What is "liquid"? Understanding the states of matter

J. A. Barker and D. Henderson

IBM Research Laboratory, Monterey and Cottle Roads, San Jose, California. 95193

Liquids exist in a relatively small part of the enormous range of temperatures and pressures existing in the universe. Nevertheless, they are of vital importance for physics and chemistry, for technology, and for life itself. A century of effort since the pioneering work of van der Waals has led to a fairly complete basic understanding of the static and dynamic physicochemical properties of liquids. Advances in statistical mechanics (the fundamental formulations of Gibbs and Boltzmann, integral equations and perturbation theories, computer simulations), in knowledge of intermolecular forces, and in experimental techniques, have all contributed to this. Thirty years ago the very existence of liquids seemed a little mysterious; today one can make fairly precise predictions of the solid–liquid–gas phase diagram and of the microscopic and macroscopic static and dynamic properties of liquids. This paper is a survey, with particular emphasis on equilibrium properties, of the theory which underlies that basic understanding, which is now at least comparable with our understanding of the physics of solids.

CONTENTS

LIST OF ABBREVIATIONS USED IN TEXT

BFW	Barker–Fisher–Watts (potential for argon)
BG	Born–Green (theory or equation)
BH	Barker–Henderson (perturbation theory)
BH1, BH2	First-order and second-order Barker–Henderson perturbation theory
CS	Carnahan–Starling (equation of state for hard spheres)
EXP	Exponential (approximation)
GH	Grundke–Henderson [parametrization of hard-sphere $y(r)$]
GMSA	Generalized mean spherical approximation
HNC	Hyper-netted chain (theory or equation)
HNC2	An extension of the hyper-netted chain theory
HS	Hard sphere
HTA	High-temperature approximation of Weeks–Chandler–Andersen
K	Kirkwood (theory or equation)
lc	Local compressibility (approximation)
LEXP	Linearized exponential approximation
LHW	Longuet–Higgins and Widom (equation of state)
MC	Macroscopic compressibility (approximation)
mc	Monte Carlo (method)
MD	Molecular dynamics (method)
MSA	Mean spherical approximation
OCT	Optimized cluster theory
ORPA	Optimized random phase approximation
OZ	Ornstein–Zernike (equation)
PY	Percus–Yevick (theory or equation)
PY2	An extension of the Percus–Yevick theory
RDF	Radial distribution function
RISM	Reference interaction site model
SA	Superposition approximation
SPT	Scaled-particle theory
SW	Square-well potential
vdW	van der Waals (theory or equation of state)
VW	Verlet–Weis (parametrization of hard-sphere radradial distribution function)
WCA	Weeks–Chandler–Andersen (theory)

I. INTRODUCTION

The existence of matter in three different phases (solid, liquid and gaseous phases) is a fact of every day experience. Solids are rigid and give sharp Bragg reflections in a diffraction experiment, demonstrating an ordered arrangement of atoms or molecules. Liquids and gases are fluid; they will flow under a shear stress however small. Further, in diffraction experiments they give no sharp Bragg reflections but diffuse rings, showing that there is no long-range ordered arrangement of molecules. Thus, there is a clear distinction between solid and fluid (though this is somewhat blurred by the existence of glasses and amorphous solids). On the other hand, there is no such qualitative distinction between liquid and gas. Van der Waals pointed out explicitly the *continuity* of liquid and gaseous states. At temperatures below the critical temperature two fluid phases can coexist in equilibrium: the denser phase is called liquid, and the less dense phase is called gas. Above the critical temperature, coexistence of fluid phases is not observed. One can pass continuously from low-temperature gas to low-temperature liquid by heating above the critical temperature, compressing, and cooling. The difference between liquid and gas is essentially a difference in *density*.

For roughly spherical molecules, and in particular for the actually spherical rare gases, only one kind of disorder is possible, namely disorder of translational motion. For molecules which are far from spherical there is also the possibility of *rotational* disorder. This may occur in a crystal which retains translational order (plastic crystals). On the other hand, rotational order may persist in a temperature range where there is translational disorder; in this case one is dealing with "liquid crystals," and many kinds of phases (nematic, smectic, cholesteric) are observed (Stephen and Straley, 1974).

The aim of the physics of liquids is to understand why particular phases are stable in particular ranges of temperature and density (phase diagrams; Fig. 1), and to relate the stability, structure, and dynamical properties of fluid phases to the size and shape of molecules, atoms, or ions and the nature of the forces between them (which in turn are determined by the electronic properties). For ordinary liquid phases we now have excellent qualitative understanding of these questions, and in simple cases this can lead to fairly rigorously *quantitative* predictions. For systems such as liquid crystals, rigorous fundamental theory is at an earlier stage, and we shall have relatively little to say on this subject. A full account of current phenomenological and semiphenomenological theoretical approaches to liquid crystals is given by Stephen and Straley (1974).

The interactions which determine the bulk properties of matter are basically electromagnetic, and in fact, apart from small relativistic and retardation effects, *electrostatic* in character; they arise from the Coulomb interactions between nuclei and electrons. Thus, one way to attempt to predict the properties of a liquid (or solid or gas) would be to solve, subject to appropriate antisymmetry conditions, the many-body Schrödinger equation describing the motion of the nuclei and

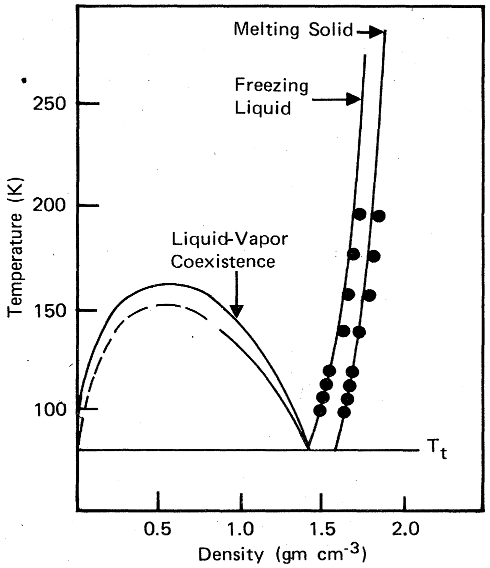

FIG. 1. Phase diagram for the 6–12 fluid, as calculated by Hansen and Verlet (1969) (solid lines), and for argon (dashed line and circles). The comparison assumes $\epsilon/k = 119.8$ K, $\sigma = 3.405$ Å.

electrons

$$\left(-\sum_i \frac{\hbar^2}{2m_i}\nabla_i^2+\sum_{i<j}\frac{q_iq_j}{r_{ij}}\right)\psi=\frac{\hbar}{i}\frac{\partial\psi}{\partial t}, \tag{1.1}$$

in which the sums are taken over all nuclei and electrons with appropriate masses m_i and charges q_i. Needless to say this would be an exceedingly difficult task!

Fortunately, there are a number of important simplifications most of which arise from the fact that nuclei are much heavier than electrons. The first is the Born–Oppenheimer (1927) approximation according to which we can solve the electronic problem for a *static* configuration of the nuclei, thus deriving a potential energy function U depending only on the *nuclear* coordinates, which can in turn be used to describe the nuclear motions. In fact, if we are prepared to determine this potential energy function experimentally (or semiempirically) we can bypass the electronic problem completely, though naturally we would like to confirm at least for a simple test case (e.g., the helium–helium interaction) that solving the electronic Schrödinger equation leads to results in agreement with our experimental determination.

A second simplification arises from the fact that the forces *between* molecules are often much weaker than *intra*molecular forces between atoms. Thus for relatively rigid molecules we can often make the approximation of ignoring any coupling between intramolecular vibrations and motions of the molecule as a whole, at least in considering many thermodynamic and transport properties (in spectroscopic studies, for example, we can certainly see intermolecular effects on intramolecular vibrations, and this is an important experimental probe). In the simplest case (rare gases) this question does not arise. For more complex molecules this approximation means that we can treat the molecules as rigid, and consider the potential energy function U_N as depending only on the positions $\vec{r}_i$ of the center of mass (say) of the molecules and their orientations Ω_i

$$U_N=U_N(\vec{r}_1,\Omega_1;\ldots;\vec{r}_N,\Omega_N). \tag{1.2}$$

Of course, this approximation would *not* be made in studying molecules with relatively free internal rotations (e.g., polymers).

A third simplification, also arising from the relatively large masses of the nuclei, is that in many cases we can describe the behavior of the molecules by *classical* mechanics and *classical* statistical mechanics, supplemented where necessary by quantum corrections (which are discussed in Sec. III.B.5). This procedure is certainly inadequate for helium and hydrogen at very low temperatures, but probably adequate for most other liquids.

A further simplification arises from the fact that intermolecular potential energies are, to a first approximation, additive. Thus, the potential energy function U_N may be written as

$$U_N=\sum_{i<j}u_2(\vec{r}_i,\Omega_i;\vec{r}_j,\Omega_j)+\sum_{i<j<k}u_3(\vec{r}_i,\Omega_i;\vec{r}_j,\Omega_j;\vec{r}_k,\Omega_k)+\ldots, \tag{1.3}$$

in which the first term is a sum of *pair* interactions, and the second a sum of *triplet* interactions (which may be chosen to vanish whenever *one* of the molecules is very distant from the other two). In the case of the rare gases, it appears to be a good approximation to neglect all terms beyond the triplet term in (1.3), and the effects of the triplet term on thermodynamic properties can be included by perturbative techniques. Whether this will prove to be true for all liquids remains to be seen.

We shall use the grand canonical ensemble which is most convenient for deriving theoretical results (Baxter, 1971). In this ensemble the probability of finding N molecules with coordinates in elements $dq_1\ldots dq_N$ at $q_1\ldots q_N$ and momenta in $dp_1\ldots dp_N$ at $p_1\ldots p_N$ is $P(dq_1\ldots dq_N)(dp_1\ldots dp_N)$ with

$$P=\left(\frac{1}{h^{fN}\Xi}\right)\exp[\beta(N\mu_0-H_N)]. \tag{1.4}$$

In this equation h is Planck's constant, $\beta=1/k_BT$, k_B is Boltzmann's constant, T is the temperature, μ_0 is the chemical potential, and f the number of degrees of freedom per molecule (3 for atoms in three dimensions, 6 for an asymmetric rotor). The q_i are generalized coordinates (center of mass coordinates and possibly angles) specifying the position and orientation of the molecule. By dq_1 we mean an f-dimensional volume element in the generalized coordinate space of molecule 1; the p_i are the momenta conjugate to the q_i. The Hamiltonian of the N-body system is H_N

$$H_N=T_N+U_N, \tag{1.5}$$

where T_N (not to be confused with the temperature T) is the kinetic energy, and U_N the potential energy. The normalizing factor Ξ is the grand partition function, given by

$$\Xi=\sum_{N=0}^{\infty}\frac{\exp[\beta N\mu_0]}{N!}\times\int_{V,\Omega}\cdots\int\exp[-\beta H_N]dq_1\ldots dq_N\,dp_1\ldots dp_N. \tag{1.6}$$

The relation with thermodynamics is given by (Kittel, 1958)

$$pV=k_BT\ln\Xi. \tag{1.7}$$

We will assume that the volume V is very large, to avoid the necessity of reiterating that the limit $V\to\infty$ is to be taken. Because the kinetic energy depends quadratically on the momenta, the integration over the p_i in (1.6) can be performed immediately for rigid molecules [similarly (1.4) can be integrated over momenta]. The result is

$$\Xi=\sum_{N=0}^{\infty}\frac{\exp[\beta N\mu]}{N!}\times\int\cdots\int\exp[-\beta U_N]d\vec{r}_1\ldots d\vec{r}_N\,d\Omega_1\ldots d\Omega_N. \tag{1.8}$$

Here $d\Omega_i$ is the volume element in the space of rotations of molecule i [cf., Kirkwood (1933b)]. For convenience we will assume $d\Omega_i$ to be normalized so that $\int d\Omega$ is 1. (Thus, for an axially symmetric molecule with the direction of its axis specified by a polar angle θ and azimuthal angle ϕ, $d\Omega$ would be $\sin\theta\, d\theta\, d\phi/4\pi$.) The quantity μ in (1.8) is equal to $\mu_0 + \ln[(2\pi m k_B T/h^2)^{\nu/2} Z'_{\mathrm{rot}}]$ in which Z'_{rot} is the free-rotator partition function for one molecule (Landau and Lifschitz, 1969), m the molecular mass, and ν the dimensionality of the space. We shall call μ (as well as μ_0) the chemical potential; it is referred to a zero or reference state different from that for μ_0.

Using (1.7) and the momentum-integrated form of (1.4) we see that the probability density P' that L *particular* molecules lie in the elements $d\vec{r}_1 \ldots d\vec{r}_L\, d\Omega_1 \ldots d\Omega_L$ is given by

$$P' = \sum_{N=0}^{\infty} \frac{\exp[N\beta\mu]}{N!\,\Xi} \times \int_{V,\Omega} \cdots \int \exp[-\beta U_N]\, d\vec{r}_{L+1} \ldots d\vec{r}_N\, d\Omega_{L+1} \ldots d\Omega_N. \tag{1.9}$$

However, there are $N(N-1)\ldots(N-L+1)$ different sets of molecules which can occupy the volume elements, so that the total probability density that *any* L molecules occupy these elements is given by

$$\begin{aligned} n^{(L)}(\vec{r}_1, \Omega_1; \ldots; \vec{r}_L, \Omega_L) &= \rho^L g(\vec{r}_1, \Omega_1; \ldots; \vec{r}_L, \Omega_L) \\ &= \sum_{N=0}^{\infty} \frac{\exp[N\beta\mu]}{(N-L)!} \\ &\quad \times \int \cdots \int \exp[-\beta U_N]\, d\vec{r}_{L+1} \ldots d\vec{r}_N\, d\Omega_1 \ldots d\Omega_N. \end{aligned} \tag{1.10}$$

The functions $n^{(L)}(\vec{r}_1, \Omega_1; \ldots; \vec{r}_L, \Omega_L)$ and $g(\vec{r}_1, \Omega_1; \ldots; \vec{r}_L, \Omega_1)$ are both called *L-particle distribution functions*. For a uniform isotropic fluid, $n^{(1)}(\vec{r}_1, \Omega_1)$ is just the number density ρ or $\langle N\rangle/V$, where $\langle N\rangle$ is the average number of molecules (recall the normalization of $d\Omega$). Also in a uniform isotropic fluid, $n^{(2)}(\vec{r}_1, \Omega_1; \vec{r}_2, \Omega_2)$ will depend only on the distance $r_{12} = |\vec{r}_1 - \vec{r}_2|$ and the orientations of the molecules with respect to one another and the direction of $\vec{r}_1 - \vec{r}_2$. The *pair distribution function* $g(1,2) = g(\vec{r}_1, \Omega_1; \vec{r}_2, \Omega_2)$ is of particular importance. The pair distribution function approaches 1 as the distance becomes large. For spherical molecules $g(1,2)$, a function of distance alone, is called the *radial distribution function*, and can be determined experimentally from neutron or x-ray diffraction experiments. The radial distribution function determined by neutron diffraction for argon in conditions close to its triple point (Yarnell *et al.*, 1973) is shown in Fig. 2. Its Fourier transform is the *static structure factor* (Chen, 1971) defined (for spherical molecules) by

$$S(|\vec{k}|) = 1 + \rho \int \exp[i\vec{k}\cdot\vec{r}]\, g(r)\, d\vec{r}. \tag{1.11}$$

For nonspherical molecules we can define the radial distribution function by

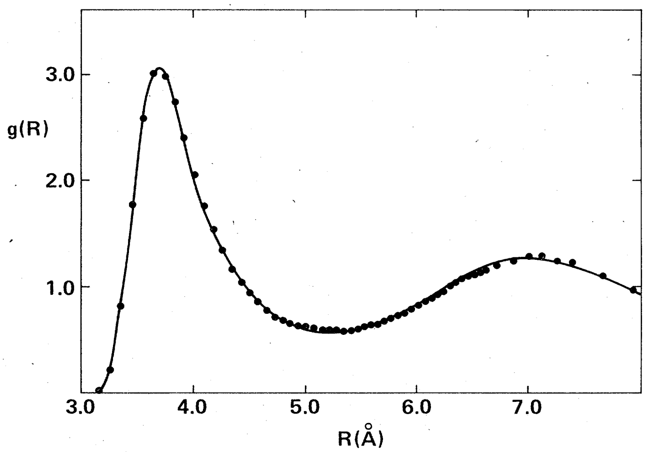

FIG. 2. Radial distribution function of liquid argon at 85 K (Yarnell *et al.*, 1973). Solid curve, from neutron diffraction experiment. Circles from Monte Carlo calculation using BFW potential of Barker *et al.* (1970) with three-body and quantum corrections. The values calculated by Verlet (1968) with the 6–12 potential are indistinguishable from the latter values on the scale of the plot.

$$g_S(r_{12}) = \int g(1,2)\, d\Omega_1 d\Omega_2. \tag{1.12}$$

To avoid ambiguity in the case of nonspherical molecules we have denoted the radial distribution function by g_s (indicating that g has been spherically averaged) and the pair distribution function by g. The distinction is unnecessary for spherical molecules.

The function h which is equal to $g-1$ is called the *net* or *total correlation function*. It is customary to define the *direct correlation function* c by means of the Ornstein–Zernike (1914) equation [as generalized for rigid nonspherical molecules by Workman and Fixman (1973)]

$$h(\vec{r}_1, \Omega_1; \vec{r}_2, \Omega_2) = c(\vec{r}_1, \Omega_1; \vec{r}_2, \Omega_2) + \rho \int h(\vec{r}_1, \Omega_1; \vec{r}_3, \Omega_3)\, c(\vec{r}_2, \Omega_2; \vec{r}_3, \Omega_3)\, d\vec{r}_3 d\Omega_3. \tag{1.13}$$

From Eqs. (1.4) and (1.6) we see that the average number of molecules [using angular brackets $\langle\,\rangle$ to denote ensemble averaging, that is averaging with the probability density of (1.4)] is given by

$$\langle N\rangle = k_B T\, \partial \ln \Xi / \partial \mu, \tag{1.14}$$

and on differentiating again, that

$$k_B T \frac{\partial\langle N\rangle}{\partial \mu} = \langle N^2\rangle - \langle N\rangle^2. \tag{1.15}$$

From the definition of $n^{(1)}, n^{(2)}$ it follows that

$$\int\int n^{(2)}(\vec{r}_1, \Omega_1; \vec{r}_2, \Omega_2)\, d\vec{r}_1 d\vec{r}_2 d\Omega_1 d\Omega_2 = \langle N(N-1)\rangle, \tag{1.16}$$

and

$$\int\int n^{(1)}(\vec{r}_1, \Omega_1)\, d\vec{r}_1 d\Omega_1 = \langle N\rangle, \tag{1.17}$$

whence

$$\int\int [n^{(2)}(\vec{r}_1,\Omega_1;\vec{r}_2,\Omega_2) - n^{(1)}(\vec{r}_1,\Omega_1)n^{(1)}(\vec{r}_2,\Omega_2)]d\vec{r}_1 d\vec{r}_2 d\Omega_1, d\Omega_2 = \langle N^2\rangle - \langle N\rangle^2 - \langle N\rangle. \tag{1.18}$$

But we have

$$\begin{aligned} k_B T\left(\frac{\partial\rho}{\partial p}\right)_{V,T} &= \frac{k_B T}{V}\left(\frac{\partial\langle N\rangle}{\partial p}\right)_{V,T}, \\ &= \left(\frac{\partial\langle N\rangle}{\partial \ln\Xi}\right)_{V,T}, \\ &= \left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T} \bigg/ \left(\frac{\partial\ln\Xi}{\partial\mu}\right)_{V,T}, \\ &= [\langle N^2\rangle - \langle N\rangle^2] \;/\; \langle N\rangle. \end{aligned} \tag{1.19}$$

Combining this with Eq. (1.18) we find

$$\begin{aligned} k_B T\left(\frac{\partial\rho}{\partial p}\right)_{V,T} &= 1 + \langle N\rangle^{-1}\int\int [n^{(2)}(\vec{r}_1,\Omega_1;\vec{r}_2,\Omega_2) - n^{(1)}(\vec{r}_1,\Omega_1)n^{(1)}(\vec{r}_2,\Omega_2)]\, d\vec{r}_1 d\vec{r}_2 d\Omega_1 d\Omega_2, \\ &= 1 + \rho\int h(r_{12},\Omega_1,\Omega_2)d\vec{r}_2 d\Omega_1 d\Omega_2. \end{aligned} \tag{1.20}$$

This is the well-known *"compressibility equation"* which relates thermodynamic properties to g or h. Note that this result is independent of any special assumptions such as pair additivity *about* the potential function. It is also valid for an oriented fluid (liquid crystal).

The thermodynamic internal energy U_i is simply the average of the total energy H_N; using (1.4) and (1.8) this becomes

$$U_i = \sum_{N=0}^{\infty}\frac{\exp[\beta N\mu]}{N!} \times \int\dots\int \exp[-\beta U_N]\{fk_B T/2 + U_N\}d\vec{r}_1\dots d\vec{r}_N d\Omega_1\dots d\Omega_N. \tag{1.21}$$

The first term in curly brackets represents the kinetic energy. For pair additive potentials [Eq. (1.3) with triplet and higher terms omitted)] the second term gives $N(N-1)/2$ equal integrals, each of which can be written in terms of $n^{(2)}(\vec{r}_i,\Omega_i;\vec{r}_j,\Omega_j)$ by virtue of (1.10). Thus, we find the result

$$U_i/\langle N\rangle = fk_B T/2 + \frac{1}{2}\rho\int g(r_{12},\Omega_1,\Omega_2)u(\vec{r}_1,\Omega_1;\vec{r}_2,\Omega_2)\,d\vec{r}_2. \tag{1.22}$$

This is the *energy equation*, which provides another route to thermodynamic properties.

We will also derive an expression for the pressure. To do this we follow the method of Born and Green (1947) and introduce in (1.8) a change of variables $\vec{r}_i = V^{1/\nu}\vec{s}_i$. Then we find

$$\Xi = \sum_{N=0}^{\infty}\frac{\exp[\beta N\mu]V^N}{N!} \times \int_{D,\Omega}\dots\int \exp[-\beta U_N(V^{1/\nu}\vec{s}_i;\Omega_i)]\; d\vec{s}_1\dots d\vec{s}_N d\Omega_1\dots d\Omega_N. \tag{1.23}$$

The region of integration D is now independent of volume (it may be considered, for example, as a sphere of unit volume centered on the origin). We can now differentiate the logarithm of (1.23) with respect to volume, to find

$$\begin{aligned} V\left(\frac{\partial\ln\Xi}{\partial V}\right)_{\mu,T} &= \sum_{N=0}^{\infty}\frac{\exp[\beta N\mu]V^N}{N!\,\Xi}\int\dots\int \exp[-\beta U_N(V^{1/\nu}\vec{s}_i,\Omega_i)]\left[N - \frac{1}{\nu k_B T}\sum_i V^{1/\nu}\vec{s}_i\cdot\vec{\nabla}_i U_N\right]d\vec{s}_1\dots d\vec{s}_N d\Omega_1\dots d\Omega_N \\ &= \left\langle N - \frac{1}{\nu k_B T}\sum_i \vec{r}_i\cdot\vec{\nabla}_i U_N\right\rangle. \end{aligned} \tag{1.24}$$

Here $\vec{\nabla}_i U_N$ is the gradient of the function U_N with respect to $\vec{r}_i$. But $(\partial\ln\Xi/\partial V)_{\mu T}$ is just $p/k_B T$, so this becomes

$$\frac{pV}{k_B T} = \left\langle N - \frac{1}{\nu k_B T}\sum_i \vec{r}_i\cdot\vec{\nabla}_i U_N\right\rangle. \tag{1.25}$$

This is known as the *virial* expression for the pressure since it can also be derived from the mechanical virial theorem of Clausius. It is also called the *pressure equation*. For additive pair potentials we must have

$$\vec{\nabla}_j u(\vec{r}_i,\Omega_i;\vec{r}_j,\Omega_j) = -\vec{\nabla}_i(\vec{r}_i,\Omega_i;\vec{r}_j,\Omega_j) \tag{1.26}$$

so (1.25) becomes

$$\begin{aligned} \frac{pV}{k_B T} &= \left\langle N - \frac{1}{\nu k_B T}\sum_{i<j}(\vec{r}_i - \vec{r}_j)\cdot\vec{\nabla}_i u(\vec{r}_i,\Omega_i;\vec{r}_j,\Omega_j)\right\rangle \\ &= \langle N\rangle - \frac{1}{2\nu k_B T}\int\int n^{(2)}(\vec{r}_1,\Omega_1;\vec{r}_2,\Omega_2) \times (\vec{r}_1 - \vec{r}_2)\cdot\vec{\nabla}_1 u(\vec{r}_1,\Omega_1;\vec{r}_2,\Omega_2)d\vec{r}_1 d\vec{r}_2 d\Omega_1 d\Omega_2 \end{aligned} \tag{1.27}$$

or

$$\frac{p}{k_B T} = \rho - \frac{\rho^2}{2\nu k_B T}\int\int(\vec{r}_1 - \vec{r}_2)\cdot\vec{\nabla}_1 u(\vec{r}_1,\Omega_1;\vec{r}_2,\Omega_2) \times g(r_{12},\Omega_1,\Omega_2)d\vec{r}_2 d\Omega_1 d\Omega_2. \tag{1.28}$$

For spherical potentials this is

$$\frac{p}{k_B T} = \rho - \frac{\rho^2}{2\nu k_B T}\int r u'(r)g(r)d\vec{r}. \tag{1.29}$$

For the hard-sphere potential which is $+\infty$ for $r < d$ and 0 otherwise, this becomes (in three dimensions)

$$\begin{aligned} \frac{p}{k_B T} &= \rho + \frac{\rho^2}{6}4\pi\int_0^{\infty}\frac{d}{dr}[\exp\{-\beta u(r)\}]r^3 y(r)dr \\ &= \rho + \frac{2\pi}{3}d^3\rho^2 y(d), \end{aligned} \tag{1.30}$$

where $y(r) = g(r)\exp\{\beta u(r)\}$ is a continuous function. The second form follows since $\exp\{-\beta u(r)\}$ is a unit step-function of $(r-d)$, so that its derivative is a δ function. The corresponding result in two dimensions is

$$\frac{p}{k_B T} = \rho + \frac{\pi d^2}{2}\rho^2 y(d). \tag{1.31}$$

Equations (1.30) and (1.31) are often written with $g(d)$ instead of $y(d)$. If this is done, strictly speaking it should be $\lim_{\epsilon\to 0} g(d+\epsilon)$ which is used. However, this more rigorous notation is rarely used.

It is appropriate to mention here the principle of corresponding states, which is remarkably useful in correlating the properties of fluids. The basic idea is that if several substances have potential functions of the same *form*, differing only in scale factors of energy and length, then their properties are identical when expressed in appropriate units. A very full discussion is given by Scott (1971); the earliest derivation from statistical mechanics was that of Pitzer (1939).

Suppose that several substances ($\lambda = 1, 2\ldots$) have potential functions of the same general form

$$U_N(\vec{r}, \Omega) = \epsilon_\lambda U_N^*(\vec{r}/\sigma_\lambda, \alpha_\lambda, \beta_\lambda, \ldots), \tag{1.32}$$

where ϵ_λ and σ_λ are dimensional constants with the dimensions, respectively, of energy and length, and $\alpha_\lambda, \beta_\lambda$ are *dimensionless* parameters [an example is the reduced three-body parameter ν^* discussed in Sec. II; see Barker *et al.* (1968)]. Then one can introduce changes of variable in the expression for the partition function to show that, for example, pV/Nk_BT is a universal function of reduced density $\rho^* = (N\sigma_\lambda^3/V)$, reduced temperature $T^* = (k_BT/\epsilon_\lambda)$, and of the *dimensionless* parameters $\alpha_\lambda, \beta_\lambda \ldots$. This will be discussed in connection with potential energy functions in Sec. II. A full account of the principle and its extensions is given by Pitzer and Brewer in Lewis and Randall (1961).

After considering intermolecular forces in Sec. II, we will discuss computer simulations (Monte Carlo and molecular dynamics methods) in Sec. III, and show that these methods give excellent agreement with experiment provided that sufficiently realistic (and complicated) potential energy functions are used (Sec. III.D.3, III.D.4). Since the computer simulation methods have been validated in this way, it is often convenient to test other theoretical methods by comparing their results for simple model potentials with the results for the *same* potentials calculated by the simulation methods. In this way uncertainties due to the adequacy or inadequacy of potential functions are avoided. It is to be emphasized that the justification for this procedure rests on the validation of the simulation methods by comparison with experiment and on their firm foundations in the principles of statistical mechanics. Without the stimulus and firm knowledge provided by computer simulations, the theory of liquids would have developed very much more slowly.

Density expansions are developed in Sec. IV. Although these expansions are most useful at low densities, they are instructive in the theory of liquids because many of the theories of the pair distribution function developed in Sec. VI can be derived conveniently from these expansions.

Before developing these theories of the pair distribution function, the scaled-particle theory is discussed in Sec. V. This theory gives good results for the equation of state of hard spheres. It was the first theory to give accurate results for a dense fluid and is presently the only convenient and accurate theory of a fluid of hard convex molecules.

The distribution function theories are developed in Sec. VI. Most of the work on the theory of liquids, at least until the last decade, has been concerned with these theories. One of these theories, the Percus–Yevick theory, has been very useful for the hard-sphere fluid. Unfortunately, these theories have been less successful so far for fluids in which attractive forces are present. We discuss methods of extending these theories so that better results can be obtained for fluids with attractive forces.

The most successful class of theories both from the point of view of numerical accuracy and of intuitive appeal are the perturbation theories developed in Sec. VII. These theories, developed largely in the last decade, explicitly demonstrate the usefulness of the concept of the continuity of the gas and liquid states discussed earlier. Liquids such as argon are, to a good approximation, a gas of hard spheres moving in a uniform background potential which results from the nonhard-core part of this potential.

Cell or lattice theories are discussed in Sec. VIII. Until recently, these methods were thought to be appropriate to solids and inapplicable to liquids. However, recent advances indicate that this is probably not so. This method may also provide the basis of a systematic theory of liquids and has the specific advantage of leading to a theory of freezing (or melting). However, the mathematical use which we make of "cells" and "lattices" should not be taken as implying that such structures have real existence in liquids. The evidence against such a view is given with great cogency in the work of Hildebrand and his colleagues (Alder and Hildebrand, 1973; Hildebrand *et al.*, 1970).

The over-all situation in the theory of liquids is that we have a good deal of insight into the factors which determine the structure and thermodynamic properties of liquids. We have integral equations (Percus–Yevick, etc.) for the distribution functions which give excellent qualitative and fair quantitative results. We have perturbation theories and ultimately computer simulations which can make precise predictions. There are possibilities for improving theories such as the Percus–Yevick theory. However, one might question whether this has reached the point of diminishing returns for spherical molecules in light of the additional insights to be gained. For nonspherical molecules, electrolytes, liquid metals, quantum liquids, etc., much more remains to be done.

This review concludes with a brief discussion of the gas–liquid interface, and of the theory of the surface tension of a liquid.

We have not included a discussion of the theoretical aspects of the dynamical properties of liquids or of the critical point region as each is a major field in itself.

II. INTERMOLECULAR FORCES

As we have seen, the most direct way to determine the potential energy function $U_N(\vec{r}_1, \Omega_1; \ldots; \vec{r}_N, \Omega_N)$

would be to solve the electronic Schrödinger equation for all relevant values of the molecular coordinates. For solids (at least undistorted lattices) this is not necessarily an impossible task—it is the aim of electronic solid state theories. However, to attain the accuracy required for meaningful thermodynamic calculations it is necessary to take account of electron correlation effects, and this has not yet been done by completely *ab initio* quantum-mechanical methods. The cohesive forces which bind nonpolar molecular crystals and liquids are largely intermolecular electron correlation effects, and are not included, for example, in a Hartree–Fock calculation, whether for two molecules or for the whole crystal. However, there are certain approximate quantum-mechanical methods which have been used with some success. Trickey *et al.* (1973) used the "augmented-plane-wave statistical-exchange" method to calculate apparently reasonable binding energies and pressures for undistorted rare-gas crystals. Similar calculations have not yet been performed for distorted crystals (these would be required to permit the study of phonon effects, etc. arising from zero-point vibrations or nonzero temperature). Similar calculations for liquids, with complete absence of symmetry, seem to be much further down the line.

With this in mind we return to Eq. (1.3), which expresses the total potential as a sum of terms arising from pairs, triplets, and so on of molecules. The pair term can, of course, be determined from calculations or measurements on two molecules, the triplet term from additional calculations or measurements on three molecules. Even the pair calculation poses difficulties for *ab initio* quantum mechanics. Liu and McLean (1974, 1975) have performed large configuration interaction calculations on the system He + He and derived an interatomic potential energy function which is in really excellent agreement with the best experimental estimates (Burgmans *et al.*, 1976) of this function (see Fig. 3). From the point of view of the physical chemist this is a milestone in the computational use of quantum mechanics! It is a little sad that we cannot proceed to make precise calculations of the phase diagram and properties of liquid helium, thus completing the bridge from Schrödinger equation to phase diagram for one substance. This is not yet possible (except at $T = 0$; see Sec. III.B.5) because the atomic motions in liquid helium are highly quantum-mechanical and exchange effects are very important below the λ temperature. Thus, liquid helium is a special problem which we shall not discuss further; a recent review with detailed references is given by ter Haar (1971). Nevertheless, the work of Liu and McLean is a valuable confirmation of present-day experimental methods for determining potential energy functions.

Similar calculations have not yet been performed for pairs of more complex atoms or molecules (nor for *three* helium atoms). Gordon and Kim (1972) and Kim and Gordon (1974) used an approximate quantum-mechanical method based on an electron-gas formulation of the energy to calculate interaction potentials for closed-shell atoms and ions. The results show quite encouraging agreement with experimental estimates, though for the present the latter must be regarded as more firmly based. Kim (1975a, b) extended this method to three-atom interactions. However, present indications (Oxtoby and Gelbart 1976) are that the resulting three-atom potentials are much too repulsive to be reconciled with experimental facts on rare-gas crystals.

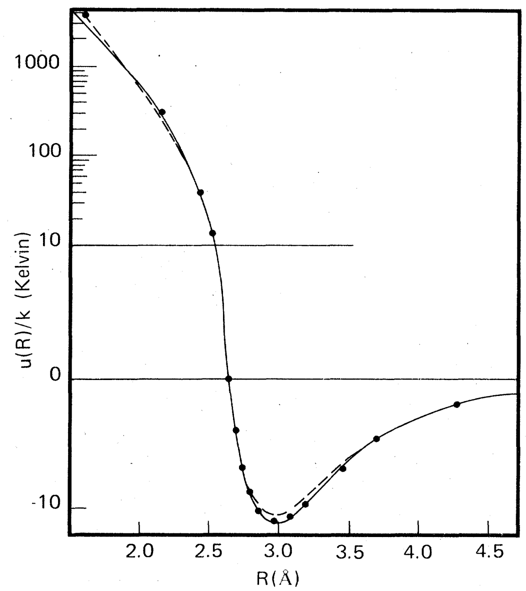

FIG. 3. The helium–helium interaction potential. Solid curve, scattering potential of Farrar and Lee (1972); dashed curve, potential from bulk data due to Beck (1968); circles, *ab initio* configuration interaction calculations of Liu and McLean (1975).

In the short-range repulsive region, Hartree–Fock calculations give fair results [see Gilbert and Wahl (1967) for calculations on rare-gas pairs].

At large atomic separations, when electronic overlap is negligible, quantum-mechanical perturbation theory can be used to relate the interactions to properties of the isolated atoms. The two-atom interaction then has the form

$$u_2(r) = -\frac{c_6}{r^6} - \frac{c_8}{r^8} - \dots . \tag{2.1}$$

The coefficient c_6 can be related to dipole oscillator strengths which are known from optical data; for rare-gas pairs the values of c_6 are known to within 1% or 2% (Leonard and Barker, 1975; Starkschall and Gordon, 1971). Leonard (1968) examined the accuracy of approximate formulae for c_6. The coefficient c_8 depends on quadrupole oscillator strengths which are not so well known (though they could fairly readily be *calculated*). Estimates of c_8 are given by Gordon and Starkschall (1972). The leading term in the three-atom interaction [corresponding to the c_6 term in (2.1)] is the so-called Axilrod-Teller interaction (Axilrod and Teller, 1943)

$$u_3 = \nu(1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3)/(R_1^3 R_2^3 R_3^3), \tag{2.2}$$

where R_i and θ_i are the sides and angles of the triangle formed by the three atoms. The coefficient ν depends on the same dipole oscillator strengths as c_6 and values for rare-gas triplets are also know accurately (Leonard and Barker, 1975). Doran and Zucker (1971) and Zucker and Doran (1976) have given estimates of dipole–quadrupole terms in third-order perturbation theory and of higher-order dipole terms; for detailed discussion and references we refer to Zucker and Doran (1976).

Konowalow and Zakheim (1972), following a suggestion of Nesbet (1968), studied a number of ways of combining repulsive interactions from Hartree–Fock calculations with the known c_6 term, using, in addition, data on second virial coefficients. One of their methods in particular (which they label P5) consistently gave good agreement with experimentally determined potentials for rare gas pairs. This is important because it demonstrates that currently practicable computations combined with minimal amounts of experimental data can lead to accurate potentials.

From the theoretical point of view little is known with certainty about shorter-ranged overlap-dependent many-body interactions, except for the work of O'Shea and Meath (1974) on hydrogen atoms. However, there is very strong *experimental* evidence (Barker, 1976; Klein and Koehler, 1976; Barker *et al.*, 1971) that their effects on thermodynamic properties of solid and liquid rare gases are very small, at least up to pressures of about 20 kbar. Thus, if one uses accurate two-atom potentials together with the many body interactions discussed above, excellent agreement with experiment for solid and liquid properties of rare gases is obtained. For detailed discussion and references on theoretical aspects of intermolecular forces we refer to the review of Certain and Bruch (1972).

We now turn to a necessarily brief discussion of experimental determinations of intermolecular pair potential functions, with emphasis on rare-gas interactions [a wider discussion is given by Scott (1971)]. Traditional methods used gas imperfection data (second virial coefficients) and gas transport coefficients (viscosities, thermal diffusion coefficients, etc.), often with a rather simple form for the pair potential, such as the Lennard–Jones 6–12 potential:

$$u(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], \tag{2.3}$$

which has just two parameters to be determined from experiment, together with the assumption that multibody interactions are negligible. Earlier work on these lines is well summarized by Hirschfelder *et al.* (1954).

Very important information was gained from high energy molecular beam measurements of I. Amdur and his colleagues, and from new and accurate viscosity measurements by E. B. Smith and his colleagues. More recently a wealth of information has been derived from low energy molecular beam differential and total scattering cross-section measurements, particularly by Y. T. Lee, U. Buck, G. Scoles, C. J. Van Mejdeningen and their co-workers; and from spectroscopic observations of vibrational levels of van der Waals molecules [Freeman *et al.* (1974); see also the review of Ewing (1975)]. In addition the detailed information on long-range and three-body interactions discussed above has become available; and solid and liquid state data have been used in the determination of potentials (Bobetic and Barker, 1970; Barker *et al.*, 1971). Detailed references to this work are given by Barker (1976).

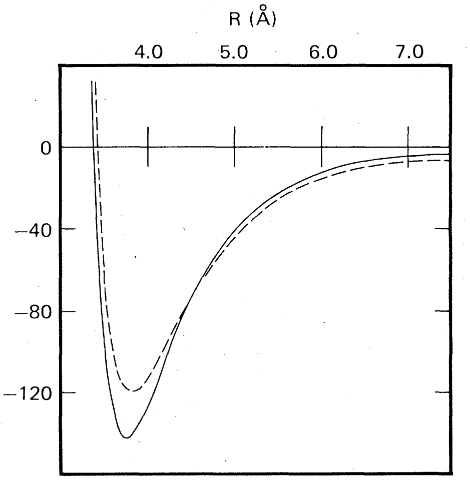

FIG. 4. The argon–argon interaction potential. Solid curve, BFW potential of Barker *et al*. (1971); dashed curve, 6–12 potential with $\epsilon/R=119.8$ K, $\sigma=3.40$ Å.

As a result of all this work interatomic potentials for homonuclear rare-gas pairs are now very accurately known, and potentials determined from different kinds of experimental data are in excellent agreement. This is shown in Fig. 4 for the case of argon. For a detailed review of the experimental data and potentials we refer to Barker (1976).

It is clear from Fig. 4 that the two-parameter 6–12 potential is quantitatively unsatisfactory (though qualitatively reasonable); this is discussed further in Sec. III. In Fig. 5 we show a comparison of calculated and experimental second virial coefficients (expressed as

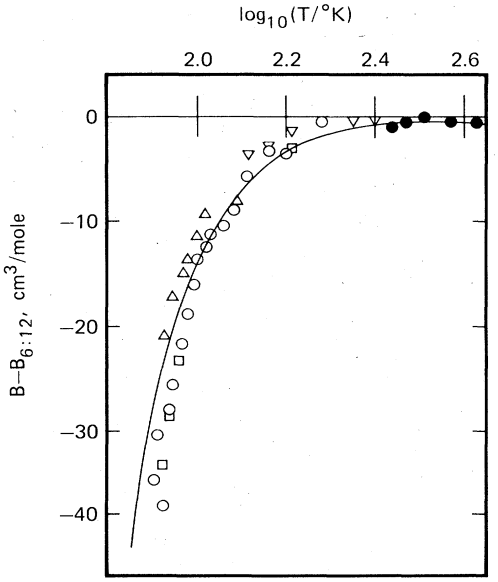

FIG. 5. Second virial coefficient of argon plotted as deviations from values calculated with 6–12 potential. Solid curve, BFW potential. The other symbols represent experimental data; for detailed references see Barker (1976).

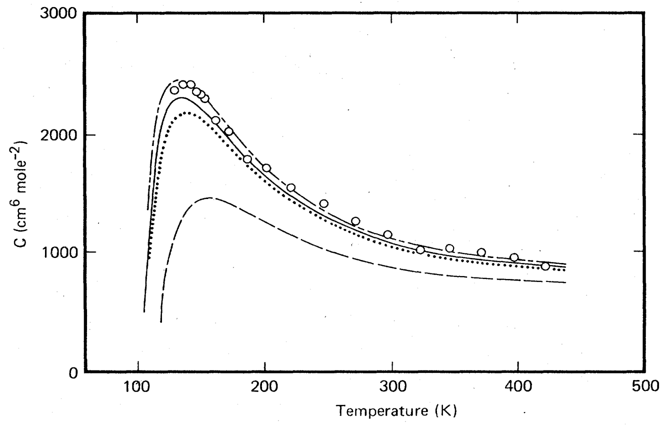

FIG. 6. Third virial coefficients of argon. The circles are experimental data (Michels *et al.*, 1958). The dashed curve is calculated with the BFW potential alone; the dotted curve includes also the Axilrod–Teller interactions; the dash-dotted curve adds third-order dipole–quadrupole interactions, and the solid curve adds fourth-order dipole interactions.

deviations from the values calculated from the 6–12 potential). In Fig. 6 we illustrate the importance of many-body interactions for argon by comparing experimental third virial coefficients with values calculated with an accurate pair potential. If no many-body interactions are included the calculated values are too low by almost a factor of 2. The Axilrod–Teller interaction corrects most of the discrepancy, and the dipole–quadrupole and fourth-order dipole interaction make relatively smaller contributions (it happens that these latter and smaller interactions almost cancel for the condensed phases of argon, so that it is a good approximation to use the Axilrod–Teller interaction as the *only* many-body interaction).

In Table I we give a comparison of the important features of the rare-gas potentials taken from Barker *et al.* (1974). With some deviation for the He–He and to a lesser extent Ne–Ne potentials, the *shapes* of the potentials are quite remarkably similar. The principle of corresponding states reflects this!

For molecules possessing permanent multipole moments there is an important contribution to the intermolecular potential energy from interactions between the permanent moments and also with moments induced in other molecules as a result of their polarizability. Values for dipole and quadrupole moments and polarizabilities may be deduced from dielectric and optical measurements. A review of these topics is given by Buckingham and Utting (1970). Note that the polarizability of the molecules introduces many-body terms in the potential energy even if they are not otherwise present (Barker, 1953; McDonald, 1974).

Potential functions for polyatomic molecules have not been studied in such detail. Evans and Watts (1975, 1976a, b) describe a relatively sophisticated benzene–benzene potential. Potential functions for interaction of water molecules are referred to in Sec. III.D.5. Harp and Berne (1970) used a Stockmayer type potential (see below) to study liquid CO and N_2, and Barojas *et al.* (1973) used a "double Lennard–Jones potential" for nitrogen. There is an extensive literature on the construction of intermolecular potential energy functions from additive atom–atom potentials which are assumed to be transferrable from one molecule to another (see for example Kitaigorodsky, 1973; Scott and Scheraga, 1966; Williams, 1967).

We mention here a number of simple model potentials which are used in theoretical studies. Two of these are the hard-sphere potential

$$\begin{aligned} u(r) &= +\infty, \quad r<d \\ &= 0, \quad r \geq d, \end{aligned} \tag{2.4}$$

and the square-well (SW) potential

$$\begin{aligned} u(r) &= +\infty, \quad r<\sigma \\ &= -\epsilon, \quad \sigma \leq r < \lambda\sigma \\ &= 0, \quad r \geq \lambda\sigma \end{aligned} \tag{2.5}$$

For polar molecules, two commonly used model potentials are the dipolar hard-sphere potential

$$u(r_{12}, \hat{\vec{\mu}}_1, \hat{\vec{\mu}}_2) = u_{\mathrm{HS}}(r) - (\mu^2/r_{12}^3) D(1,2), \tag{2.6}$$

TABLE I. "Corresponding states" comparison of potentials.

	ϵ/k_B(K)	r_m(Å)	C_6^{*f}	r_0^*	$(u'')^{*g}$	$(u''')^{*h}$	ν^{*i}	Λ^{*j}
He [a]	11.0	2.96						
He [b]	10.4	2.969	1.42	0.888	74.3		0.0082	2.29
Ne [c]	42.0	3.102	1.22	0.891	79.6	−1507	0.0110	0.485
Ar [d]	142.1	3.761	1.11	0.893	81.3	−1701	0.0249	0.154
Kr [e]	201.9	4.007	1.06	0.892	81.7	−1667	0.0296	0.084
Xe [e]	281.0	4.362	1.05	0.892	78.6	−1576	0.0361	0.052
6–12			2.00	0.891	72.0	−1512		

[a] Scattering potential of Farrar and Lee (1972).

[b] Potential from bulk data, based on the work of Beck (1968).

[c] Potential from scattering and solid state data, Farrar *et al.* (1973).

[d] Potential due to Barker *et al.* (1971).

[e] Potentials due to Barker *et al.* (1974).

[f] $C_6^* = C_6/(\epsilon r_m^6)$.

[g] $(u'')^*$ is the reduced second derivative at the minimum.

[h] $(u''')^*$ is the reduced third derivative at the minimum.

[i] ν^* is the reduced coefficient of the Axilrod-Teller interaction $\nu/(\epsilon r_m^9)$.

[j] Λ^* is the reduced de Broglie wavelength $h/(r_m\sqrt{m\epsilon})$.

and the Stockmayer potential

$$u(r_{12},\hat{\vec{\mu}}_1,\hat{\vec{\mu}}_2)=u_{6-12}(r)-\frac{\mu^2}{r_{12}^3}D(1,2), \tag{2.7}$$

where $\hat{\vec{\mu}}_1$ and $\hat{\vec{\mu}}_2$ are unit vectors specifying the orientations of the two dipoles whose magnitude is μ

$$D(1,2)=3(\hat{\vec{\mu}}_1\cdot\hat{\vec{\mathrm{r}}}_{12})(\hat{\vec{\mu}}_2\cdot\hat{\vec{\mathrm{r}}}_{12})-\vec{\mu}_1\cdot\vec{\mu}_2, \tag{2.8}$$

$\hat{\vec{\mathrm{r}}}_{12}=\vec{\mathrm{r}}_{12}/r_{12}$, and $u_{\mathrm{HS}}(r)$ and $u_{6-12}(r)$ are given by Eqs. (2.4) and (2.3), respectively. Triplet and higher multibody interactions are not present in any of these model systems, defined by (2.4) to (2.7).

We mention the Kihara (1963) "core" potential model for nonspherical molecules. In this model the molecules are assumed to have cores which may be lines or two-dimensional figures (e.g., a plane hexagon for benzene). If ρ is the *shortest* distance between the cores of two molecules, the potential energy is assumed to be a function $u(\rho)$ of ρ alone. If $u(\rho)$ is the hard-sphere potential for diameter σ then the model describes hard nonspherical molecules. If the core is a line of length $x\sigma$, the molecules are "hard spherocylinders."

III. COMPUTER SIMULATIONS AND EXPERIMENTS

A. Introduction

The most severe difficulties in the theory of liquids arise because there is no obvious way of reducing the complex many-body problem posed by the motion of the molecules to a one-body or few-body problem, analogous to the phonon analysis of motions in crystals, or the virial series for dilute gases discussed in Sec. IV. The most straightforward way of meeting this problem is head-on, via a computer solution of the many-body problem itself. Clearly this can be done in principle; the only bothersome questions might be: How "many" is many-body? This question has been explored very fully by a large amount of work in the last two decades. The answer has turned out to be that a few tens to a few hundreds is "many" enough for almost all purposes. By studying systems of this number of molecules one can obtain very good estimates of the behavior of macroscopic systems in almost all conditions; the most notable exception is the neighborhood of the critical point.

There are two important methods to be considered: The *"Monte Carlo"* (MC) method, which evaluates *ensemble averages* in the sense of statistical mechanics; and the method of *molecular dynamics* (MD) in which the dynamical equations of motion of the molecules are solved and *time averaging* is used. There are advantages in both of these methods. Molecular dynamics gives, obviously, full dynamical information and can be used to study time-dependent phenomena. On the other hand the Monte Carlo method can yield certain thermodynamic properties (in particular, though with some difficulty, the entropy) which cannot easily be obtained from molecular dynamics. The choice of method is determined by the problem to be solved.

A key idea in both methods is the use of periodic boundary conditions to enhance the ability of small systems to simulate the behavior of large systems. This idea was introduced in the very earliest applications of both methods [by Metropolis *et al.* (1953) for Monte Carlo; by Alder and Wainwright (1957, 1959) for molecular dynamics]. The technique is to consider a certain basic region, usually a cube, containing a certain number N of molecules; and then to imagine the whole of space filled by periodic images of this basic unit. In this way, one can consider configurations of an infinite system (which must of course be periodic) while only considering a limited number N of molecules. The great advantage is that *surface effects*, which would otherwise be very large for small N, are avoided. Often one uses the "nearest image distance convention" according to which a given molecule i is supposed to interact only with that periodic image of another molecule j which lies closest to i. In fact, if the range of the molecular interactions is less than half the edge of the cube this includes *all* interactions; it is often convenient to *force* this by truncating the potential at some distance $R_{\max}$ and to take account of the long-range tail of the interaction (if necessary) by perturbative techniques.

Although cubical (or at least rectangular) periodic volumes have almost always been used, it is by no means clear that this is optimal. For some purposes it might be preferable to use, for example, the dodecahedral Wigner–Seitz cell of the face-centered cubic lattice. Determination of the "nearest image distance" would be more complicated, but this might be more than outweighed by other savings, particularly if the potentials are complicated.

It is convenient to mention here the use of "near-neighbor tables," based on the work of Verlet (1967). The purpose of this is to save unnecessary labor in calculating distances between molecules which are certain to be too far apart to interact. One constructs a table listing, for each molecule i, those molecules j which are within a certain distance $R_2(>R_{\max})$ of i. The distance R_2 is chosen so that during a number p of time-steps or Monte Carlo steps there is negligible probability that a molecule which was initially at a distance greater than R_2 from i will come closer than $R_{\max}$ to i. Then, after constructing the table, one need only scan through the molecules in the table to calculate energy and forces, rather than scanning through *all* molecules. After p steps one must, of course, construct the table again. If p is relatively large this can lead to substantial savings of computer time if (but *only* if) the number of entries in the table for molecule i is much less than the total number of molecules. Another procedure, to be preferred for still larger numbers of molecules, is described by Quentrec and Brot (1973).

In Sec. III.B and III.C we proceed to discuss the Monte Carlo and molecular dynamics methods. The reader interested only in the results should turn immediately to Sec. III.D.

B. The Monte-Carlo method

1. The canonical ensemble

Most Monte Carlo calculations in statistical mechanics have been performed using the canonical or (T, V, N) ensemble of Gibbs in which the number of N molecules, the volume V and the temperature T are fixed. It will be convenient to describe the method in this context, and to describe the use of other ensembles (constant pressure, grand canonical) at a later stage.

The general term "Monte Carlo method" refers to the use of random sampling techniques (for which a roulette wheel could be used) to estimate averages or integrals. In the context of statistical mechanics it refers to a particular and very efficient "importance sampling" method introduced by Metropolis *et al.* (1953) in which one generates a chain of configurations of a many-body system in such a way that the probability of a particular configuration, of energy U, appearing in the chain is proportional to $e^{-\beta U}$. Then the unweighted average of any function over the configurations of the chain gives an estimate of the canonical average of that function; for example, the pressure may be estimated by averaging the virial, the thermodynamic energy by averaging U, and so on.

The way in which the chain of configurations is generated may be described in words as follows. Suppose that we have generated M configurations and that the Mth configuration is a certain configuration j with energy U_j. The $(M+1)$th configuration is chosen as follows. Select a molecule at random and consider the configuration l derived from j by moving this molecule from its position (x,y,z) to a new position $(x+u,y+v,z+w)$, where u,v,w are numbers chosen randomly in the interval $(-\delta,\delta)$; let U_l be the energy of the configuration l. Compute $E=\exp[-\beta(U_l-U_j)]$ and select a number r chosen randomly in the interval $(0,1)$. If $E\geq r$, the $(M+1)$th configuration is l, otherwise it is j. Note that if $U_l<U_j$ the $(M+1)$th configuration is l irrespective of the value of r, so that it is not really necessary to compute the exponential. We have assumed tacitly that only the Cartesian coordinates are relevant. If, for example, molecular orientations are relevant then in generating the configuration l from j one should also rotate the molecule through an angle randomly chosen on the interval $(-\psi,\psi)$ about an axis which may be either completely randomly selected, or selected with equal probability as the x-, y-, or z-axis (Barker and Watts, 1969). The process is otherwise unchanged. The values of δ and ψ can be chosen to optimize convergence.

It can be shown that in a sufficiently long chain generated by these rules configurations l appear with probability proportional to $\exp[-\beta U_l]$, as we require for canonical averaging. However it is clear that only those configurations will appear which can be reached in a finite number of steps from the initial configuration. If not all configurations can be so reached all is not necessarily lost. For example in a hard-sphere solid at high densities in a finite system, interchange of molecules may be impossible; but configurations differing by interchange of molecules are identical and of equal weight, so correct canonical averages would still be found [cf., Ree (1971)].

A justification for the statements made above can be given briefly as follows [for more detailed discussions see Ree (1971), Wood (1968a), and especially Metropolis *et al.* (1953)]. The rules given above amount to a specification of conditional probabilities p_{jl} that the $(M+1)$th state is l given that the Mth state is j (because the probabilities for the $(M+1)$th state depend only on the Mth state the process is a *Markov process*). These transition probabilities have the property (for which they were designed) that

$$\exp[-\beta U_j]p_{jl}=\exp[-\beta U_l]p_{lj}. \tag{3.1}$$

Now it is known from the theory of Markov processes (Feller, 1950) that the probability of occurrence of configurations l (within the class of configurations accessible from the initial configuration) approach for very long chains *unique* limits w_l which are determined by the equations

$$\sum_j w_j p_{jl}=w_l. \tag{3.2}$$

These equations state that the long chain approaches a steady state in that the probability of entering a state is equal to the probability of being found in the state. But (3.2) is certainly satisfied by

$$w_l=c\exp[-\beta U_l], \tag{3.3}$$

where c is a constant, because if (3.3) is satisfied then (3.2) is a consequence of (3.1), which may be recognized as the "principle of microscopic reversibility." Thus, since the solution of (3.2) is unique it must be given by (3.3), and this is what we wished to prove.

Note that we have not used any special assumption, such as pair additivity, about the potential energy U; the method as outlined is valid in the presence of many-body forces. Choice of p_{jl} so that (3.1) is satisfied is the only (but *vital*!) requirement. However in the presence of three-body forces the calculation of (U_l-U_j) becomes very much more time consuming. In calculations on argon with three-body forces (Barker *et al.*, 1971; Barker and Klein, 1973) the three-body interactions were treated by perturbation theory, with the average of the three-body potential evaluated by summing over a subset of the chain (every 1000th configuration). For *short-range* three-body interactions the direct calculation of (U_l-U_j) at every step would not pose such serious problems.

In the procedure outlined above the basic Monte Carlo move was a displacement (translation and possibly rotation) of a single molecule. While this is most commonly used it is by no means essential. Ree (1970) performed calculations for hard disks in which *two* molecules were moved simultaneously in such a way that the center of mass remained fixed. It would also be possible to move *all* molecules simultaneously.

The quantities which can be evaluated by the Monte Carlo method are those which can be expressed as canonical averages of functions of configuration, such as pressure, energy, radial distribution function, etc. The radial distribution function is calculated in a *discrete representation* in which the number N_i of intermolecular distances in the range r_i to r_{i+1} is evaluated. We mention here a method due to Verlet (1968) for extending the range over which the radial distribution function $g(r)$ can be calculated. In general $g(r)$ is only determined for a limited range of r, say $r<R_{\max}$. However for $r>R_{\max}$ it is usually an excellent approximation to assume that the direct correlation function $c(r)$ is given by $-\beta u(r)$, where $u(r)$ is the pair potential. But if we know $g(r)$ for $r<R_{\max}$ and $c(r)$ for $r>R_{\max}$, then the Ornstein–Zernike equation can be solved to give $g(r)$ for $r > R_{\max}$. This method was tested by Verlet and found to give excellent results.

One can also evaluate some quantities, such as the specific heat C_v, which can be expressed as variances or covariances of functions of configuration, though these quantities are found with less accuracy because of the inherent difficulties of determining variances and covariances by sampling a distribution. However it is *not* possible to determine directly by the canonical Monte Carlo method the free energy A or entropy S. In fact $\exp[-\beta A]$ is the normalizing factor for the probabilities w_l, and the nature of the process of Metropolis *et al.* (1953) makes it impossible to determine this.

On the other hand one can evaluate *derivatives* of the free energy either with respect to thermodynamic variables such as V and T or with respect to parameters which appear in the potential energy function U describing the system, since these derivatives can be expressed as canonical averages. Thus, if the potential energy function $U(\vec{r},\lambda)$ depends on the parameter λ as well as on the configuration of the system (represented by the shorthand symbol $\vec{r}$ describing positions and orientations of all molecules) then we have

$$\begin{aligned}\frac{\partial A}{\partial \lambda} &= -k_B T\,\frac{\partial}{\partial\lambda}\left[\ln\int\cdots\int \exp[-\beta U]d\vec{r}\right]\\ &= \int\cdots\int \frac{\partial U}{\partial\lambda}\exp[-\beta U]d\vec{r}\Big/\int\cdots\int\exp[-\beta U]d\vec{r}\\ &= \left\langle\frac{\partial U(\vec{r},\lambda)}{\partial\lambda}\right\rangle_{\lambda}, \qquad (3.4)\end{aligned}$$

in which $\langle\,\rangle_\lambda$ means canonical averaging for the system with potential energy $U(\vec{r},\lambda)$. Hence, by performing Monte Carlo calculations for a number of values of λ one can evaluate $\partial A/\partial\lambda$ for a range of values of λ; by integrating numerically the results, free energy *differences* can be evaluated, according to the equation

$$A(\lambda) - A(\lambda_0) = \int_{\lambda_0}^{\lambda}\left\langle\frac{\partial U(\vec{r},\lambda)}{\partial\lambda}\right\rangle_{\lambda} d\lambda. \qquad (3.5)$$

Perhaps the most familiar example of this is the case where λ is the *volume* V, introduced into the potential energy by the "scaling" transformation discussed in Sec. I. In this case (3.5) becomes the thermodynamic relation

$$A(V_1) - A(V_0) = -\int_{V_0}^{V_1} p\,dV, \qquad (3.6)$$

with the pressure given by the virial expression,

$$\frac{pV}{Nk_BT} = 1 - \left\langle\sum_i \vec{r}_i\cdot(\partial U/\partial\vec{r}_i)_v\right\rangle\Big/(\nu N k_B T), \qquad (3.7)$$

where ν is the dimensionality of the system. These results have been used to calculate the free energy of dense fluid systems by integrating from low densities (large volumes), where the free energy is known, to high densities. Results have been obtained in this way for hard disks and spheres (Alder *et al.*, 1968; Hoover and Ree, 1968) and for the 6–12 fluid (Hansen and Verlet, 1969). It should be noted that these integrations must be carried out along paths which are *reversible* in the thermodynamic sense, in order that the derivative be uniquely defined. This created special difficulties in the study of the 6–12 liquid made by Hansen and Verlet, since an isothermal path from low (gas) density to high (liquid) density had to pass through density ranges in which one-phase states were metastable and unstable with respect to two-phase states. To avoid this difficulty, Hansen and Verlet imposed constraints limiting the possible fluctuations in the number of molecules in subvolumes of their system, thus preventing phase separation. Because the subvolumes themselves contained a relatively large number of molecules these constraints were expected to have little effect on thermodynamic functions.

A rather similar idea was used to calculate the free energy of hard-sphere and hard-disk solids (Hoover and Ree, 1968) and of the 6–12 solid (Hansen and Verlet, 1969). In these cases the systems studied were "single-occupancy" models in which the volume was divided into cells each constrained to hold exactly one molecule. These systems behave reversibly as volume is increased so that the free energy difference between systems at solidlike densities and very low densities can be calculated from (3.6) and (3.7). However at very low densities the free energy can be calculated exactly. Furthermore, at solidlike densities the cell constraints have no effect (they are automatically satisfied). Thus, in this way the free energy of the solid phase can be determined. But knowing the free energy and pressure for solid, liquid and gaseous phases one can proceed by thermodynamics to construct the phase diagram; we shall return to this in Sec. III.D.

Hansen and Pollock (1975) calculated the free energy of the 6–12 solid by integrating (3.6) from a high density at which the harmonic approximation becomes valid, and confirmed the results of Hansen and Verlet (1969).

Another familiar result is found if we choose the parameter λ to be temperature T. In this case (3.5) can be cast in the form

$$A(T_1)/T_1 - A(T_0)/T_0 = -\int_{T_0}^{T_1}\langle U\rangle_T (dT/T^2), \qquad (3.8)$$

which will be recognized as an integrated form of the Gibbs–Helmholtz equation

$$A = E - TS = E + T(\partial A/\partial T). \qquad (3.9)$$

Using (3.8) one can calculate, by performing Monte Carlo simulations at a series of temperatures, the temperature variation of the free energy, and if the free energy is known at one temperature (e.g., near $T = 0$) the absolute free energy can be determined. For example, at sufficiently low temperatures the free energy of the 6–12 solid can be determined by standard methods of lattice dynamics (Klein and Koehler, 1976), since the motions become essentially harmonic. By using these results together with (3.8) the free energy could be calculated at all temperatures. This procedure, which was proposed by Hoover and Ree (1968), provides an alternative to the procedure of Hansen and Verlet (1969) discussed above, but has not so far been implemented.

Another possibility for calculating the free energy of a *liquid* is to use both (3.6) and (3.8), by integrating with (3.6) from low density to high density at a high temperature (sufficiently above the critical temperature to avoid two-phase and critical regions); and then to integrate using (3.8) down to a low temperature (at constant volume). In this way one makes use of van der Waals' "continuity of gaseous and liquid states"! This method was used by Lee *et al.* (1973) to calculate the free energy of clusters of 6–12 molecules, but has not so far been implemented for bulk fluids. In fact by combined use of (3.6) and (3.8) one could calculate free energy changes along any reversible path in the (T, V) plane.

The usefulness of (3.5) is by no means confined to the case where λ is a thermodynamic variable such as V or T. One can, in a very general way, introduce a parameter λ (or several parameters) into $U(r, \lambda)$ which changes a system of simple or known properties ($\lambda = \lambda_0$) into a more complicated system which is the system of interest ($\lambda = \lambda_1$). For example, the parameter may modify the pair potential, so that we have

$$U(\vec{r}, \lambda) = \sum_{i<j} u(r_{ij}; \lambda), \tag{3.10}$$

where for example $u(r_{ij}; \lambda_0)$ might be the hard-sphere potential and $u(r_{ij}; \lambda_1)$ the 6–12 potential or some other realistic potential. If we follow this idea and replace the integral in (3.5) by a truncated Taylor series

$$\begin{aligned} A(\lambda_1) - A(\lambda_0) = {} & \left[\frac{\partial}{\partial\lambda}\langle U(\vec{r}, \lambda)\rangle_\lambda\right]_{\lambda=\lambda_0} (\lambda_1 - \lambda_0) \\ & + \frac{1}{2}\left[\frac{\partial^2}{\partial\lambda^2}\langle U(\vec{r}, \lambda)\rangle_\lambda\right]_{\lambda=\lambda_0} (\lambda - \lambda_0)^2 + \dots \end{aligned} \tag{3.11}$$

we are led to the perturbation theories which are discussed in Sec. VII. The great advantage of (3.11) is that it requires detailed information only on the reference system (with $\lambda = \lambda_0$); the corresponding penalty is that the Taylor series is not necessarily rapidly convergent (though it *is* rapidly convergent for the example of hard-sphere and 6–12 potentials given above). In cases where $(\lambda_1 - \lambda_0)$ is a natural "smallness parameter" (for example, for the three-body interactions and quantum corrections discussed in Sec. III.D below) Eq. (3.11) is a very useful and powerful result. But Eq. (3.5) will always work, provided that the computer does enough work!

This perturbation technique can also be used to evaluate quantities other than free energy. Thus suppose that we have a system for which the potential energy is given by

$$U = U_0 + \lambda U_1 \tag{3.12}$$

and that we wish to evaluate for this system, to first order in λ, the average of some function X of configuration, which may also depend on λ according to

$$X = X_0 + \lambda X_1. \tag{3.13}$$

Then we have

$$\begin{aligned} \langle X\rangle_\lambda &= \langle X \exp[-\beta\lambda U_1]\rangle_0 / \langle \exp[-\beta\lambda U_1]\rangle \\ &= [\langle X_0\rangle_0 + \lambda\langle X_1\rangle_0 - \beta\lambda\langle X U_1\rangle_0] / [1 - \beta\lambda\langle U_1\rangle_0] + 0(\lambda^2) \\ &= \langle X_0\rangle_0 + \lambda\langle X_1\rangle_0 - \beta\lambda[\langle X_0 U_1\rangle_0 - \langle X_0\rangle_0\langle U_1\rangle_0] + 0(\lambda^2). \end{aligned} \tag{3.14}$$

Thus, for this purpose we must evaluate the covariance of X_0 and U_1 in addition to the averages of X_0 and X_1. In these equations X could be the virial, required to determine the pressure; or the energy itself, $(U_0 + \lambda U_1)$; or the radial distribution function (RDF) (N_i in the discrete representation). These formulae were used by Barker *et al.* (1971) and Barker and Klein (1973) to evaluate three-body and quantum corrections to the pressure, energy and specific heat of argon, and explicit formulae for these cases are given in the two cited papers. They were also used by Barker (1973) to evaluate three-body and quantum corrections to the RDF of argon; the resulting RDF was compared with their experimental data, with excellent agreement, by Yarnell *et al.* (1973). Note that in (3.14) there are distinct terms of order λ. The first, $\lambda\langle X_1\rangle_0$, is the direct contribution of λX_1 to the average; the second, covariance, term is an indirect contribution due to the modification of the structure of the system by λU_1 which in turn modifies the average of X_0. These terms are in general of comparable order of magnitude.

Squire and Hoover (1969) used Eq. (3.5) to evaluate the free energy of formation of vacancies in a crystal. In Sec. IX we discuss a parametrization based on a modified periodic boundary condition which changes a bulk liquid into a set of slabs, thus creating free surfaces and permitting the calculation of surface free energy (i.e., surface tension). The invention of such processes is a fertile field. The power of the Monte Carlo method lies in the fact that the Gedanken experiments of classical thermodynamics can actually be performed quantitatively.

The relatively large number of Monte Carlo calculations that may be required to evaluate the integral in (3.5) has motivated a number of attempts to find methods for calculating $A(\lambda_1) - A(\lambda_0)$ when λ_1 is not necessarily very close to λ_0 using Monte Carlo data only for the systems with $\lambda = \lambda_0$ and $\lambda = \lambda_1$ (so-called "direct" methods) (McDonald and Singer, 1967; Bennett and Alder, 1971; Valleau and Card, 1972; Torrie, *et al.*, 1973; Patey and Valleau, 1973; Torrie and Valleau, 1974; Bennett, 1974; Torrie and Valleau, 1976).

Given two systems with potential energy functions U_0 and U_1, the difference between their free energies is given by

$$\begin{aligned} A_1 - A_0 &= -kT \ln\left[\int e^{-\beta U_1} d\vec{r} \Big/ \int e^{-\beta U_0} d\vec{r}\right], \\ &= -kT \ln\langle e^{-\beta\Delta}\rangle_0, \end{aligned} \tag{3.15}$$

where

$$\Delta = U_1 - U_0. \tag{3.16}$$

An optimized procedure for evaluating this free-energy difference using purely Boltzmann averages for the systems and 0 and 1 is described by Bennett (1974). This procedure was used for the calculation of surface tension of a liquid by Miyazakai *et al.* (1976).

Equation (3.15) can be written in the form

$$A_1 - A_0 = -kT \ln\left[\int_{-\infty}^{\infty} f_0(\Delta U) \exp(-\beta\Delta U) d\Delta U\right], \tag{3.17}$$

where $f_0(\Delta U)$ is the probability density of ΔU in the canonical ensemble for U_0. Unfortunately, direct Boltzmann averaging usually does not lead to good estimates of $f_0(\Delta U)$ in the range of values of ΔU which contribute importantly to the integral in (3.17). This can be remedied, as Valleau and co-workers have shown, by generating a Markov chain with limiting probabilities proportional to $W(\vec{r})\exp(-\beta U_0)$ rather than simply $\exp(-\beta U_0)$. We shall denote averages over such a chain by $\langle\,\rangle_W$. The weighting function W can be chosen by trial and error to optimize the estimate of $f_0(\Delta U)$. The weighting functions used by Valleau and co-workers had the form

$$W(\vec{r}) = W(\Delta U). \tag{3.18}$$

The Boltzmann average of an arbitrary function $\theta(\vec{r})$ can be recovered from the non-Boltzmann average by the relation

$$\langle\theta\rangle_0 = \langle\theta/W\rangle_W/\langle 1/W\rangle_W. \tag{3.19}$$

Similarly the probability density $f_0(\Delta U)$ can be recovered from the probability density $f_W(\Delta U)$ in the weighted system by the relation

$$f_0(\Delta U) = f_W(\Delta U)/[W(\Delta U)\langle 1/W\rangle_W]. \tag{3.20}$$

Use of these methods leads to substantial gains in computational efficiency. A more detailed review is given by Valleau and Torrie (1976a,b).

Another procedure for calculating the free energy of a fluid was explored for the case of the hard-sphere fluid by Adams (1974). This was based on a result for the chemical potential derived by Widom (1963), that μ is given by

$$\mu = -k_B T\{\ln(V/N) + \tfrac{3}{2}\ln(2\pi m k_B T/h^2) + \ln[\langle\exp(-\beta\psi)\rangle_N]\}. \tag{3.21}$$

Here ψ is the potential energy change due to adding one more molecule to a system of N molecules; the canonical average $\langle\,\rangle_N$ is evaluated for the system of N molecules. This method, which gave reasonable results for densities which were not too high, is closely related to the grand canonical method discussed below. It is also related to the ideas of the Scaled Particle Theory (Sec. V), and Adams used his results to test that theory.

2. The constant-pressure ensemble

The constant-pressure or (T,N,p) ensemble is most conveniently described by introducing dimensionless variables scaled by the edge L of the fundamental cube (Wood, 1968a,b; 1970)

$$\vec{r}_i' = \vec{r}_i/L. \tag{3.22}$$

The un-normalized weighting function $P(\vec{r}',L)$, which in the canonical case is just $\exp(-\beta U)$, becomes in this case $\exp\{-\beta[U(L\vec{r}') + pL^\nu - \nu N\ln L]\}$, with ν the dimensionality of the system. A Monte Carlo chain for this ensemble can be generated exactly as described for the canonical ensemble, except that the basic step involves not only changing the dimensionless coordinates $\vec{r}_i'$ of one of the molecules i, but also changing L by a number uniformly distributed on the interval $(-\delta_L, \delta_L)$ where δ_L may be chosen to optimize convergence. The quantity which determines acceptance or otherwise of a move is not just ΔU, as in the canonical case, but $\Delta[U(L\vec{r}') + pL^\nu - \nu N\ln L]$. This method has obvious advantages if we are actually interested in results at a particular pressure, usually zero pressure. It was used by McDonald (1969) to calculate excess enthalpies and volumes of mixtures at zero pressure. Vorontstov-Vel'yaminov *et al.* (1970) also used this ensemble to study a single-component fluid.

The average of a function $F(\vec{r})$ of configuration in the constant pressure ensemble is given by

$$\langle F\rangle = \int_0^\infty dL \int d\vec{r}' F(L\vec{r}')P(\vec{r}',L) \Big/ \int_0^\infty dL \int d\vec{r}' P(\vec{r}',L). \tag{3.23}$$

For "hard-sphere" particles in any number of dimensions, Wood (1968a,b; 1970) showed that an alternative and convenient realization of the constant pressure ensemble could be obtained by explicitly performing the integrations over L in (3.23). For details of this we refer to the original papers. This method has the advantage that the pressure is obtained directly rather than by extrapolating the RDF $g(r)$ to the hard-sphere diameter d.

3. The grand-canonical ensemble

The grand-canonical ensemble or $(TV\mu)$ ensemble in which the chemical potential is fixed rather than the number of molecules had not been used for Monte Carlo calculations on realistic potentials until fairly recently. However Norman and Filinov (1969), Adams (1974, 1975) and Rowley *et al.* (1975) have used different methods to implement the use of this ensemble. The great advantage is that it leads directly to estimates of the free energy (since the chemical potential is fixed).

Using the same "scaled" coordinates as for the constant pressure ensemble, the un-normalized weighting function $P(\vec{r}',N)$, where N is the number of molecules, is given by

$$P(\vec{r}',N) = \exp\{-[k_B T\ln N! + N k_B T\ln V + U(\vec{r}',N) - N\mu]/k_B T\}. \tag{3.24}$$

If N were a continuous variable, one could proceed exactly as described for the constant pressure ensemble, with acceptance of a move being decided by the Metropolis procedure applied to (3.23). However N, if it is to change, must change by at least ±1, and except for low densities and/or high temperatures the probability of this is very low. Thus, it is essential to consider a Markov process with three possible steps: (i) a molecule is moved (probability α_0); (ii) a molecule is added (probability α_+); (iii) a molecule is removed (probability α_-). One requires $\alpha_+ = \alpha_-$, $\alpha_0 + \alpha_+ + \alpha_- = 1$. In adding a molecule its position is chosen randomly in the cell. Norman and Filinov (1969) used essentially this procedure, with the type of move [(i), (ii), or (iii)] being decided randomly. They tried moves in which more than one molecule was added or removed, and found $\Delta N = \pm 1$ only to be preferred—except at low densities the probability of adding or removing more than one molecule is negligible, so that attempts at such moves are wasted labor. By varying α_0 they found that $\alpha_0 = \alpha_+ = \alpha_- = 1/3$ appeared to be optimal.

In this process the number of molecules, and hence the density, must be determined by averaging N; the pressure may be determined by averaging the virial and the energy by averaging U as usual. Norman and Filinov generated only short Monte Carlo chains (approximately 10^4 steps) and their results were therefore essentially qualitative for the liquid phase. However they were able to demonstrate the abrupt change of density (gas–liquid phase transition) at a particular chemical potential (for a 6–12 fluid), and their gas-phase pressure agreed well with that obtained from the virial series.

Adams (1974, 1975) used a very similar process except that moves of type (i) and of type (ii) or (iii) were performed *in turn*, with the choice between (ii) and (iii) being made randomly (with equal probabilities). Thus the overall numbers of types (i), (ii), and (iii) were in the ratios 1/2, 1/4, 1/4. Results were obtained for hard spheres (Adams, 1974) up to density $\rho\sigma^3=0.7912$ and even at this relatively high density were in good agreement with the accurate equation of state of LeFevre (1972). Note that in this paper Adams described an *approximate* grand canonical method to be used if one wishes to fix the *excess* (over ideal gas) chemical potential μ', and an *exact* method to be used if one wishes to fix $(\mu'+k_BT\ln\langle N\rangle)$. Since the latter quantity is just the absolute chemical potential μ (apart from a constant involving the known volume V) it is much better to fix this and to use the exact method. One cannot determine the excess of the chemical potential over that of an ideal gas at the same density until the density is known! Adams (1975) also obtained results for the 6–12 fluid at high temperatures ($T^*=2.0$ and 4.0). At $T^*=2.0$ the results gave reasonable agreement for pressure and energy with those interpolated from the canonical ensemble results of Verlet and Weis (1972a)—note however that this agreement does not check the chemical potentials or free energies. It is perhaps worth noting that Adams mentions that the ensemble averages can show great sensitivity to shortcomings in the random number generator used.

In his calculations Adams added a long-range correction to compensate for the truncation of the potential at each step of the calculation, in particular in calculating the value of ΔU on which the decision whether to accept a move is based. The long-range correction is given, if $R_{\max}$ is the distance at which the potential is truncated by

$$U_{1r}=\frac{N^2}{V}2\pi\int_{R_{\max}}^{\infty}r^2u(r)dr. \tag{3.25}$$

If this is done the Helmholtz free energy A can be calculated straightforwardly from the equation

$$A/N=\mu-(pV/N), \tag{3.26}$$

where p is the pressure for the *untruncated* potential. If the long-range correction is *not* added in this way then care must be taken in adding it at a later stage. In particular, the pressure for the truncated potential [which must be used in (3.26) if one wishes to calculate the Helmholtz free energy for the truncated potential] is *not* given by the truncated integral of the virial

$$\frac{pV}{Nk_BT}=1-\frac{2\pi\rho}{3}\int_0^{R_{\max}}r^3u'(r)g(r)dr. \tag{3.27}$$

but rather by the expression

$$\frac{pV}{Nk_BT}=1-\frac{2\pi\rho}{3}\int_0^{R_{\max}}r^3u'(r)g(r)dr+\frac{2\pi}{3}\rho R_{\max}^3u(R_{\max})g(R_{\max}), \tag{3.28}$$

in which the last term arises from the δ function in $u'(r)$, $-u(R_{\max})\delta(r-R_{\max})$, at the point of truncation. Usually one replaces $g(R_{\max})$ by 1. For potentials behaving like r^{-6} for $r\geq R_{\max}$ the last term is equal to the long-range energy per particle U_{1r}/N, with U_{1r} given by (3.25); it is also equal to *one-half* of the usual "long-range pressure correction" given by

$$-\frac{2\pi\rho}{3}\int_{R_{\max}}^{\infty}r^3u'(r)dr.$$

Of course it is not necessary in practice to evaluate the logarithm of $N!$ in the exponent of (3.24), which is given purely for clarity of exposition. Because of the obvious result,

$$e^{-\Delta\ln N!}=\frac{1}{N+1},\quad \Delta N=1$$
$$=N,\quad \Delta N=-1, \tag{3.29}$$

the probabilities of adding a molecule [type (ii) move] or removing one [type (iii)] are given by the Metropolis criterion as $\min[VZe^{-\beta\Delta U}/(N+1),1]$ and $\min[Ne^{-\beta\Delta U}/(VZ),1]$ respectively, where Z is $e^{\beta\mu}$.

An alternative and less transparent implementation of the grand canonical ensemble is given by Rowley *et al.* (1975). In this formulation one considers a set of M molecules (M being larger than the maximum number of molecules that can fit in the available volume). With each molecule there is associated an "occupation number" n_i having the value 0 or 1; if n_i is 0 the molecule is regarded as "fictitious" and not included in calculating the energy, if it is 1 the molecule is regarded as "real" and included in calculating the energy. Apart from this the "real" and "fictitious" molecules are treated on equal footing. A mathematical argument leads to the following transition probability rules: select in order a molecule from *all* real and fictitious molecules; with probability 1/2, simply move it as in the canonical method; *or*, also with total probability 1/2, change it from fictitious to real with probability $\min[ZVe^{-\beta\Delta U}/(M-N),1]$ (if fictitious) or from real to fictitious with probability $\min[(M-N+1)e^{-\beta\Delta U}/(ZV),1]$ (if real). Mathematically, the ensemble generated by these rules appears to be identical with the grand canonical ensemble. There is a "memory" effect in that a "fictitious" molecule remains in the neighborhood of the "hole" from which it is removed, and so may be more likely to be made "real" again at a subsequent attempt. However there is no reason why this should lead to incorrect results.

Rowley *et al.* (1975) made several calculations for the 6–12 fluid at the reduced temperature $T^*=1.15$. Their results for the free energy at liquid densities differed substantially from those calculated using the restricted canonical ensemble by Hansen and Verlet (1969). The differences were much larger than the combined statistical uncertainties. Torrie and Valleau (1974) obtained a value for the free energy at $T^*=1.15$ using their "direct" canonical method which agreed almost exactly with that of Hansen and Verlet. Miyazaki and Barker (1975) used a grand canonical method very similar to that of Adams (1975) to calculate free energies at $T^* = 1.15$ and four densities in the liquid range; their values agreed closely with those of Hansen and Verlet. Finally the Barker–Henderson perturbation theory and the optimized cluster theory of Weeks, Chandler, and Andersen (see Sec. VII.D) give results agreeing very closely with those of Hansen and Verlet. Thus, it is almost certain that the results of Rowley *et al.* are incorrect. The discrepancy is of the same order of magnitude as the long-range corrections discussed above, but its origin is unclear.

The grand-canonical methods work best at higher temperatures and low densities. At higher densities the methods of Torrie and Valleau (1974) or Bennett (1974) are to be preferred.

4. The microcanonical ensemble

For the sake of completeness we mention here that the method of molecular dynamics discussed below may be regarded (if used for equilibrium studies) as generating configurations of the microcanonical or (EVN) ensemble. Strictly speaking, the total momentum is also fixed, and this leads to corrections of order $1/N$ (Ree, 1971). Thermodynamic calculations like those described in connection with the canonical ensemble can also be made using this method, via the relation

$$TdS = dE - p dV, \tag{3.30}$$

in which now both T and p are statistical quantities, the temperature T being derived from the mean kinetic energy,

$$\langle KE \rangle = (\nu/2) k_B T, \tag{3.31}$$

for a monatomic fluid, and p from the average of the virial. However, to our knowledge (3.30) has not been used in this way.

5. Quantum statistical mechanics

The methods of classical statistical mechanics so far discussed are valid for all substances at sufficiently high temperatures, but at low temperatures there are quantum-mechanical deviations from classical behavior. These are of two kinds: (i) effects of statistics (and possibly spin), and (ii) diffraction effects. The effects of statistics (and spin) are very small for all liquids except for liquid helium below or just above the λ temperature, and will not be discussed further. The diffraction effects, on the other hand, are appreciable at higher temperatures. They arise from the fact that paths other than the classical paths contribute to the evolution of the system.

For most liquids these effects on equilibrium properties are adequately described by an expansion in powers of h^2 (for analytic potentials; Wigner, 1932; Kirkwood, 1933a, b) or h (for non-analytic potentials; Gibson, 1975a, b), of which the first two or three terms are readily evaluated by the Monte Carlo procedures already described.

For spherical molecules with analytic potentials (but not necessarily pair-additive potentials) the Helmholtz free energy is given by

$$\begin{aligned} A/Nk_BT &= \frac{A_{\rm cl}}{Nk_BT} + \frac{h^2}{96\pi^2 (k_BT)^2 m} \left\langle \sum_i \nabla_i^2 U \right\rangle_{\rm cl} + 0(h^4) \\ &= \frac{A_{\rm cl}}{Nk_BT} + \frac{h^2}{96\pi^2 (k_BT)^2 m} \left\langle \sum_i (\vec{\nabla}_i U)^2 \right\rangle_{\rm cl} + 0(h^4) . \end{aligned} \tag{3.32}$$

Exchange effects are not included in the above expansion. Such exchange effects are negligibly small at the high temperatures at which (3.32) can reasonably be applied (Hill, 1968, 1974; Bruch, 1973). The identity of the two forms for (3.32) can be shown by an integration by parts (Green 1951). Alternatively, the canonical partition function Z_N is given to order h^2 by

$$Z_N = \frac{\lambda^{-3N}}{N!} \int \exp\left[-\beta\left(U + \frac{h^2}{96\pi^2 m k_B T} \sum_i \nabla_i^2 U\right)\right] d\vec{r}_1 \cdots d\vec{r}_N, \tag{3.33}$$

where $\lambda = h/(2\pi m k_B T)^{1/2}$. By differentiating this with respect to temperature and volume one can derive expressions for thermodynamic energy and pressure which are valid to order h^2; these are given explicitly by Barker *et al.* (1971) and have the general form given in Eq. (3.14). Although these results are correct it must be noted that the exponential in (3.32) is *not* the correct configuration-space probability density to order h^2. The quantum corrections in (3.31) and (3.33) include corrections *both* to potential energy and kinetic energy; expressions for the kinetic energy corrections are given by Gibson (1974, 1975a, b). The correct configuration-space probability density w is given, for analytic potentials, to order h^2 by (Landau and Lifschitz, 1969)

$$w = \text{const} \times \exp\left[-\beta\left\{U - \frac{h^2}{96\pi^2 (k_BT)^2 m} \sum_i (\vec{\nabla}_i U)^2 + \frac{h^2}{48\pi^2 (k_BT)^2 m} \sum_i \nabla_i^2 U\right\}\right]. \tag{3.34}$$

This result was used by Barker (1973) in conjunction with Eq. (3.14) to calculate quantum corrections to the radial distribution function of liquid argon. Landau and Lifschitz (1969) also give results for the momentum-space probability density. Note that in quantum mechanics (even to order h^2) the configuration-space and momentum-space probabilities are correlated, not independent as in classical statistical mechanics.

Hansen and Weis (1969) calculated both h^2 and h^4 corrections to the free energy for the 6–12 potential, and applied their results to liquid neon. Detailed expressions for the term of order h^4 are well known and are given for example by Hill (1968). The term of order h^4 proved to be negligible for liquid neon, and therefore *a fortiori* for heavier inert gas liquids.

The above results are valid for spherical molecules. The basic theory for calculation of quantum effects for nonspherical molecules was given by Kirkwood (1933b). Detailed results for axially symmetrical molecules to order h^2, with dipolar and quadrupolar interactions, are given by Singh and Datta (1970), McCarty and Babu (1970), and Pompe and Spurling (1973). These results are given for second virial coefficients but the extension to higher densities is obvious if one is prepared to use the Monte Carlo method. Pompe and Spurling (1973) also evaluate the term of order $\hbar^4$, which was earlier evaluated by Wang Chang (1944). Extension to nonaxially symmetric molecules could be made following the methods of Kirkwood (1933b).

If the quantum effects are so large that the Wigner–Kirkwood expansion discussed above does not show satisfactory convergence there is no generally satisfactory method which has been applied to liquids at nonzero temperatures. Bruch *et al.* (1974) have proposed the use of essentially classical methods with $\exp[-\beta u(r)]$ replaced by a two-body Slater sum. While this is not exact, if may prove to be a useful approximation.

For the *ground* state of liquid helium, if one assumes a variational wave function ψ, the expression for the expectation value of the energy can be cast in the form of a "canonical" average for a fictitious classical liquid with $|\psi|^2$ replacing $e^{-\beta U}$ (McMillan, 1965), and the classical Monte Carlo method may be used to evaluate the expectation value of the Hamiltonian (Schiff and Verlet, 1967; Hansen *et al.*, 1971; Murphy and Watts, 1970; Murphy, 1971). The ground-state energy of liquid helium has been calculated in this way using Jastrow wave functions [i.e., wave functions of the form $\prod_{i<j} f(r_{ij})$]. However, this method cannot be used at nonzero temperatures.

Perhaps the most promising approach to a quantum-mechanical method for nonzero temperature is use of the Feynman path integral formulation of quantum statistical mechanics (Feynman and Hibbs, 1965) or the equivalent Wiener integral formulation, which has been used successfully for evaluating second and third virial coefficients of helium by Fosdick and Jordan (Fosdick and Jordan, 1966; Jordan and Fosdick, 1968; see also Storer, 1968; Klemm and Storer, 1973; Jorish and Zitserman, 1975). A form of the quantum-mechanical partition function which has exactly the form of a *classical* partition function is given by Bruch (1971); this may be derived either as a Riemann sum approximation to the path-integral expression for the partition function (Feynman and Hibbs, 1965), or by a variational method developed by Golden (1965). If there are N molecules in the system and an L-point Riemann sum is used then the partition function has the form of a classical partition function for a system of $L \times N$ molecules, so that the Metropolis Monte Carlo technique could, in principle, be applied for a many-body system. However no results for many-body systems using this method have been published. Actually Bruch's results are presented for a two-body system (second virial coefficient) but they can be generalized in an obvious way to many-body systems.

Kalos (1970) describes a method for solving the Schrödinger equation by a Monte Carlo technique for iterating the kernel of an integral equation, and this has been applied to liquid helium by Kalos *et al.* (1974). It may be possible to generalize this method to nonzero temperatures. Another possible method (Fermi–Ulam method) based on a diffusive process with birth and death has been discussed most recently by Anderson (1975).

Quantum mechanical study of *dynamical* properties poses an even more difficult problem which has not been attacked by computer simulation. Heller (1975) describes a "wavepacket path integral formulation of semiclassical dynamics" which indicates one possible line of attack.

6. Long-range interactions

In plasmas, fused salts, and aqueous solutions of ions the Coulomb potential plays a very important role, and the truncation of the potential which is used in most simulation studies is unsatisfactory. This problem has been met by using the Ewald summation technique to sum the interactions to infinite distance, using the periodicity resulting from periodic boundary conditions (Brush *et al.*, 1966; Barker, 1965). Since the Coulomb potential will not be discussed further, we give no details but refer to the original publications.

The dipole–dipole potential is also long ranged and this gives rise to serious difficulties in connection with the dielectric properties of dipolar fluids, since truncating the potential produces a "depolarizing" field which suppresses fluctuations in the polarization. Two ways dealing with this difficulty are available: the inclusion of an Onsager reaction field to cancel the depolarizing field produced by truncating the potential (Barker and Watts, 1973; Watts, 1974) and the use of the Ewald summation method (Jansoone, 1974). Recent unpublished Monte Carlo work by Adams and McDonald (1976) indicates that these two different methods lead to similar but not identical results. A useful examination of this question is given by Smith and Perram (1975). Further investigation is required.

C. The method of molecular dynamics

1. General remarks

The computational procedure in molecular dynamics involves numerical solution of the Newtonian equations of motion (for spherical molecules) or the coupled Newton–Euler equations of motion for translations and rotations (for rigid nonspherical molecules). These are sets of several hundred to several thousand ordinary differential equations which can be handled quite readily by modern computers. Difficulties arise when there are very fast and very slow motions present, since a time-step small enough to describe the fast motions will require unreasonably long computations to describe the slow motions. This has so far prevented detailed study of polymer motions, for example. For the kinds of molecules we are going to discuss this is not a serious problem (except to some extent in the case of water), and we shall not discuss it further.

Many important computations were made for hard-sphere and square-well potentials, for which a particularly convenient algorithm is available. We will discuss this briefly before considering continuous potentials.

2. Hard-sphere and square-well potentials

The first molecular dynamics calculations (Alder and Wainwright, 1957, 1959; Alder *et al.*, 1972) were made using hard-sphere and square-well potentials. These potentials have the property that the forces between the particles are zero except for implusive forces when the particles reach particular distances (the hard-sphere diameter σ and the distance $\lambda\sigma$ corresponding to the outer wall of the square well). Thus the dynamics breaks down essentially into a series of binary collisions between which the molecules move in straight lines. Given a set of molecular coordinates and velocities immediately *after* a collision one can calculate when the *next* collision will occur and proceed immediately to that time to evaluate the changes of velocities of the two particles concerned by conservation of energy and momentum. Thus the basic time-step for the computation is effectively equal to the mean time between collisions, whereas for *continuous* potentials the time-step must be small compared to the *duration* of a collision, a much shorter time. This leads to very fast computations, so that the dynamics can be followed over relatively long times. A full account of the method for these potentials is given by Alder and Wainwright (1959), and a briefer account by Ree (1971).

3. Continuous potentials

Several algorithms have been used for continuous potentials for spherical molecules. Gibson *et al.* (1960), who performed molecular dynamics calculations in connection with radiation damage in solids, used a two-step central difference algorithm

$$\vec{v}_i(t+\Delta t/2)=\vec{v}_i(t-\Delta t/2)+(\Delta t/m)\vec{f}_i(\vec{r}(t)) \tag{3.35}$$

and

$$\vec{r}_i(t+\Delta t)=\vec{r}_i(t)+(\Delta t)\vec{v}_i(t+\Delta t/2), \tag{3.36}$$

where $\vec{f}_i$ is the force on the ith particle, $-\vec{\nabla}_i U$. Rahman (1964), who made the first dynamics computations for fluids with continuous potentials, first used a predictor-corrector method, but in later work on water (Rahman and Stillinger, 1971) adopted a higher-order method of the type described by Nordsieck (1962). The latter method gives high-order accuracy while requiring explicit evaluation only of the forces (not derivatives of the forces). Verlet (1967) introduced a simple one-step central difference algorithm

$$\vec{r}_i(t+\Delta t)=-\vec{r}_i(t-\Delta t)+2r_i(t)+(\Delta t)^2/m\vec{f}_i(r_i(t)). \tag{3.37}$$

With this algorithm the velocities are not required, but may be evaluated by the central difference formula

$$\vec{v}_i(t)=[\vec{r}_i(t+\Delta t)-\vec{r}_i(t-\Delta t)]/(2\Delta t). \tag{3.38}$$

The initial coordinates may be chosen in a number of ways. At the beginning of a problem one may start from a perfect crystal lattice; if the equilibrium state is liquid, the configuration normally rapidly approaches liquid-like states. Most often one will start with a near-equilibrium configuration from the end of a previous computation. The velocities are normally given an initial Maxwell distribution to speed the approach to equilibrium. We note that the equations of motion are such that the initial periodicity due to the periodic boundary conditions is maintained at all later times.

The longest time over which meaningful dynamical results can be obtained is of the order L/c, where L is the edge of the periodic box, and c the velocity of sound. For times longer than this the periodic boundary condition can lead to spurious behavior.

4. Evaluation of static and dynamic properties

The static equilibrium properties are evaluated by means of time averages

$$\langle A\rangle=\frac{1}{\Theta}\int_0^{\Theta}A(t)dt \simeq\frac{1}{M}\sum_{m=1}^{M}A(m\Delta t), \tag{3.39}$$

in which A could be, for example, the kinetic energy, from which the temperature may be evaluated, the virial, the RDF, etc. In (3.39) it is assumed that the system has reached equilibrium at $t=0$, and Θ is a sufficiently long time, normally the whole duration of the computer "experiment," apart from the preliminary "equilibration" stage.

Those measurable dynamical properties, such as (frequency-dependent) viscosity, self-diffusion constant, thermal conductivity, the results of neutron and optical spectroscopic measurements etc., which involve the linear response to an external probe, can be expressed (Berne, 1971) by means of Green–Kubo formulae in terms of *equilibrium* averages of time correlation functions of the form

$$\langle A(0)A(\tau)\rangle=\frac{1}{\Theta}\int_0^{\Theta}A(t)A(t+\tau)dt \simeq\frac{1}{M-n}\sum_{m=1}^{M-n}A(m\Delta t)A(\{m+n\}\Delta t),\quad \tau=n\cdot\Delta t. \tag{3.40}$$

The nature of the functions A corresponding to various measurable properties is described by Berne (1971). In particular the dynamic structure factor $S(\vec{k},\omega)$ is given by

$$S(\vec{k},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}I(\vec{k},\tau)d\tau, \tag{3.41}$$

where

$$I(\vec{k},\tau)=\frac{1}{N}\sum_{l,m=1}^{N}\langle\exp[-i\vec{k}\cdot\vec{r}_l(0)]\exp[i\vec{k}\cdot\vec{r}_m(\tau)]\rangle \tag{3.42}$$

(Chen, 1971). This function has been studied for the 6–12 fluid by Levesque *et al.* (1973), who also evaluated viscosity and the self-diffusion coefficient [the latter quantity had also been evaluated by Rahman (1964) and Levesque and Verlet (1970)]. Levesque *et al.* (1973) find evidence for the existence of a large-time "tail" in the Green–Kubo function for viscosity [cf., Alder and Wainwright (1967, 1970)], which means that the precise evaluation of viscosity by this route may be very difficult.

As an alternative to the study of transport properties using equilibrium time correlation functions one can use *nonequilibrium* molecular dynamics to study a system in which, for example, velocity gradients are present (for the case of viscosity). This has been done by Ashurst and Hoover (1975), Hoover and Ashurst (1975), and Gosling *et al.* (1973).

D. Results of computer simulations

1. Hard spheres in ν dimensions

Hard-sphere systems, with potential given by Eq. (2.4), are of great interest because of the light they cast on the question of the melting transition and because of their use as reference systems for perturbation theories. We note that the partition function for the *one-dimensional* hard-sphere system can be evaluated exactly (Tonks 1936); the pressure is given by

$$\frac{pL}{Nk_BT}=\frac{1}{1-(L/Nd)}\,. \tag{3.43}$$

There is no phase transition, in accord with the theorem of van Hove, which states that there can be no phase transition for a one-dimensional system with interactions of finite range.

There have been very extensive and careful studies by both Monte Carlo and molecular dynamics methods of the equilibrium properties of two-dimensional and three-dimensional hard-sphere systems. The work up to about 1967 is summarized and analyzed critically by Wood (1968a); later references are Hoover and Ree (1967, 1968), Alder *et al.* (1968), Alder and Hecht (1969), Chae *et al.* (1969), Barker and Henderson (1971a, 1972), Young and Alder (1974). Another excellent discussion is given by Ree (1971).

A major conclusion is that both two-dimensional and three-dimensional hard-sphere systems show first-order phase transitions from fluid at low densities to solid at high densities. For three dimensions this has appeared almost certain since the work of Alder and Wainwright (1957) and Wood and Jacobson (1957). For two dimensions the results of Alder and Wainwright (1962) were also compelling; in particular Fig. 7, taken from their paper, indicates very clearly the coexistence of solid and fluid phases. Such coexistence has not been observed in three-dimensional systems, where much larger systems would be required. However a finally convincing proof of the existence of the two phases was given by Hoover and Ree (1967, 1968), who calculated the free energy of both phases by methods already discussed in Sec. III.B, and determined the pressure and densities of the coexisting phases by thermodynamic methods (equating pressures and chemical potentials in the two phases). The results of these calculations are given in Table II; and pV/Nk_BT as a function of density is shown in Figs. 8 and 9.

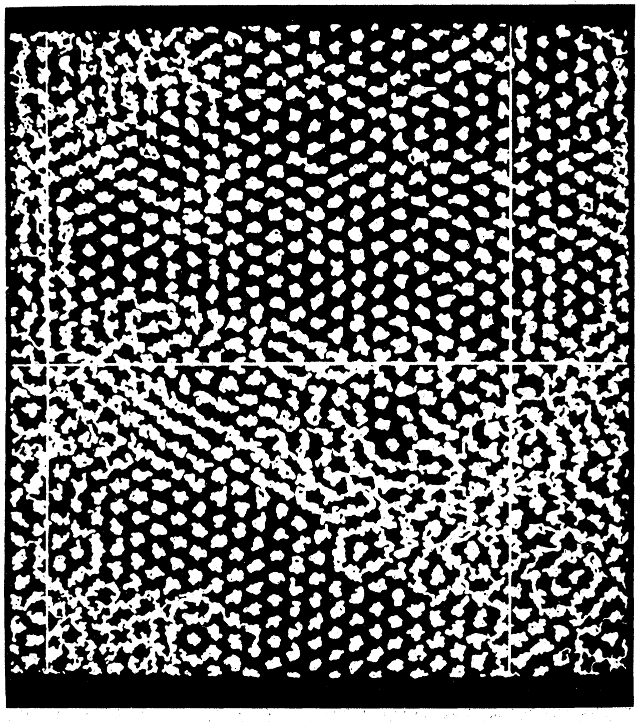

FIG. 7. Particle trajectories of hard-disk system in "two-phase" region from molecular dynamics calculation (Alder and Wainwright, 1962).

TABLE II. Fluid–solid transition data for hard spheres in two and three dimensions.[a]

	ρ/ρ_0(Fluid)	ρ/ρ_0(Solid)	$p/(\rho_0k_BT)$
Two-dimensions	0.761	0.798	8.08
Three-dimensions	0.667 ± 0.003	0.736 ± 0.003	8.27 ± 0.13

[a] Taken from Hoover and Ree (1968) and Ree (1971). The close-packed density is ρ_0.

The reader who wishes to form his own assessment of the evidence for these phase transitions should undoubtedly read the discussion of Wood (1968a), who wrote before seeing the work of Hoover and Ree, "it seems fair to state that the molecular dynamics and Monte Carlo results *in toto* certainly *suggest* a first-order phase transition. To ask that they *prove* the existence of one is perhaps asking too much of methods which are presently constrained to the use of relatively small numbers of molecules." However under "Additional references" he listed the papers of Hoover and Ree (1967, 1968), with the comment, "These important papers essentially decide the question of the existence of a first-order phase transition."

It is sometimes felt that the existence of the two-dimensional phase transition contradicts a result found by Peierls (1936) and Landau (1937), according to which the root-mean-square displacement of a particle in a two-dimensional solid of infinite extent is infinite. In fact,

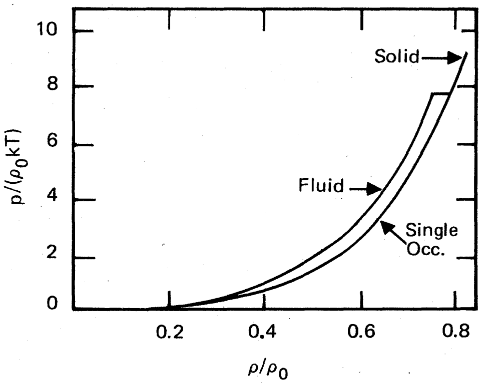

FIG. 8. Equation of state of unconstrained and single-occupancy hard disk system (Hoover and Ree, 1968). The quantity ρ_0 is the close-packed density.

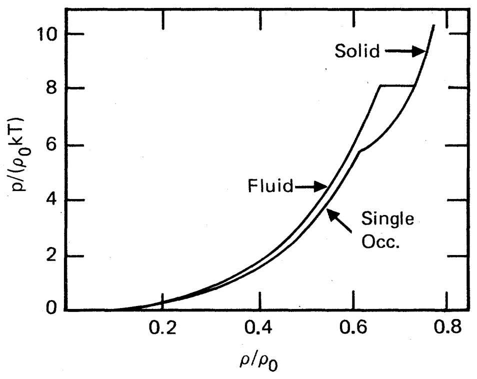

FIG. 9. Equation of state of unconstrained and single-occupancy hard sphere systems (Hoover and Ree, 1968). The quantity ρ_0 is the close-packed density.

there is no such contradiction (Frenkel, 1946; Mikeska and Schmidt, 1970; Hoover *et al.*, 1973). Since this is not universally known we will expand on the point. If one writes an expression for the mean-square thermal displacement of a particle in a solid as an integral over phonon or fluctuation wave number $\vec{k}$, the resulting integral (for an infinite crystal) diverges near $k=0$ like $1/|\vec{k}|$ in one dimension and like $\ln|\vec{k}|$ in two dimensions, but is convergent in three dimensions [the situation is slightly complicated by the fact that Landau and Lifschitz (1969) exhibit the integral correctly but state incorrectly that it is logarithmically divergent in one dimension and convergent in two and three dimensions]. Frenkel (1946) states categorically and partly correctly that "the increase of the quadratic fluctuations in the relative positions of the atoms with increase of their average distance apart in the case of linear and plane lattices has no bearing whatsoever on the question of their mechanical or thermodynamical stability... it is only possible to draw the conclusion that one- and two-dimensional crystals must scatter x-rays in a way similar to that which characterizes ordinary three-dimensional liquids." However, even the latter limited conclusion is not valid for finite two-dimensional crystals. Hoover *et al.* (1974) calculate explicitly the root-mean-square displacements for finite two-dimensional crystals containing N atoms [it is proportional to $(\ln N)^{1/2}$], and show that a crystal the size of the known universe (radius 10^{10} light years) would still have r.m.s. displacement less than 10 Å! Further Mikeska and Schmidt (1970) show that a two-dimensional crystal would possess Bragg reflections, since "the Bragg scattering peaks of a (two-dimensional) crystal turn out to be only slightly weakened as compared to the usual δ-function spikes of the structure function."

It is not easy to find convincing *experimental* examples of truly two-dimensional solids, though Frenkel cites graphite, in which the interlayer bonding is very much weaker than the intralayer bonding. However, Elgin and Goodstein (1974) in their thermodynamic study of ^{4}He absorbed on Grafoil find, as well as fluid phases, both a *registered* (or "lattice gas") solid and a *nonregistered* solid phase. It is the latter which one might regard as a "genuine" two-dimensional solid. It is a little surprising that the melting transition for this solid appears to be a second-order transition. However it is strictly only for the classical hard-sphere system that we know that the transition is first-order in two dimensions. Helium on Grafoil is neither classical, nor hard-sphere (nor, one must add at the risk of weakening the argument, strictly two-dimensional).

The most extensive tabulation of the RDF for three-dimensional hard spheres is that of Barker and Henderson (1971a, 1972). Barker and Henderson (1972) present a parameterized equation giving the covariances $\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle$ of the discrete radial distribution function N_i derived from Monte Carlo calculations. Chae *et al.* (1969) present radial distribution functions for two-dimensional hard spheres at several densities.

Alder *et al.* (1970) made a molecular dynamics study of the transport properties (diffusion coefficient, shear and bulk viscosity and thermal conductivity) of three-dimensional hard spheres over the whole fluid range of densities by evaluating equilibrium time-correlation functions. They compared their results with the Enskog theory, which involves a nearly exponentially decaying time correlation function and takes account of *static* but not *dynamic* many-body effects. They observed deviations from exponential decay (large-time tails) persisted for many collision times, indicating highly collective effects. Near the solidification density the shear viscosity was larger than the Enskog value by about a factor of 2, and the diffusion coefficient was smaller than the Enskog value by about the same factor. The thermal

TABLE III. Comparison of Monte Carlo and molecular dynamic results for 6–12 potential with experimental data for argon.[a]

T (K)	V (cm^3/mole)	P (atm) Exptl	MC or MD	$-U$ (cal/mole) Exptl	MC or MD
A. Monte Carlo results:					
97.0	28.48	214	200 ± 14	1386	1413 ± 2
97.0	28.95	141	141 ± 10	1371	1388 ± 2
97.0	29.68	39	17 ± 12	1340	1360 ± 2
108.0	28.48	451	443 ± 12	1360	1387 ± 2
108.0	31.72	16	−16 ± 10	1244	1258 ± 2
117.0	28.48	619	605 ± 16	1334	1372 ± 2
117.0	29.68	386	399 ± 14	1289	1319 ± 2
117.0	30.92	219	174 ± 13	1245	1278 ± 2
127.0	30.92	367	331 ± 13	1219	1261 ± 2
127.0	33.51	137	69 ± 12	1137	1170 ± 2
127.0	35.02	65	13 ± 13	1094	1117 ± 2
136.0	30.30	585	607 ± 14	1214	1264 ± 2
136.0	32.52	313	289 ± 13	1144	1192 ± 2
136.0	38.01	60	33 ± 10	1010	1022 ± 2
B. Molecular dynamics results:[b]					
86.1	27.98	95	91		1457
91.0	27.98	205	208		1445
93.7	27.98	272	270		1438
94.2	27.98	282	273		1440
105.4	27.98	513	507	1389	1414
128.1	31.71	292	299	1190	1235
128.3	31.71	295	295	1190	1230

[a] Comparison assumes $\epsilon/k = 119.8$K, $\sigma = 3.405$ Å; taken from McDonald and Singer (1969).

[b] Molecular dynamics results of Verlet (1967).

TABLE IV. Liquid–gas transition data for 6–12 fluid and argon.[a]

		p^*	ρ^*_{gas}	ρ^*_{liquid}	L^*
6–12[b]	$T^*=0.75$	0.0025	0.0035	0.825	6.62
Argon	$T^*=0.75$	0.0031	0.0047	0.818	6.50
6–12[b]	$T^*=1.15$	0.0597	0.073	0.606	4.34
Argon	$T^*=1.15$	0.0664	0.093	0.579	3.73

[a] Taken from Hansen and Verlet (1969). All quantities are reduced in terms of ϵ and σ; argon data assume $\epsilon/k=119.8$ K, $\sigma=3.405$ Å; L^* is the reduced latent heat of evaporation.

[b] Derived from Monte Carlo calculations.

conductivity and bulk viscosity were much closer to the Enskog values. The product of shear viscosity and diffusion constant remained roughly constant, in accord with the Stokes relation. Dymond and Alder (1971) find experimental evidence for these effects in the diffusion coefficients of krypton, methane and carbon dioxide.

Hoover *et al.* (1971) made Monte Carlo studies of *soft* spheres (with repulsive r^{-n} potentials) and compared the results with the predictions of several theoretical results.

2. The square-well potential

Fairly extensive Monte Carlo (Rotenberg, 1965; Lado and Wood, 1968; Henderson, Madden, and Fitts, 1976) and molecular dynamics (Alder *et al.*, 1972) results for the square-well potential with $\lambda=1.5$ are available. These results are discussed in Secs. VI and VII.

3. The Lennard-Jones 6-12 potential

Pressures, energies and radial distribution functions (RDF) for the 6–12 fluid have been calculated by Monte Carlo and molecular dynamics methods. The first Monte Carlo calculations were those of Wood and Parker (1957) for a supercritical isotherm; more recent work includes that of Verlet and Levesque (1967) and McDonald and Singer (1967, 1969). Molecular dynamics results for thermodynamic properties are given by Verlet (1967), and for the RDF, including an extensive tabulation, by Verlet (1968). In Table III we compare some calculated pressures and energies with experimental data for argon. At high densities the agreement is really remarkably good. However, the energies show discrepancies of up to 4% at larger volumes, as one would expect from the discrepancies in second virial coefficients.

TABLE V. Fluid–solid transition data for 6–12 fluid and argon.[a,b]

	T^*	p^*	ρ^*_{fluid}	ρ^*_{solid}	ΔV^*	L^*
6–12	2.74	32.2	1.113	1.179	0.050	2.69
Argon	2.74	37.4				2.34
6–12	1.35	9.00	0.964	1.053	0.087	1.88
Argon	1.35	9.27	0.982	1.056	0.072	1.63
6–12	1.15	5.68	0.936	1.024	0.091	1.46
Argon	1.15	6.09	0.947	1.028	0.082	1.44
6–12	0.75	0.67	0.875	0.973	0.135	1.31
Argon	0.75	0.59	0.856	0.967	0.133	1.23

[a] Taken from Hansen and Verlet (1969). All quantities are reduced in terms of ϵ and σ; argon data assume $\epsilon/k=119.8$ K, $\sigma=3.405$ Å; L^* is the reduced latent heat of fusion.

[b] The 6–12 values are derived from Monte Carlo calculations.

TABLE VI. Triple point properties of the 6–12 potential.

	T^*_t	p^*_t
Machine simulation[a]	0.68 ± 0.02	
PY(E)	0.70	0.0020
BH2	0.66	0.0006

[a] Hansen and Verlet (1969).

Hansen and Verlet (1969) evaluated free energies and constructed the phase diagram as discussed in Sec. III.B. The phase diagram is shown in Fig. 1, with the experimental results for argon for comparison. The qualitative and semi-quantitative agreement is extremely satisfying. This diagram undoubtedly represents a major achievement of statistical mechanics in explaining the phase relationships of solid, liquid and gas. The Lennard-Jones parameters used for argon are $\epsilon/k_B=119.8$K and $\sigma=3.405$Å; these were determined solely from gas properties by Michels *et al.* (1949).

Some detailed numerical results are given for the liquid-vapor equilibrium in Table IV and for the fluid-solid equilibrium in Table V.

Estimates for the triple point properties and critical constants of the 6–12 fluid based on the Monte Carlo and molecular dynamics results are given in Tables VI and VII. Values for the free energy (actually A/Nk_BT) and pressure (actually pV/Nk_BT) are given in Tables VIII and IX.

The quantitative differences between the calculated and experimental liquid–gas coexistence curve in the neighborhood of the critical point in Fig. 1 are probably partly due to the long-range fluctuations which are not taken into account by the computation, though there may be a substantial contribution from the shortcomings of the 6–12 potential. The deviations in liquid density at lower temperatures, and particularly in the latent heat at $T^*=1.15$ (Table IV) are almost certainly due to the latter cause.

Streett *et al.* (1974) and Ravechḗ *et al.* (1974) made very detailed Monte Carlo calculations for the 6–12 substance in the neighborhood of the solid–fluid transition

TABLE VII. Critical constants for the 6–12 potential.

	T^*_c	ρ^*_c	p^*_c	p_cV_c/Nk_BT_c
MD[a]	1.32–1.36	0.32–0.36	0.13–0.17	0.30–0.36
Exptl	1.26	0.316	0.117	0.293
BG(P)[b]	(1.45)	(0.40)	(0.26)	(0.44)
BG(C)	1.58	0.40	0.30	0.48
PY(P)[b]	(1.25)	(0.29)	(0.11)	(0.30)
PY(C)	1.32	0.28	0.13	0.36
PY(E)	1.34	0.34	0.14	0.31
HNC(P)[b]	(1.25)	(0.26)	(0.12)	(0.35)
HNC(C)	1.39	0.28	0.15	0.38
BH2	1.38	0.33	0.16	0.35
OCT[c]	1.35	0.35	0.15	0.32

[a] Verlet (1967).

[b] Obtained by extrapolation.

[c] Sung and Chandler (1974).

TABLE VIII. Values of A/Nk_BT for 6–12 potential.

k_BT/ϵ	$\rho\sigma^3$	Simul.[a]	PY(E)	BH1(PY)	BH1	BH2	Var.(PY)	Var.(VW)	WCA[b] (PY)	WCA[b] (VW/GH)	ORPA[c]
2.74	0.60	−0.34	−0.33	−0.31	−0.31	−0.33	−0.19	−0.18	−0.32	−0.33	−0.34
	0.70	+0.01	+0.01	+0.04	+0.02	+0.01	+0.20	+0.21	+0.02	+0.01	+0.00
	0.80	0.43	0.43	0.45	0.46	0.42	0.65	0.69	0.43	0.41	0.41
	0.90	0.93	0.95	0.97	0.99	0.95	1.21	1.27	0.97	0.92	0.92
	1.00	1.59	1.61	1.65	1.66	1.62	1.92	2.01	1.66	1.56	1.56
1.35	0.60	−1.77	−1.75	−1.67	−1.65	−1.75	−1.59	−1.57	−1.73	−1.74	−1.76
	0.70	−1.65	−1.62	−1.54	−1.51	−1.63	−1.42	−1.39	−1.62	−1.63	−1.64
	0.80	−1.41	−1.37	−1.30	−1.26	−1.41	−1.13	−1.07	−1.39	−1.41	−1.42
	0.90	−1.02	−0.99	−0.90	−0.84	−1.01	−0.67	−0.57	−0.98	−1.02	−1.03
	0.95	−0.72	−0.72	−0.62	−0.55	−0.72	−0.35	−0.23	(−0.67)	(−0.74)	(−0.75)
1.15	0.60	−2.29	−2.28	−2.16	−2.15	−2.30	−2.10	−2.09	−2.25	−2.26	−2.29
	0.70	−2.25	−2.23	−2.11	−2.10	−2.26	−2.02	−1.99	−2.23	−2.24	−2.25
	0.80	−2.06	−2.06	−1.95	−1.92	−2.10	−1.81	−1.74	−2.08	−2.09	−2.10
	0.90	−1.79	−1.74	−1.61	−1.56	−1.76	−1.40	−1.29	−1.73	−1.77	−1.77
0.75	0.60	−4.24		−3.99	−3.99	−4.29	−4.01	−3.99	−4.17	−4.18	−4.25
	0.70	−4.53	−4.50	−4.26	−4.26	−4.28	−4.24	−4.24	−4.51	−4.51	−4.54
	0.80	−4.69	−4.63	−4.38	−4.37	−4.74	−4.38	−4.30	−4.69	−4.69	−4.71
	0.90		−4.55	−4.29	−4.26	−4.67	−4.22	−4.08	(−4.60)	(−4.62)	(−4.63)

[a] Verlet and Levesque (1967), Verlet (1967), Levesque and Verlet (1969), Hansen and Verlet (1969), Hansen (1970).
[b] HTA of WCA.
[c] ORPA correction to WCA (VW/GH) calculated by Anderson (1972).

at several temperatures, with particular emphasis on structural properties, the effect of initial conditions and the possibility of "crystallization" in a Monte Carlo calculation (which they observed for "nucleated" systems). They estimated coexisting fluid and solid densities by a Maxwell construction (which has some uncertainty due to inability to obtain satisfactory averages in the "unstable" region). Their coexisting densities were about 4% lower than those of Hansen and Verlet (1969). These differences are discussed by Hansen and Pollock (1975) and Raveché *et al.* (1975). The latter authors believe that there is agreement within the combined uncertainties. We have already discussed (in Sec. III.B.2) other calculations which tend to confirm the accuracy of

TABLE IX. Values of pV/Nk_BT for 6–12 potential.

k_BT/ϵ	$\rho\sigma^3$	Simul.[a]	Simul.[b]	PY(E)	BH1(PY)	BH1	BH2	Var.(PY)	Var.(VW)	WCA[a] (PY)	WCA[c] (VW/GH)	ORPA[d]
2.74	0.65	2.22		2.23	2.23	2.24	2.22	2.48	2.54	2.21	2.18	2.20
	0.75	3.05		3.11	3.11	3.14	3.10	3.43	3.54	3.11	3.04	3.05
	0.85	4.38		4.42	4.42	4.48	4.44	4.79	4.98	4.50	4.30	4.31
	0.95	6.15		6.31	6.37	6.41	6.40	6.69	6.97	6.57	6.10	6.10
1.35	0.10	0.72		0.72	0.77	0.77	0.74	0.78	0.78	0.77	0.77	0.73
	0.20	0.50		0.51	0.54	0.55	0.52	0.56	0.56	0.53	0.53	0.51
	0.30	0.35		0.36	0.35	0.39	0.36	0.39	0.39	0.32	0.31	0.35
	0.40	0.27		0.29	0.25	0.26	0.26	0.31	0.32	0.17	0.17	0.25
	0.50	0.30		0.33	0.29	0.31	0.27	0.39	0.43	0.18	0.18	0.27
	0.55	0.41		0.43	0.40	0.43	0.35	0.53	0.58	0.27	0.27	0.35
	0.65	0.80		0.85	0.85	0.91	0.74	1.08	1.19	0.72	0.71	0.77
	0.75	1.73		1.72	1.77	1.87	1.64	2.14	2.34	1.70	1.64	1.68
	0.85	3.37		3.24	3.36	3.54	3.36	3.92	4.24	3.51	3.28	3.30
	0.95	6.32		5.65	5.96	6.21	6.32	6.67	7.16	(6.58)	(5.90)	(5.91)
1.00	0.65	−0.25		−0.22	−0.25	−0.21	−0.36	−0.10	+0.04	−0.51	−0.50	−0.38
	0.75	+0.58	0.48	+0.57	+0.62	+0.71	+0.53	+0.95	1.20	+0.43	+0.40	+0.47
	0.85	2.27	2.23	2.14	2.30	2.48	2.25	2.90	3.32	2.41	2.20	2.23
	0.90	~3.50		3.33	3.57	3.79	3.53	4.34	4.84	(3.96)	(3.55)	(3.57)
0.72	0.85	0.40	0.25	0.33	0.50	0.70	0.25	1.05	1.59	0.43	0.26	0.32
	0.90		~1.60	1.59	1.90	2.15	1.63	2.73	3.39	(2.24)	(1.83)	(1.87)

[a] Verlet and Levesque (1967), Verlet (1967), Levesque and Verlet (1969).
[b] McDonald and Singer (1969).
[c] HTA of WCA.
[d] ORPA correction to WCA (VW/GH) calculated by Andersen (1972).

the results of Hansen and Verlet.

Dynamical properties of the 6–12 fluid have been studied by Rahman (1964, 1968), Levesque and Verlet (1970), and Levesque *et al.* (1973) using the equilibrium time-correlation method, and by Ashurst and Hoover (1975) using nonequilibrium methods. A more detailed discussion of their methods is given by Hoover and Ashurst (1975). Rahman and Levesque and Verlet found diffusion coefficients within 15% of experimental values for argon, but the shear viscosity calculated by Levesque *et al.* (1973) for a thermodynamic state close to the triple point was over 30% higher than the experimental value for argon. The results of Ashurst and Hoover indicate that when properly extrapolated to infinite-width systems the equilibrium and *nonequilibrium* results agree with one another and with experimental data for argon. This large finite-system effect seems to occur only near the triple point. The "nonequilibrium" results had to be corrected for non-Newtonian behavior by extrapolation to zero shear rate. Ashurst and Hoover found good agreement between their calculated viscosities and experimental data for argon in a wide range of conditions. The noneqilibrium methods appear to have substantial advantages in terms of computer time requirements.

Fehder (1969, 1970) has made a molecular dynamics study of the two-dimensional 6–12 fluid. A thorough Monte Carlo investigation of the same system, showing both liquid-gas and solid-fluid transitions, is given by Tsien and Valleau (1974).

4. Argon with realistic potentials

The accurate BFW (Barker *et al.* 1971) pair potential for argon and the Axilrod–Teller three-body interaction have been discussed in Sec. II, and methods for including the three-body interaction and quantum corrections in computer simulations in Sec. III.B. Calculated properties for fluid and solid argon calculated with these potentials and methods are compared with experiment in Table X. The agreement with experiment is excellent over a very wide range of conditions, including both fluid and solid phases at pressures up to 20 kbar on the melting line. The agreement with experiment is better than for the 6–12 potential even at high liquid densities, but not much better because the 6–12 potential happens to give good agreement in the neighborhood of the triple point. However the real failure of the 6–12 potential to describe the properties of argon is seen at gaseous densities, as discussed in Sec. II.

In Tables XI and XII we exhibit the separate two-body, three-body and quantum contributions to the energy and pressure for liquid argon. The three-body contributions are quite large. If one wished to treat the 6–12 potential as a true pair potential and include three-body and quantum effects, there would be very large discrepancies with experiment.

Low-temperature properties of solid argon as given by the BFW and Axilrod–Teller potentials are discussed by Barker *et al.* (1971), Barker (1976), and Fisher and Watts (1972a); the latter paper discusses elastic constants at temperatures up to the melting point.

The radial distribution function for liquid argon near its triple point has been calculated with corrections for three-body interactions and quantum effects (Barker, 1973) and the results are in excellent agreement with experiment (Yarnell *et al.*, 1973); the comparison is shown in Fig. 2. Note, however that the 6–12 potential, using the results of Verlet (1967b), gives equally good agreement. The radial distribution function at high densities is quite insensitive to the details of the attractive potential, being determined primarily by the hard-core repulsions (cf., Sec. VII).

It would be interesting to repeat the calculation of the phase diagram using these potentials, particularly near the critical point to see how much of the discrepancy in Fig. 1 is due to the use of the 6–12 potential. Unfortunately this has not been done. However, the calculated pressures in Table X for the critical isotherm ($T = 150.87$K) are very close to the experimental values.

Fisher and Watts (1972b) calculated diffusion coefficients for the BFW potential *without* the Axilrod–Teller interaction, and found results rather similar to those found with the 6–12 potential at the same densities. It seems likely that the Axilrod–Teller interaction, which is a relatively slowly-varying interaction, does not

TABLE X. Calculated[a] and experimental energies and pressures for solid or fluid argon.

V (cm^3/mole)	T (K)	U_{calc} (cal/mole)	U_{expt} (cal/mole)	p_{calc} (bar)	p_{expt} (bar)
		Solid on melting line[b]			
23.75	63.10	−1786	···	1	0
24.30	77.13	−1727	···	28	0.25
24.03	108.12	−1664	···	1028	1051
23.05	140.88	−1624	···	2650	2708
22.55	160.4	−1574	···	3808	3805
22.09	180.15	−1525	···	4964	4999
21.70	201.32	−1462	···	6199	6335
21.47	197.78	−1459	···	6593	6140
20.12	273.11	−1178	···	11974	11380
19.92	273.11	−1150	···	12686	···
19.41	323.14	−941	···	15988	15354
		Fluid on melting line[b]			
23.66	180.15	−1297	···	4907	4999
22.96	197.78	−1235	···	6319	6140
23.10	201.32	−1236	···	6143	6335
21.31	273.11	−940	···	11645	11380
21.09	273.11	−924	···	12585	···
20.46	323.14	−664	···	15513	15354
		Fluid[c]			
27.04	100.00	−1423	−1432	655	661
29.66	100.00	−1313	−1324	118	106
30.65	140.00	−1213	−1209	588	591
35.36	140.00	−1061	−1069	170	180
41.79	140.00	−906	−922	18	37
48.39	150.87	−784	−789	54	62
57.46	150.87	−679	−689	48	51
70.73	150.87	−573	−591	50	50
91.94	150.87	−462	−481	50	50

[a] Values calculated by Monte Carlo method using BFW pair potential and Axilrod–Teller interaction.

[b] Barker and Klein (1973).

[c] Barker *et al*. (1971).

TABLE XI. Contributions to the internal energy of argon.[a]

T (°K)	V (cm^3/mole)	$U_i(2b)$ (cal/mole)	$U_i(3b)$ (cal/mole)	$U_i(Q)$ (cal/mole)	U_i(theor) (cal/mole)	U_i(exp) (cal/mole)
100.00	27.04	−1525.2	87.1	15.6	−1423	−1432
100.00	29.66	−1393.6	67.9	12.5	−1313	−1324
140.00	30.65	−1284.7	62.8	9.3	−1213	−1209
140.00	41.79	−951.4	39.5	6.4	−906	−922
150.87	70.73	−603.8	26.6	4.6	−573	−591

[a] All entries taken from Barker *et al*. (1971).

have a great effect on dynamical properties at high densities.

5. Other simulation studies

Extensive molecular dynamics studies of nonpolar liquids with diatomic molecules, with emphasis on dynamical properties have been made by Berne and coworkers, and are well reviewed by Berne (1971).

Liquid water has been studied extensively by molecular dynamics (Rahman and Stillinger, 1971; Stillinger and Rahman, 1972, 1974) and Monte Carlo methods (Barker and Watts, 1969, 1973; Watts 1974; Popkie *et al.*, 1973; Kistenmacher *et al.* 1974; Lie and Clementi, 1975). Stillinger and Rahman made thorough studies of static and dynamic properties using successively improved empirical potentials. Clementi and coworkers emphasize the pair potential, starting from Hartree–Fock quantum mechanical calculations and including correlation effects. Note that Zeiss and Meath (1975) recently made a careful estimate of c_6 for water which is appreciably smaller than that used by Kistenmacher *et al.* (1974). The work of Barker and Watts emphasized the problem of dielectric properties already discussed in Sec. III.B.6. Evans and Watts (1974) compared second virial coefficients for some of the potentials used in these studies with experiment. Shipman and Scheraga (1974) derived an empirical water-water potential.

McDonald (1974) made Monte Carlo calculations for polar molecules interacting with the Stockmayer potential; he also examined the effects of polarizability of the molecules using formal results due to Barker (1953). Patey and Valleau (1974, 1976) made similar studies for dipolar and quadrupolar hard spheres. McDonald and Rasaiah (1975) studied by Monte Carlo the average force between ions in a "Stockmayer" solvent. Patey and Valleau (1975) made similar studies for charged hard spheres in a dipolar hard sphere solvent.

There is a very extensive literature on Monte Carlo methods for polymers (Lowry, 1970; Lal and Spencer, 1973). Much of this work did not use the Metropolis scheme. Curro (1974) describes an application of the Metropolis method to multichain system of oligomers containing 15 and 20 units. For a general account of the statistical mechanics of polymers the book by Flory (1969) is indispensable.

TABLE XII. Contributions to the pressure of argon.[a]

T (°K)	V (cm^3/mole)	$p(2b)$ (atm)	$p(3b)$ (atm)	$p(Q)$ (atm)	p(theor) (atm)	p(exp) (atm)
100.00	27.04	+239.9	364.2	42.2	646	652
100.00	29.66	−148.0	238.8	25.3	116	105
140.00	30.65	+348.9	214.3	16.7	580	583
140.00	41.79	−33.7	49.0	2.7	18	37
150.87	70.73	+34.5	13.2	1.2	49	49

[a] All entries taken from Barker *et al*. (1971).

Liquid metals differ from simpler liquids in that the "effective" pair potentials are oscillatory (March 1968). Monte Carlo calculations for liquid sodium are described by Murphy and Klein (1973), Fowler (1973) and Schiff (1969), and molecular dynamics results are given by Rahman (1970).

Monte Carlo calculations on rigid nonspherical molecules include those of Levesque *et al.* (1969) and Vieillard–Baron (1972) on hard ellipses and of Few and Rigby (1973) and Vieillard–Baron (1974) on hard spherocylinders. These results are referred to in Sec. V.B.

In the work on the two-dimensional hard ellipse system Vieillard–Baron observed two first-order phase transitions, with an oriented solid phase stable at high densities, a nematic phase with orientational order but no translational order stable at intermediate densities, and a liquid phase disordered both in orientations and translations stable at low densities. In the three-dimensional hard spherocylinder system Vieillard–Baron was unable to observe a nematic phase. It is possible that this was due to the nature of the initial conditions used in the Monte Carlo work, which resembled more closely a smectic (layered) phase. It would be worthwhile to make a Monte Carlo study starting from a nematic structure with perfect orientational order, which could be generated by applying an affine transformation $x'=x$, $y'=y$, $z'=az$ to a *fluid* configuration of hard spheres (this would lead to a nematiclike configuration of hard ellipsoids).

IV. DENSITY EXPANSIONS AND VIRIAL COEFFICIENTS

A. Introduction

In the limit of zero density, the equation of state of a gas is given by the *perfect gas* law

$$pV/Nk_BT=1. \tag{4.1}$$

As the density is increased, deviations from (4.1) occur. A gas exhibiting these deviations may be called an *imperfect gas*. It is observed experimentally that the equation of state of an imperfect gas at low densities is given by

$$\frac{pV}{Nk_BT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots, \tag{4.2}$$

where B, C, D, etc. are called the second, third, fourth, ... virial coefficients and V_m is the molar volume.

In this section the relation between these virial coefficients and the coefficients in the density expansion of other quantities and the intermolecular forces will be explored. Although Eq. (4.2) does not provide the basis of a satisfactory theory of liquids, this expansion is useful for imperfect gases at low densities. The virial coefficients can be calculated for model or real potentials and can be regarded as another source of quasi-experimental data similar to the computer simulations discussed above. Moreover, density expansions can be used to introduce theories which do apply to the liquid state. For simplicity, systems with pairwise-additive central forces will be considered in detail. Thus,

$$U_N(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i<j=1}^{N} u(r_{ij}), \tag{4.3}$$

where $r_{ij} = |\vec{r}_{ij}|$ and $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$. Generalizations to more complex systems will be considered briefly.

Additional discussion of density expansions can be found in Kihara (1953a, 1955), Hirschfelder *et al.* (1954), Uhlenbeck and Ford (1962), Dymond and Smith (1969), and Mason and Spurling (1969).

B. General expressions for the virial coefficients

1. Second virial coefficient

The equation of state depends only on the partition function

$$Z_N = \frac{\lambda^{-3N}}{N!} \int \prod_{i<j=1}^{N} e_{ij} d\vec{r}_1 \cdots d\vec{r}_N, \tag{4.4}$$

where $\lambda = h/(2\pi m k_B T)^{1/2}$ results from the integration of the kinetic energy variables,

$$e(r) = \exp\{-\beta u(r)\}, \tag{4.5}$$

and $e_{ij} = e(r_{ij})$. Equation (4.4) can be regarded as an average over N- molecule configurations of noninteracting molecules. Thus

$$\begin{aligned} A/k_BT &= -\ln Z_N \\ &= -N \ln V - \ln \left\langle \prod_{i<j=1}^{N} e_{ij} \right\rangle, \end{aligned} \tag{4.6}$$

where the terms which are independent of V and which do not contribute to the equation of state have been dropped.

The factors e_{12} and e_{13} are independent. Hence,

$$\langle e_{12} e_{13} \rangle = \langle e_{12} \rangle^2. \tag{4.7}$$

However, the three functions e_{12}, e_{13}, and e_{23} are not independent. Thus,

$$\langle e_{12} e_{13} e_{23} \rangle \neq \langle e_{13} \rangle^2. \tag{4.8}$$

At sufficiently low densities, only interactions between pairs of molecules occur with high probability, and configurations in which all three of the functions in (4.8) differ from unity are rare. Under such conditions, the equality in (4.8) can be introduced as an approximation. If products involving more than three molecules are treated similarly,

$$A/k_BT = -N \ln V - \tfrac{1}{2} N^2 \ln \langle e_{12} \rangle, \tag{4.9}$$

where the factor in front of the logarithm arises because there are $\frac{1}{2}N(N-1) \simeq \frac{1}{2}N^2$ pairs of molecules. The function $e(r)$ differs from unity only for values of r which are a few molecular diameters. Hence, it is convenient to introduce the function

$$f(r) = e(r) - 1, \tag{4.10}$$

which is called the *Mayer f-function.* Thus,

$$A/k_BT = -N \ln V - \tfrac{1}{2} N^2 \ln(1 + \langle f_{12} \rangle), \tag{4.11}$$

where

$$\begin{aligned} \langle f_{12} \rangle &= V^{-2} \int f_{12} d\vec{r}_1 d\vec{r}_2 \\ &= V^{-1} \int f_{12} d\vec{r}_2. \end{aligned} \tag{4.12}$$

The integral in (4.12) is of the order of a molecular volume. Hence, the logarithm in (4.11) can be expanded to give

$$A/k_BT = -N \ln V + B(N/V_m), \tag{4.13}$$

where B is independent of the volume and is given by

$$\begin{aligned} B &= -\frac{N_m}{2} \int f(r_{12}) d\vec{r}_2, \\ &= -2\pi N_m \int_0^\infty f(r) r^2 dr, \end{aligned} \tag{4.14}$$

where N_m is Avogadro's number. The latter form of (4.14) is valid only for a spherically symmetrical potential. Differentiating to obtain the pressure gives

$$\frac{pV}{Nk_BT} = 1 + \frac{B}{V_m} \tag{4.15}$$

so that B, given by (4.14), is the second virial coefficient.

2. Third virial coefficient

To second order in V^{-1}, the error in (4.13) and (4.15) is due to the neglect of three-molecule correlations. Hence, for each triplet of molecules, the above approximation to Z_N must be multiplied by the factor

$$I = \langle e_{12} e_{13} e_{23} \rangle / \langle e_{12} \rangle^3. \tag{4.16}$$

If this expression is written in terms of the f- functions and expanded, then

$$\begin{aligned} I &= \langle (1+f_{12})(1+f_{13})(1+f_{23}) \rangle / \langle 1+f_{12} \rangle^3 \\ &= \frac{1 + 3\langle f_{12} \rangle + 3\langle f_{12} \rangle^2 + \langle f_{12} f_{13} f_{23} \rangle}{1 + 3\langle f_{12} \rangle + 3\langle f_{12} \rangle^2 + \langle f_{12} \rangle^3}. \end{aligned} \tag{4.17}$$

The factor $\langle f_{12} \rangle$ is of order V^{-1}, and $\langle f_{12} f_{13} f_{23} \rangle$ is of order V^{-2}. Thus,

$$I = 1 + \langle f_{12} f_{13} f_{23} \rangle + 0(V^{-3}). \tag{4.18}$$

Therefore,

$$A/k_BT = -N \ln V + B(N/V_m) - \tfrac{1}{6} N^3 \ln(1 + \langle f_{12} f_{13} f_{23} \rangle), \tag{4.19}$$

where the factor in front of the logarithm arises because there are $\frac{1}{6}N(N-1)(N-2) \simeq N^3/6$ triplets of molecules. Expanding the logarithm gives

$$A/k_BT = -N \ln V + B(N/V_m) + \tfrac{1}{2}C(N/V_m^2)\,, \tag{4.20}$$

where C is independent of the volume and is given by

$$\begin{aligned} C &= -\frac{N_m^2}{3V}\int f_{12}f_{13}f_{23}\,d\vec{r}_1 d\vec{r}_2 d\vec{r}_3\,, \\ &= -\frac{N_m^2}{3}\int f_{12}f_{13}f_{23}\,d\vec{r}_2 d\vec{r}_3\,. \end{aligned} \tag{4.21}$$

Differentiation gives a result consistent with (4.2) so that C is the third virial coefficient.

For spherically symmetric potentials (4.21) can be simplified by using r_{12}, r_{13}, and r_{23} as variables. It is easy to show that

$$d\vec{r}_3 = 2\pi\frac{r_{13}r_{23}}{r_{12}}\,dr_{13}dr_{23} \tag{4.22}$$

so that

$$C = -\frac{8\pi^2 N_m^2}{3}\int f_{12}f_{13}f_{23}r_{12}r_{13}r_{23}\,dr_{12}dr_{13}dr_{23}\,, \tag{4.23}$$

where the integration is over all r_{12}, r_{13}, and r_{23} which form a triangle.

3. Higher-order virial coefficients

Higher-order virial coefficients can be obtained in a manner similar to that given above. We shall not give details. The general scheme for obtaining these virial coefficients was first given by Mayer and his colleagues between 1937 and 1942. This procedure has been reviewed by Mayer (1940, 1958), Uhlenbeck and Ford (1962), and van Kampen (1961). We have followed van Kampen's treatment because of its relative simplicity.

The higher-order virial coefficients are sums of integrals whose integrands are products of f functions. It is convenient to represent these *cluster integrals* by diagrams (often called *Mayer diagrams*) in which a bar represents the function $f(r)$. The junction of two bars (often called a *field point*) represents a molecule whose coordinates are integrated while a circle at the end of a bar (often called a *root point*) represents a molecule whose position is fixed. Molecule 1 is taken as the origin. Thus $d\vec{r}_i$ represents $d(\vec{r}_i - \vec{r}_1)$. Some examples of these diagrams are

$$\circ\!\!-\!\!\circ = f_{12} \tag{4.24}$$

and

$$\triangle = \int f_{12}f_{13}f_{23}\,d\vec{r}_2 d\vec{r}_3. \tag{4.25}$$

Sometimes it will be convenient to use diagrams with $rdf(r)/dr$ and $-de(r)/d\beta$ as bonds. These bonds will be represented by --- and ∿∿, respectively. The diagrams contributing to B, C, and D are given in Fig. 10. The diagrams which contribute to the virial coefficients are said to be *irreducible* because they cannot be factored into products of simpler terms.

The expressions for B, C, and D in terms of the diagrams in Fig. 10 are

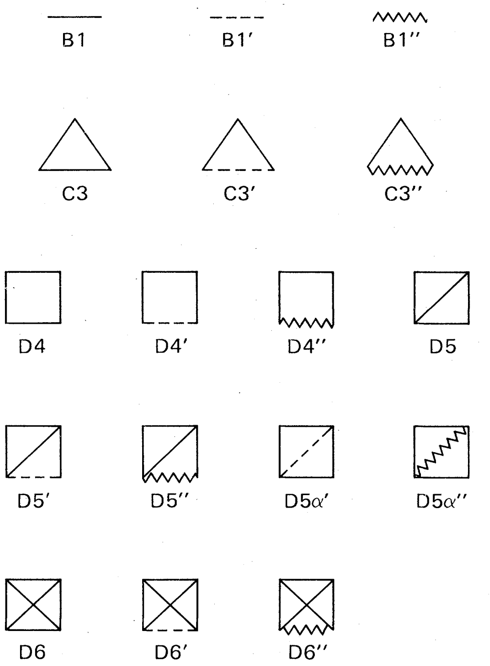

FIG. 10. Irreducible diagrams contributing to B, C, and D.

$$B = -(N_m/2)B1, \tag{4.26}$$

$$C = -(N_m^2/3)C3, \tag{4.27}$$

and

$$D = -(N_m^3/8)[3(D4) + 6(D5) + D6]. \tag{4.28}$$

Expressions for the fifth- and higher-order virial coefficients can be written down. However, the number of irreducible cluster integrals contributing to the virial coefficient increases rapidly with order. For example, ten irreducible cluster integrals contribute to the fifth virial coefficient. Thus, the enumeration of the diagrams contributing to the virial coefficients becomes a difficult problem as the order of the coefficient increases. The diagrams contributing up to the seventh virial coefficient have been enumerated by Uhlenbeck and Ford (1962).

4. Virial coefficients for some model potentials

The simplest potential which can be used in the calculation of virial coefficients is that of the so-called Gaussian molecules where

$$f(r) = -\exp\{-r^2/a^2\}. \tag{4.29}$$

This potential is a soft repulsive potential. Although it is unrealistic (for example, the potential is temperature dependent) it has the virtue of yielding simple analytic expressions for the virial coefficients. Earlier, this was a great advantage because, for other potentials, the higher-order cluster integrals are complex. However, the advent of modern computers permits numerical evaluation of the complex cluster integrals. For this reason Gaussian molecules are no longer of great interest and will not be considered here. Another simple model system which is simple enough to permit relatively easy evaluation of virial coefficients is the parallel hard cube system (Geilikman, 1950; Zwanzig, 1956; Hoover and DeRocco, 1961, 1962). This system consists of hard cubes whose edges are all constrained to be parallel to Cartesian coordinate axis.

The simplest model potential which will be considered in detail is the hard-sphere potential, where

$$f(r)=\begin{cases}-1, & r<d\\ 0, & r>d.\end{cases} \tag{4.30}$$

Thus,

$$B=N_m b\,, \tag{4.31}$$

where $b=2\pi d^3/3$ is four times the volume of a hard sphere. The third virial coefficient for hard spheres can most easily be obtained by first calculating the following integral

$$c_2(r_{12})=\int f_{13}f_{23}\,d\vec{r}_3. \tag{4.32}$$

For hard spheres, $c_2(r)$ is just the volume common to two spheres of diameter d separated by a distance r. This is easily obtained and is

$$c_2(r)=\begin{cases}\dfrac{4\pi d^3}{3}\left[1-\frac{3}{4}(r/d)+\frac{1}{16}(r/d)^3\right], & r<2d\\ 0, & r>2d.\end{cases} \tag{4.33}$$

Thus

$$C3=\int f(r)c_2(r)\,d\vec{r}$$

$$=-5\pi^2 d^6/6. \tag{4.34}$$

Hence

$$C/B^2=\tfrac{5}{8}. \tag{4.35}$$

The fourth virial coefficient for hard spheres can also be obtained easily from (4.33). The results are

$$D4=\int [c_2(r)]^2\,d\vec{r}$$

$$=(272/105)b^3\,, \tag{4.36}$$

and

$$D5=\int f(r)[c_2(r)]^2\,d\vec{r},$$

$$=-\frac{6347}{3360}b^3\,. \tag{4.37}$$

The fully connected integral $D6$ is more difficult. It is most simply obtained from

$$d_3'(r_{12},r_{13},r_{23})=\int f_{14}f_{24}f_{34}\,d\vec{r}_4, \tag{4.38}$$

which for hard spheres is the volume common to three spheres of diameter d. This volume and the resulting value for $D6$ can be obtained analytically (van Laar, 1899; Boltzmann, 1899; Nijboer and van Hove, 1952; Rowlinson, 1963; Powell, 1964). The result for $D6$ is

$$D6=\int f_{12}f_{13}f_{23}d_3'(r_{12},r_{13},r_{23})\,d\vec{r}_2\,d\vec{r}_3$$

$$=\frac{4131\cos^{-1}(1/3)-712\pi-438\sqrt{2}}{560\pi}\,b^3=1.2669b^3. \tag{4.39}$$

Hence

$$D/B^3=0.2869. \tag{4.40}$$

Numerical values for the fifth virial coefficient for hard spheres have been obtained by several authors (Katsura and Abe, 1963; Kilpatrick and Katsura, 1966; Rowlinson, 1964a; Ree and Hoover, 1964a; Oden *et al.*, 1966; Barker and Henderson, 1967c; Kim and Henderson, 1968a). The value of Kim and Henderson (1968a) should be the best because seven of the ten cluster integrals are obtained analytically in their calculation. Ree and Hoover (1964a, 1967) have obtained numerical values for the sixth and seventh hard-sphere virial coefficients. The results of these calculations are listed in Table XIII. All the known hard-sphere virial coefficients are positive. However, there is evidence that some of the higher-order virial coefficients may be negative (Ree and Hoover, 1964b).

The equations of state of hard spheres predicted by truncated virial expansions are plotted in Fig. 11. As more terms are included, the agreement with machine simulations improves. For hard spheres, the virial series seems convergent at all densities at which the hard spheres are fluid. Extrapolations using Padé approximants, which are ratios of polynomials in the density in which the coefficients are constrained to fit the known virial coefficients, are in good agreement with the computer simulations. For more realistic potentials with attractive forces, the convergence is much poorer (Barker and Henderson 1967c).

The virial coefficients for the square-well potential have been obtained by Katsura (1959, 1966), Barker and Monaghan (1962a, 1966), and Barker and Henderson (1967c). Henderson *et al.* (1975) have obtained virial coefficients for hard spheres with a Yukawa tail.

The third, fourth, and fifth virial coefficients have been obtained numerically for the 6–12 potential. Barker *et al.* (1966) give a convenient tabulation. The simpler cluster integrals can be obtained straightforwardly.

TABLE XIII. Hard sphere virial coefficients.

	B/N_mb	C/B^2	D/B^3	E/B^4	F/B^5	G/B^6
Exact	1	0.625	0.2869	0.1103[a]	0.0386[b]	0.0138[c]
SPT	1	0.625	0.2969	0.1211	0.0449	0.0156
CS	1	0.625	0.2813	0.1094	0.0156	0.0132
BG(P)	1	0.625	0.2252	0.0475		
BG(C)	1	0.625	0.3424	0.1335		
K(P)	1	0.625	0.1400			
K(C)	1	0.625	0.4418			
PY(P)	1	0.625	0.2500	0.0859	0.0273	0.0083
PY(C)	1	0.625	0.2969	0.1211	0.0449	0.0156
HNC(P)	1	0.625	0.4453	0.1447	0.0382	
HNC(C)	1	0.625	0.2092	0.0493	0.0281	

[a] Kim and Henderson (1968a).

[b] Ree and Hoover (1964a).

[c] Ree and Hoover (1967).

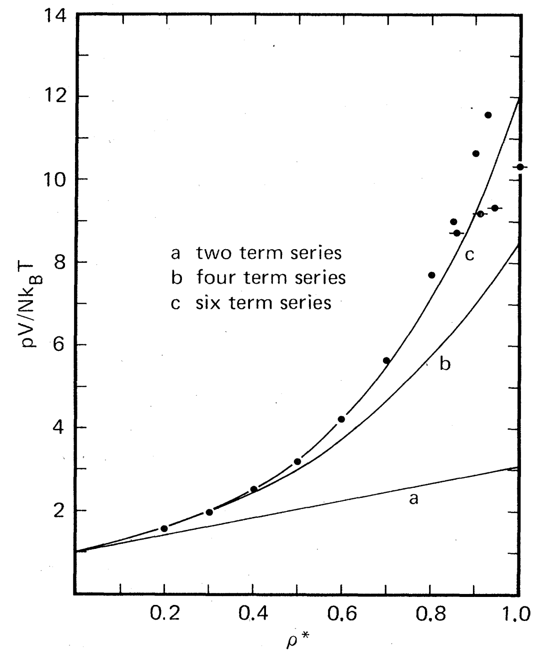

FIG. 11. Equation of state of hard spheres. The curves give the results calculated from truncated virial series. The points denoted by ● and -●- give the computer simulation results of Barker and Henderson (1971a, 1972) and Alder and Wainwright (1960) for fluid and solid hard spheres, respectively. The reduced density ρ^* is Nd^3/V.

The more complex integrals, such as $D6$, are most accurately obtained by expanding the integrand in spherical harmonics (Barker and Monaghan, 1962b). Results for B, C, D, and E for the 6–12 potential are plotted in Fig. 12. At high temperatures, where the repulsive forces dominate, the virial coefficients are positive. However, at low temperatures they are negative. The temperature for which $B = 0$ is called the *Boyle temperature*. For this temperature, the isotherm of pV/Nk_BT approaches unity with zero slope as $\rho \to 0$. Qualitatively, one may say that the attractive forces are important below this temperature.

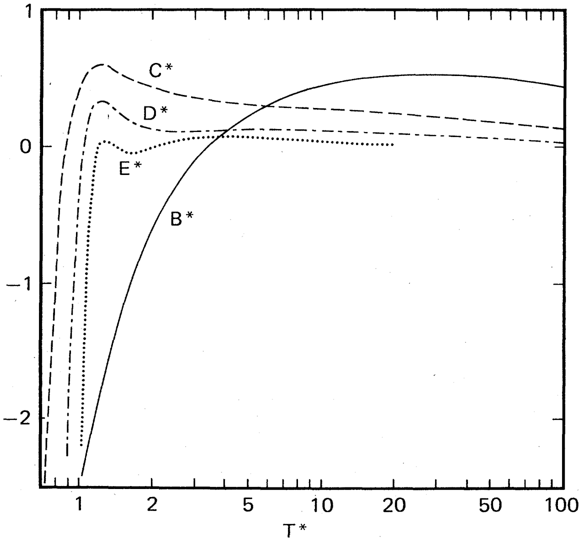

FIG. 12. Virial coefficients for 6–12 fluid. The nth virial coefficient is reduced by the factor $(2\pi N_m \sigma^3/3)^{n-1}$.

C. Density expansion of the radial distribution function

The distribution functions can also be expanded in powers of V^{-1}, or more conventionally ρ. At low densities, where only pairs of molecules interact, the radial distribution function (RDF) is given by

$$g(r) = e(r). \tag{4.41}$$

The higher-order terms can be obtained by a method similar to that given above. The result is

$$g(r) = e(r)y(r), \tag{4.42}$$

where

$$y(r) = 1 + \sum_{n=1}^{\infty} \rho^n y_n(r), \tag{4.43}$$

and $y_1(r) = c_2(r)$,

$$y_2(r) = d_3(r) + 2d_4(r) + \tfrac{1}{2}\{c_2^2(r) + d_5(r)\}, \tag{4.44}$$

where the doubly-rooted cluster integral integrals, $c_2, \ldots, d_5$ are given in Fig. 13. It is to be noted that $c_2^2(r)$ decomposes into a product of simpler integrals. Thus, some of the cluster integrals contributing to $g(r)$ or $y(r)$ can be decomposed. On the other hand, the expansion of $\ln g(r)$ consists only of integrals which cannot be decomposed. For example,

$$\ln g(r) = -\beta u(r) + \ln y(r), \tag{4.45}$$

where

$$\ln y(r) = \sum_{n=1}^{\infty} \rho^n \xi_n(r), \tag{4.46}$$

$\xi_1(r) = y_1(r)$, and

$$\xi_2(r) = y_2(r) - \frac{1}{2} y_1^2(r),$$

$$= d_3(r) + 2d_4(r) + \frac{1}{2} d_5(r). \tag{4.47}$$

If Eqs. (4.42) and (4.43) are substituted into the compressibility, pressure or energy equations, the virial expansion is obtained. This, of course, is expected since, once (4.3) is assumed, everything is exact. The compressibility equation yields (4.26) to (4.28) directly. The pressure equation yields these expressions because

$$B1' = -3(B1), \tag{4.48}$$

$$C3' = -2(C3), \tag{4.49}$$

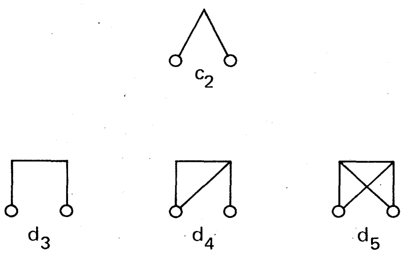

FIG. 13. Irreducible diagrams contributing to $y_1(r)$ and $y_2(r)$.

$$4(D4') = -9(D4), \tag{4.50}$$

$$4(D5') + D5\alpha' = -9(D5), \tag{4.51}$$

and

$$2(D6') = -3(D6). \tag{4.52}$$

Equations (4.48)–(4.52) are established by integration by parts. The energy equation yields (4.26)–(4.28) because

$$\partial B1/\partial\beta = B1'', \tag{4.53}$$

$$\partial C3/\partial\beta = C3'', \tag{4.54}$$

$$\partial D4/\partial\beta = D4'', \tag{4.55}$$

$$\partial D5/\partial\beta = 4(D5'') + D5\alpha'', \tag{4.56}$$

and

$$\partial D6/\partial\beta = 6(D6''). \tag{4.57}$$

The triplet distribution function has the expansion

$$g_{123} = g_{12}g_{13}g_{23}[1 + \rho d_3'(123) + \ldots], \tag{4.58}$$

where d_3' has been defined in (4.38). If d_3' and all higher-order terms are neglected then one has the superposition approximation of Kirkwood (1935).

For hard spheres, $c_2(r)$, and thus $y_1(r)$, is given by (4.33). For this system, Nijboer and van Hove (1952) have calculated $y_2(r)$ and Ree *et al.* (1966) have calculated $y_3(r)$. McQuarrie (1964), Hauge (1965), and Barker and Henderson (1967c) have calculated $y_1(r)$ and $y_2(r)$ for the square-well potential. Henderson (1965), Henderson and Oden (1966), Henderson *et al.* (1967), Kim, Henderson, and Oden (1969) have computed $y_1(r)$, $y_2(r)$ and $y_3(r)$ for the 6–12 potential.

D. Virial coefficients for more complex systems

1. Quantum effects

Systems such as liquid helium, which have large quantum mechanical effects, are beyond the scope of this article. However, for systems such as argon, and even neon and gaseous hydrogen and helium at high temperatures, the quantum effects are small and can be treated by an expansion in h^2, where h is Planck's constant. For additive interactions which are analytic (other than at $r = 0$), the free energy is given by the expansion

$$A = A_{\rm cl} + \frac{h^2}{24\pi m k_B T} N_\rho \int \nabla^2 u(r) g_{\rm cl}(r) r^2 dr + \cdots, \tag{4.59}$$

where $A_{\rm cl}$ and $g_{\rm cl}$ are the free energy and RDF of the classical system (i.e., $h \to 0$ or $m \to \infty$). An alternative form of (4.59), which is suited to machine simulations, has been given earlier, Eq. (3.31). Combining (4.59) with the density expansion of $g_{\rm cl}(r)$ gives the quantum correction to the virial coefficients. Kim and Henderson (1966, 1968b) have calculated the correction of order h^2 to B, C, D, and E for the 6–12 potential. The higher-order h^4 and h^6 corrections to B are derived and tabulated by Haberlandt (1964) for the 6–12 potential.

For potentials such as the hard-sphere potential, which are not analytic, (4.59) is not valid. For hard spheres, Hemmer (1968) and Jancovici (1969a) have obtained

$$\frac{A}{Nk_BT} = \frac{A_{\rm cl}}{Nk_BT} + \frac{\pi}{\sqrt{2}}\lambda\rho d^2 g_{\rm cl}(d) + \cdots, \tag{4.60}$$

where $\lambda = h/(2\pi m k_B T)^{1/2}$. For hard spheres, the quantum corrections are of order h rather than h^2 as in (4.59). Combining (4.60) with the density expansion of $g_{\rm cl}(d)$ gives the quantum correction to the hard-sphere virial coefficients. Jancovici (1969b) has obtained the second-order quantum correction to the hard-sphere free energy also. This result can be used to obtain the quantum corrections to the virial coefficients. Jancovici (1969b) gives the quantum corrections, to order λ^2, to the hard-sphere B and C. The quantum corrections to order λ^6 for the hard-sphere B have been given by Nilsen (1969) who extended the lower-order calculations of Uhlenbeck and Beth (1936), Handelsman and Keller (1966), Hemmer and Mork (1967), Hill (1968), and Gibson (1970).

Gibson (1972) has obtained the first quantum correction to the free energy for the square-well potential and from this deduced the first quantum corrections to the virial coefficients. The first quantum correction to B for the square-well potential has been obtained earlier. References are given by Gibson (1972).

The first quantum correction to the RDF for an analytic potential have been obtained by Singh and Ram (1973, 1974) and Gibson (1974). These expressions can be used to obtain expressions for the first quantum corrections to the $y_n(r)$. Singh and Ram give some numerical results for these corrections to the $y_n(r)$. Equivalent expressions in the discrete representation can be obtained easily from (3.14) and (3.34). Singh (1974), Gibson and Byrnes (1975) and Gibson (1975a, b) have obtained the first quantum correction to the RDF for non-analytic potentials.

2. Three-body interactions

An expression for the free energy, which is valid to first-order in the strength of the three-body interaction and which is useful for machine simulations, has been given in (3.14). Written in terms of distribution functions, this becomes

$$A = A_{2b} + \frac{1}{6}N\rho^2 \int g_{2b}(123)\, u(123)\, d\vec{r}_2\, d\vec{r}_3, \tag{4.61}$$

where A_{2b} and $g_{2b}(123)$ are the free energy and triplet distribution function in the absence of three-body forces. It is to be remembered that (4.61) is valid only to first-order in the strength of the three-body interactions, ν. For simple fluids, such as argon, this is not a practical limitation because the ν^2 terms are negligibly small. From (4.61) it is seen that there is no three-body force contribution to the second virial coefficient. The third virial coefficient is

$$C = \frac{N_m^2}{3}\left[-C3 + \int e_{12}e_{13}e_{23}u_{123}\, d\vec{r}_2\, d\vec{r}_3\right]. \tag{4.62}$$

A diagrammatic notation to represent the three-body terms has been devised. For example, see Rushbrooke and Silbert (1967).

In Fig. 14 the third virial coefficient of argon, calculated using the BFW (Barker *et al.*, 1971) pair-potential and the triple-dipole (Axilrod–Teller), dipole-dipole–quadrupole, and fourth-order triple-dipole three-body potentials. These results were obtained by Barker (1976) and Caligaris and Henderson (1975). The agreement with experiment is good only if the three-body terms are included. Johnson and Spurling (1971b) have calculated the contributions of the dipole–quadrupole–quadrupole and triple–quadrupole forces to C and has found them to be small. For comparison, the second virial coefficient, calculated from the BFW potential, is also plotted in Fig. 14. Casanova *et al.* (1970), Dulla *et al.* (1971), and Johnson and Spurling (1974) have calculated three-body force contributions to D.

Lee *et al.* (1975) and Caligaris and Henderson (1975) have calculated the second and third virial coefficients (including three-body interactions) of Ar + Kr and Kr + Xe mixtures.

There have been no calculations of the effects of three-body forces on the $y_n(r)$, the coefficients in the density expansion of the RDF.

3. Nonspherical potentials

For a nonspherical potential, the second virial coefficient is given by a straightforward generalization of (4.14). Thus,

$$B=-\frac{N_m}{2V}\int f(1,2)d\vec{r}_1 d\vec{r}_2 d\Omega_1 d\Omega_2, \tag{4.63}$$

where the $d\vec{r}_i$ are the position volume elements and the $d\Omega_i$ are the angle volume elements normalized so that the integral of $d\Omega_i$ is unity. Appropriate generalizations of (4.26) to (4.28) give C and D.

There has been a great deal of work on the evaluation of virial coefficients for a wide variety of angle-dependent potentials. Here we will attempt only to review work on nonspherical potentials which have also been used in the theory of liquids.

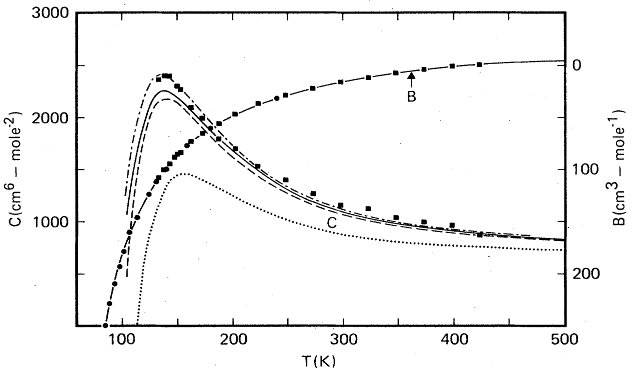

FIG. 14. Second and third virial coefficients of argon. For B, the solid curve gives the results calculated using the BFW pair-potential. For C, the curves marked · · ·, ----, –––, and the solid curve give the results calculated using just the BFW pair potential, the BFW pair potential and *ddd*, *ddd* +*ddq*, and *ddd* +*ddq* +*ddd*$_4$, respectively, where *ddd*, *ddq*, and *ddd*$_4$ are the dipole–dipole–dipole (Axilrod–Teller), dipole–dipole–quadrupole, and fourth-order dipole–dipole–dipole terms. The points ■ and ● give the experimental results of Michels *et al*. (1949, 1958) and Weir *et al*. (1967), respectively.

a. Spherical cores

For dipolar hard spheres, the potential energy is given by

$$\begin{aligned} u(r_{12},\Omega_1,\Omega_2)&=\infty,\ r<\sigma \\ &=-(\mu^2/r_{12}^3)D(1,2),\ r>\sigma, \end{aligned} \tag{4.64}$$

where the angle-dependent term $D(1,2)$ is

$$\begin{aligned} D(1,2)&=3(\hat{\vec{\mu}}_1\cdot\hat{\vec{r}}_{12})(\hat{\vec{\mu}}_2\cdot\hat{\vec{r}}_{12})-\hat{\vec{\mu}}_1\cdot\hat{\vec{\mu}}_2 \\ &=2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2), \end{aligned} \tag{4.65}$$

and $\hat{\vec{\mu}}_i$ and $\hat{\vec{r}}_{12}$ are unit vectors. The second virial coefficient is

$$B=-\frac{N}{4}\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta_1 d\theta_1\int_0^{\pi}\sin\theta_2 d\theta_2\int_0^{\infty}r_{12}^2 f(1,2)dr_{12}. \tag{4.66}$$

The original method (Keesom 1912) for evaluating (4.66) was to expand $f(1,2)$ in (4.66) in powers of β and integrate over r_{12}. The subsequent integration over the angles results in the vanishing of the odd powers of β. The result is

$$B=b[1-x^2/3-x^4/75-29x^6/55125-\cdots], \tag{4.67}$$

where $x=\beta\mu^2/\sigma^3$. With the advent of computers, Eq. (4.66) could be evaluated by direct numerical integration. Watts (1972) has calculated C for dipolar hard spheres. Keesom (1915) has also calculated B for quadrupolar hard spheres.

Stockmayer (1941), Rowlinson (1949), and Barker and Smith (1960) have calculated B for the Stockmayer potential

$$u(r)=4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right\}-\frac{\mu^2}{r^3}D(1,2). \tag{4.68}$$

Rowlinson (1951a) has calculated C for this potential. Rowlinson (1951b) has also calculated B and C for a 6–12 potential with both dipolar and quadrupolar terms. Pople (1954a, b) and Buckingham and Pople (1955) have considered methods of calculating B for a 6–12 potential with a variety of multipolar terms. A review of these techniques has been given by Mason and Spurling (1969).

b. Nonspherical cores

For hard spheres, $B=N_m b$. For hard nonspherical molecules, we can write

$$B=N_m bf, \tag{4.69}$$

where b is the second virial coefficient of hard spheres of the same volume as the nonspherical molecules (i.e., four times the volume of N_m hard spheres) and $f>1$ is a shape-dependent factor. Isihara (1950), Isihara and Hayashida (1951a, b) and Kihara (1951, 1953a, b) have shown that for *convex* molecules f is related to the volume, V_1, surface area, S_1, and mean radius of curvature, $\bar{R}_1$, of the molecule. In fact,

$$f=1+\left(\frac{\bar{R}_1 S_1}{4V_1}-\frac{3}{4}\right), \tag{4.70}$$

so that

TABLE XIV. $\bar{R}_1$, S_1, and V_1 for several shapes.

Shape	Size	$\bar{R}$	S_1	V_1
Sphere	Radius $=a$	a	$4\pi a$	$4\pi a^3/3$
Rectangular Parallelopiped	Length of edges l_1, l_2, l_3	$(l_1+l_2+l_3)/4$	$2(l_1l_2+l_1l_3+l_2l_3)$	$l_1l_2l_3$
Regular tetrahedron	Side $=l$	$3l(\tan^{-1}\sqrt{2})/2\pi$	$\sqrt{3}\,l^2$	$\sqrt{2}\,l^3/12$
Cylinder	Length $=l$ Radius $=a$	$\frac{1}{4}(l+\pi a)$	$2\pi a(l+a)$	$\pi a^2 l$
Prolate (cigar shaped) Spherocylinder	Length $=l$ Radius $=a$	$l/4+a$	$2\pi a(l+2a)$	$\pi a^2(l+4a/3)$
Prolate ellipsoid of revolution	Major semi-axis $=a$	$\frac{a}{2}\left(1+\frac{1-\epsilon^2}{2\epsilon}\ln\frac{1+\epsilon}{1-\epsilon}\right)$	$2\pi b^2\left(1+\frac{\sin^{-1}\epsilon}{\epsilon(1-\epsilon^2)^{1/2}}\right)$	$4\pi ab^2/3$
Oblate ellipsoid of revolution	Minor semi-axis $=b$ $\epsilon^2=(a^2-b^2)/a^2$	$\frac{b}{2}\left(1+\frac{\sin^{-1}\epsilon}{\epsilon(1-\epsilon^2)^{1/2}}\right)$	$2\pi a^2\left(1+\frac{1-\epsilon^2}{2\epsilon}\ln\frac{1+\epsilon}{1-\epsilon}\right)$	$4\pi a^2 b/3$

$$B=N_m[V_1+\bar{R}_1S_1]. \tag{4.71}$$

The quantities V_1, S_1, and $\bar{R}_1$ are given for several shapes in Table XIV. Gibbons (1969), using the scaled-particle theory which will be discussed in Sec. V, has shown that, for this theory,

$$C=N_m^2\left[V_1^2+2(\bar{R}_1S_1)V_1+\frac{1}{3}(\bar{R}_1S_1)^2\right], \tag{4.72}$$

and

$$D=N_m^3[V_1^3+3(\bar{R}_1S_1)V_1^2+(\bar{R}_1S_1)^2V_1]. \tag{4.73}$$

In addition, Gibbons has obtained approximations to the higher-order virial coefficients. Equation (4.72) is exact for hard spheres.

In the special case of prolate spherocylinders of length l and diameter σ

$$\frac{B}{N_m b}=\frac{1+\alpha}{4}, \tag{4.74}$$

$$\frac{C}{N_m^2 b^2}=\frac{1+2\alpha+\alpha^2/3}{16}, \tag{4.75}$$

$$\frac{D}{N_m^3 b^3}=\frac{1+3\alpha+\alpha^2}{64}, \tag{4.76}$$

where

$$b=\frac{2\pi}{3}\sigma^3\left(1+\frac{3x}{2}\right), \tag{4.77}$$

$x=l/\sigma$, and

$$\begin{aligned}\alpha&=\bar{R}_1S_1/V_1,\\&=3(1+x)(1+x/2)/(1+3x/2).\end{aligned} \tag{4.78}$$

For hard spheres $x=0$ and $\alpha=3$. Rigby (1970) has calculated D, for $x=0.4$ and 0.8, by a Monte Carlo method and obtained the results in Table XV. Equations (4.72) and (4.75) are probably exact for prolate spherocylinders as well as for hard spheres.

By considering the second virial coefficient of a gas of hard rods, Onsager (1942, 1949) found a first-order phase change to an anisotropic phase which is similar to a nematic liquid crystal. Zwanzig (1963) obtained similar results using the virial coefficients up to seventh, calculated from the results of Hoover and DeRocco (1961, 1962), of a gas of long hard parallelopipeds constrained to point only in three mutually perpendicular directions.

Kihara (1951, 1953a) has studied convex molecules using nonspherical potentials which have the form $u=u(\rho)$, where $u(r)$ is some simple central potential (for example, the 6–12 potential) and ρ is the shortest distance between the *cores* (not the centers) of the molecules. For such simplified potentials B can be calculated with relative ease. The hard convex molecules considered above are of this form.

Chen and Steele (1969, 1970) have calculated the virial coefficients of linear dumbell molecules composed of fused hard spheres. Their results and the Monte Carlo results (Rigby 1970) for virial coefficients of this system are given in Table XV. The quantity x is l/σ, where l is the separation of the centers of the spheres. Spherical harmonic contributions to the coefficients of the density expansion of $g(r_{12}, \Omega_1, \Omega_2)$ were also calculated. Sweet and Steele (1967, 1969) have made similar calculations for diatomic 6–12, a Kihara core potential for a linear convex molecule, and a Stockmayer poten-

TABLE XV. Virial coefficients for hard prolate spherocylinders and fused diatomic hard spheres.

	Prolate spherocylinders				
x	0	0.4		0.8	
α	3	3.15		3.44	
B/N_mb	1	1.038 [a]		1.109 [a]	
$C/N_m^2b^2$	0.625	0.663 [a]	0.665 [b]	0.738 [a]	0.740 [b]
$D/N_m^3b^3$	0.2869	0.318 [a]	0.301 [b]	0.361 [a]	0.336 [b]
	Fused hard spheres				
x	0	0.4		0.6	
B/N_mb	1	1.053 [c]		1.119 [c]	
$C/N_m^2b^2$	0.625	0.68 [c]	0.684 [b]	0.75 [c]	0.757 [b]
$D/N_m^3b^3$	0.2869		0.318 [b]		0.359 [b]

[a] Equations (4.74)–(4.76).

[b] Monte Carlo calculations (Rigby, 1970).

[c] Chen and Steele (1969, 1970).

tial.

The fused hard spheres and diatomic 6–12 potentials are examples of what may be called interaction-site potentials in which the pair-potential of the molecule is built up out of central pair potentials between interaction sites within the molecule. These would usually be the nuclei (or some subset of the nuclei) within the molecule in which case they are often referred to as atom-atom potentials. Evans and Watts (1975, 1976b) have used such interaction site potentials to compute B for benzene.

Ladanyi and Chandler (1975) have reformulated the Mayer cluster expansion in terms of f functions for the site–site interactions rather than in terms of the molecular f functions. Because the site–site f functions are functions only of the scalar distance between the interaction sites, Ladanyi and Chandler hope that a simplification will be obtained even though the number of diagrams has increased.

Rowlinson (1951b) has used a four-charge model with a central 6–12 potential to obtain a pair potential for water. He has used a multipole expansion based on this model and, retaining only the dipolar and quadrupolar terms, has calculated B and C. Johnson and Spurling (1971a) and Johnson *et al.* (1972) have made similar calculations. With the availability of modern computers, there is no need to restrict oneself to only the dipolar and quadrupolar terms. Evans and Watts (1974) have calculated B for the full Rowlinson potential, the Ben-Naim and Stillinger (1972) potential and for some potentials arising from Hartree–Fock calculations of the interactions between water molecules.

Kirkwood (1933b), Wang Chang (1944), McCarty and Babu (1970), Singh and Datta (1970), and Pompe and Spurling (1973) have calculated quantum corrections to the virial coefficients for nonspherical molecules.

V. SCALED-PARTICLE THEORY

A. Hard spheres

It has already been pointed out in Sec. I that, for hard spheres of diameter d, the equation of state is given by

$$pV/Nk_BT = 1 + 4\eta g(d), \tag{5.1}$$

where $\eta = (\pi/6)\rho d^3$. The factor $\pi d^3/6$ is the volume of a hard sphere. Thus, for hard spheres it is only necessary to find $g(d)$. Reiss *et al.* (1959) have developed a simple but accurate method, called the *scaled-particle theory* (SPT), for obtaining $g(d)$ and thus p.

Let $p_0(r)$ be the probability that there is no molecule whose center lies within a sphere of radius r, centered about some specified point. Thus, $-dp_0/dr$ is the probability of finding an empty sphere whose radius lies between r and $r+dr$. This is equal to the product of the probability of having no molecule within the radius r and the conditional probability, $4\pi\rho G(r)r^2dr$, of there being a center of at least one molecule within dr of r when no molecule is inside the sphere of radius r. The significance of $G(r)$ arises from the fact that an empty sphere of radius d affects the remainder of the fluid precisely like another molecule (hence the name scaled-particle theory), i.e., $G(d) = g(d)$.

Thus,

$$-dp_0(r)/dr = p_0(r)4\pi\rho r^2 G(r). \tag{5.2}$$

Also,

$$p_0(r) = \exp\{-\beta W\}, \tag{5.3}$$

where $W(r)$ is the reversible work necessary to create a cavity of radius r in the fluid. It is to be noted that p_0, W, and G depend upon ρ as well as r. However, for notational simplicity we do not show this dependence explicitly. Combining (5.2) and (5.3) gives

$$dp_0/p_0 = -\beta dW = -4\pi\rho G(r)r^2dr. \tag{5.4}$$

Hence,

$$dW = pdV + \gamma dS = k_BT\rho G(r)dV, \tag{5.5}$$

where γ is the surface tension and S and V are the surface area and the volume of the system, respectively. Therefore,

$$G(r) = (\rho k_BT)^{-1}\left(p + \frac{2\gamma}{r}\right). \tag{5.6}$$

It is to be noted that (5.6) gives

$$G(\infty) = pV/Nk_BT = 1 + 4\eta G(d). \tag{5.7}$$

To proceed further we need to know the r dependence of γ. For r not too small, it is reasonable to assume

$$\gamma(r) = \gamma_0\{1 + \delta(d/r)\}, \tag{5.8}$$

where γ_0 and δ are constants to be determined. Substitution of (5.8) into (5.6) gives

$$G(r) = (\rho k_BT)^{-1}\left(p + \frac{2\gamma_0}{r} + \frac{4\gamma_0\delta d}{r^2}\right). \tag{5.9}$$

To determine γ_0 and δ it is necessary to consider $p_0(r)$ again. For $r<d/2$, no more than one molecular center can lie within a sphere or radius r and, therefore, $p_0(r)$ is equal to unity minus the probability of there being a molecular center within the sphere. Thus,

$$p_0(r) = 1 - (4\pi/3)r^3\rho, \quad r<d/2. \tag{5.10}$$

Hence, combining (5.2) and (5.10), we have

$$\begin{aligned} -dp_0/dr &= p_0(r)4\pi r^2\rho G(r) \\ &= 4\pi r^2\rho, \end{aligned} \tag{5.11}$$

for $r<d/2$. Thus, $p_0(r)G(r) = 1$ and

$$G(r) = [1 - (4\pi/3)r^3\rho]^{-1}, \quad r<d/2. \tag{5.12}$$

Consequently, Eq. (5.12) is valid for all $r<d/2$ and Eq. (5.9) is valid for r not too small. For $d/2<r<d/\sqrt{3}$, two molecular centers can lie within the sphere and $p_0(r)$ and $G(r)$ cannot be determined without first knowing $g(r)$.

However, as an approximation we can assume that (5.9) is valid for all $r>d/2$. *This is the central approximation of the SPT.* Hence, approximately

$$G(r) = \frac{p}{\rho k_BT} + A\left(\frac{d}{r}\right) + B\left(\frac{d}{r}\right)^2, \quad r<d/2, \tag{5.13}$$

where $A = 2\gamma_0/\rho k_BTd$ and $B = 4\gamma_0\delta/\rho k_BTd^2$. Solving Eqs. (5.7) and (5.13) for $p/\rho kT$ and $G(r)$ gives

$$\frac{p}{\rho kT} = \frac{1 + 4\eta(A+B)}{1 - 4\eta}\ . \tag{5.14}$$

and

$$G(r)=[1-8\eta(r/d)^3]^{-1},\quad r<d/2$$

$$=\frac{1+4\eta(A+B)}{1-4\eta}+\frac{A}{r}+\frac{B}{r^2},\quad r>d/2. \tag{5.15}$$

Expressions for A and B, and thus γ_0 and δ can be obtained by requiring that $G(r)$ and dG/dr be continuous at $r=d/2$. The resulting values for A and B are

$$A=-\frac{3\eta(1+\eta)}{2(1-\eta)^3}, \tag{5.16}$$

and

$$B=\frac{3\eta^2}{4(1-\eta)^3}. \tag{5.17}$$

Therefore,

$$\frac{p}{\rho k_BT}=\frac{1+\eta+\eta^2}{(1-\eta)^3}. \tag{5.18}$$

Thus, in the SPT

$$g(d)=\frac{4-2\eta+\eta^2}{4(1-\eta)^3}. \tag{5.19}$$

Equation (5.18) gives an exact second and third virial coefficient and, as may be seen in Table XIII, gives reasonable values for the higher virial coefficients also. On the other hand, (5.18) must fail at high densities since it predicts that p remains finite and monotonically increasing for all $\eta<1$ and, therefore, for densities greater than close packing. However, for the densities at which hard spheres are fluid, Eq. (5.18) is in good agreement with the machine simulation results, as may be seen in Fig. 15.

The SPT result for γ_0, obtained from (5.16), is

$$\gamma_0=-\frac{9}{2\pi}\left(\frac{k_BT}{d^2}\right)\eta^2\frac{1+\eta}{(1-\eta)^3}. \tag{5.20}$$

Expanding (5.20) in powers of the density gives

$$\gamma_0=-\frac{\pi}{8}k_BTd^4\rho^2+\cdots, \tag{5.21}$$

which agrees exactly with the known first term in the density expansion of γ_0 (Kirkwood and Buff, 1949). The fact that the surface tension is negative may be, at first sight, surprising. However, it is an immediate consequence of the fact that the hard-sphere fluid has no attractive forces and so can be maintained at finite volume only by means of an external pressure.

The SPT also gives expressions for the equations of state of two-dimensional hard discs and one-dimensional hard rods (Helfand *et al.*, 1961). The expressions are

$$\frac{pA}{Nk_BT}=\frac{1}{(1-y)^2}, \tag{5.22}$$

where $y=(\pi/4)\rho d^2$, and

$$\frac{pL}{Nk_BT}=\frac{1}{1-\rho d}, \tag{5.23}$$

respectively, for hard discs and hard rods. Equation (5.22) is a good approximation to the machine simulation results for hard discs and (5.23) is exact.

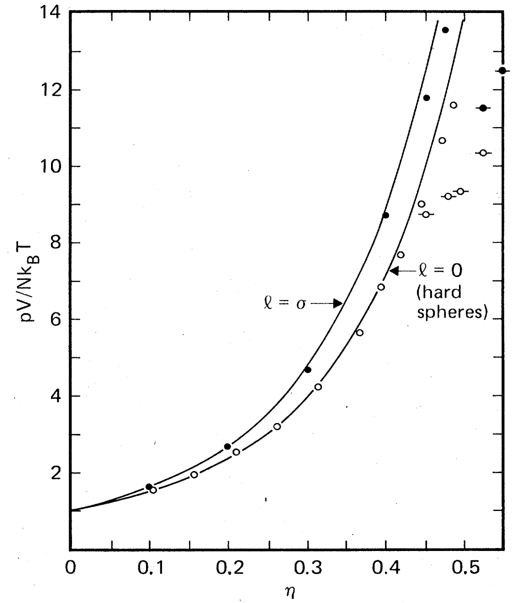

FIG. 15. Equation of state of hard spheres and hard prolate spherocylinders. The points marked ○ and ● give the simulation results of Barker and Henderson (1971a, 1972) and Few and Rigby (1973) for fluid hard spheres and spherocylinders, respectively, and the points marked -○- and -●- give the simulation results of Alder and Wainwright (1960) and Few and Rigby (1973) for solid hard spheres and spherocylinders, respectively. The curves give the SPT results. The quantity η is ρV_1, where V_1 is the volume of a molecule.

Carnahan and Starling (1969) have empirically observed that results even better than those of (5.18) can be obtained by a simple empirical modification of (5.18). Carnahan and Starling (CS) added the factor $\lambda\eta^3/(1-\eta)^3$ to (5.18) and chose λ to be the integer which gave the closest approximation to D (and, coincidently, to E and F also). The CS equation of state is

$$\frac{p}{\rho k_BT}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}. \tag{5.24}$$

Thus, in this approximation

$$g(d)=\frac{4-2\eta}{4(1-\eta)^3}. \tag{5.25}$$

The virial coefficients and equation of state, calculated from Eq. (5.24), are given in Table XIII and Fig. 16, respectively. Both are in excellent agreement with the exact results. It is to be noted, however, that (5.24) predicts that densities greater than close packing can be obtained and so must fail at high densities. The CS expression for the free energy of a hard-sphere fluid may be obtained by integration. The result is

$$\frac{A}{Nk_BT}=3\ln\lambda-1+\ln\rho+\frac{4\eta-3\eta^2}{(1-\eta)^2}, \tag{5.26}$$

where $\lambda=h/(2\pi mkT)^{1/2}$. Henderson (1975b) has empirically modified (5.22) to obtain a very accurate expression for the hard-disc equation of state. His expression is

$$\frac{pA}{Nk_BT}=\frac{1+y^2/8}{(1-y)^2}. \tag{5.27}$$

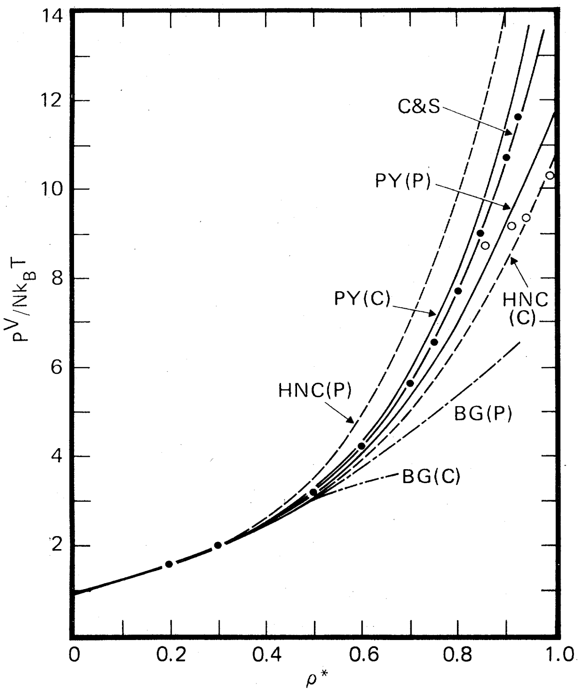

FIG. 16. Equation of state of hard spheres. The points marked ● and ○ give the machine simulation results of Barker and Henderson (1971a, 1972) for fluid hard spheres and of Alder and Wainwright (1960) for solid hard spheres. The curves give the results of various theories. The BG results were calculated by Kirkwood *et al*. (1950) and Levesque (1966). The HNC results were calculated by Klein (1963). The reduced density ρ^* is Nd^3/V.

The SPT can also be used to obtain the equation of state of hard-sphere mixtures (Lebowitz, Helfand, and Praestgaard, 1965). Their result is

$$\frac{p}{\rho k_B T}=\frac{1+\xi+\xi^2}{(1-\xi)^3}-\frac{\pi}{2}\frac{\rho}{(1-\rho)^3}\sum_{i<j=1}^{m}x_i x_j(d_{ii}-d_{jj})^2\,[2d_{ij}+d_{ii}d_{jj}X], \tag{5.28}$$

where d_{ii} are the diameters of the m components,

$$\xi=\frac{\pi}{6}\rho\sum_{k=1}^{m}x_k d_{kk}^3, \tag{5.29}$$

$$X=\frac{\pi}{6}\rho\sum_{k=1}^{m}x_k d_{kk}^2, \tag{5.30}$$

$$d_{ij}=\frac{d_{ii}+d_{jj}}{2}, \tag{5.31}$$

$$x_i=\frac{N_i}{N}, \tag{5.32}$$

N_i is the number of hard spheres of species i, and N is the total number of molecules in the mixture. Equation (5.28) also gives B and C correctly and is in good agreement with the machine results for hard sphere mixtures. In addition, for the extreme case of a binary mixture in which $d_{11}\to 0$, Eq. (5.28) yields the result

$$\frac{p}{\rho k_B T}=\frac{1+(1-3x_1)\xi+\xi^2}{(1-\xi)^3}, \tag{5.33}$$

where $\xi=(\pi/6)\rho d_{22}^3 x_2$. Equation (5.33) can be written in the form

$$\frac{p}{\rho k_B T}=\frac{x}{1-\xi}+x_2\frac{1+\xi+\xi^2}{(1-\xi)^3}$$

$$=\frac{x_1}{1-\xi}+x_2\left(\frac{pV}{Nk_BT}\right)_2. \tag{5.34}$$

Equation (5.34) is exact if an exact expression for $(pV/Nk_BT)_2$ is used. Equation (5.34) may be obtained directly by observing that in the limit $d_{11}\to 0$ all the volume unoccupied by the big spheres is available to the point spheres.

B. Hard convex molecules

Gibbons (1969, 1970) and Boublik (1974) have applied the SPT to mixtures of hard convex (not necessarily spherical) molecules. The result is

$$\frac{p}{\rho k_B T}=\frac{1}{1-Y\rho}+\frac{AB\rho}{(1-Y\rho)^2}+\frac{1}{3}\frac{B^2C\rho^2}{(1-Y\rho)^3}, \tag{5.35}$$

where

$$A=\sum_{i=1}^{m}x_i\bar{R}_i, \tag{5.36}$$

$$B=\sum_{i=1}^{m}x_i S_i, \tag{5.37}$$

$$C=\sum_{i=1}^{m}x_i\bar{R}_i^2, \tag{5.38}$$

$$Y=\sum_{i=1}^{m}x_i V_i, \tag{5.39}$$

and $\bar{R}_i$, S_i, and V_i are the mean radius of curvature, surface area, and volume, respectively, of a molecule of species i. Expressions for these quantities are given in Table XIV for molecules for various shapes. For the particular case of a pure fluid, Eq. (5.35) becomes

$$\frac{p}{\rho k_B T}=\frac{1}{1-V_1\rho}+\frac{\bar{R}_1S_1\rho}{(1-V_1\rho)^2}+\frac{1}{3}\frac{\bar{R}_1^2S_1^2\rho^2}{(1-V_1\rho)^3}. \tag{5.40}$$

For hard spheres, $\bar{R}_i=d_{ii}/2$, $S_i=\pi d_{ii}^2$, $V_i=(\pi/6)d_{ii}^3$, and (5.40) and (5.35) give (5.18) and (5.28) respectively. Equations (5.40) and (5.35) give the correct second virial coefficient and, for hard spheres, give the correct third virial coefficient. For prolate spherocylinders, (5.40) gives an accurate third virial coefficient (Rigby 1970). Thus, one may conjecture that the SPT gives the correct third coefficient for all hard convex molecules.

For hard prolate spherocylinders of length l and diameter σ, Eq. (5.40) becomes

$$\frac{p}{\rho kT}=\frac{3+(3\alpha-6)\eta+(\alpha^2-3\alpha+3)\eta^2}{(1-\eta)^3}, \tag{5.41}$$

where α is given by Eq. (4.78) and $\eta=V_1\rho$. For hard spheres $\alpha=3$. Few and Rigby (1973) and Vieillard-Baron (1974) have made Monte Carlo calculations for prolate spherocylinders for $\alpha=3.6$ ($l=\sigma$) and $\alpha=4.5$ ($l=2\sigma$), respectively. The $\alpha=3$ (spheres) and $\alpha=3.6$ results are plotted in Fig. 15. The SPT works well for hard spherocylinders as well as for hard spheres. Presumably, the SPT is reliable for any isotropic fluid of hard convex molecules.

Cotter and Martire (1970a) have used the SPT to obtain an equation of state for perfectly aligned, as well as isotropic, hard spherocylinders. Cotter and Martire (1970b) and Timling (1974) have also made calculations for partially aligned spherocylinders. They have used these two models as models of a nematic liquid crystal. They find a liquid–liquid phase change from the isotropic to the aligned phase at high densities. Vieillard–Baron (1974) has attempted to find this phase change for $\alpha = 4.5$ by the Monte Carlo method. He believes his results to show that, for this system, the phase change, if present, occurs at a higher density than that predicted by the SPT. Vieillard–Baron was unable to establish the existence or non-existence of a liquid–liquid phase transition for this system at high densities because of its extreme slowness in achieving equilibrium for $\eta > 0.54$. Some reasons for this have been mentioned in Sec. III.D.5. However, his calculations indicate that the value of η at which melting occurs increases as $x = l/\sigma$ increases, whereas Few and Rigby (1973) reached the opposite conclusion. Actually, both Vieillard–Baron and Few and Rigby may be correct if the volume change on melting increases as x increases. Finally, it is worth noting that the SPT calculations of Cotter and Martire for the aligned phase are for simplified versions of the SPT. Thus, it is possible that better results for the aligned phase can be obtained from the SPT. The more rigorous calculations of Timling only established a lower bound for the fluid-fluid transition.

C. Further developments

We have seen that Eq. (5.18) for the hard-sphere equation of state results from the approximation

$$G(r) = G_0 + G_1/r + G_2/r^2, \tag{5.42}$$

which is *assumed* valid for $r \geq d/2$, together with the conditions

$$G(d/2) = 1/(1-\eta) \tag{5.43}$$

and

$$\left.\frac{dG}{dr}\right|_{r=d/2} = \frac{6\eta}{d(1-\eta)^2}, \tag{5.44}$$

which result from (5.12) together with the condition that $G(r)$ and $dG(r)/dr$ are continuous at $r = d/2$, and the conditions

$$G(d) = g(d) \tag{5.45}$$

and

$$G_0 = (pV/Nk_BT) = 1 + 4\eta G(d). \tag{5.46}$$

To make further progress, we must gain further understanding of $G(r)$. For hard spheres this function can be obtained from $p_0(r)$ through (5.2). Now $p_0(r)$ is the probability of finding an empty sphere of at least radius r. Thus,

$$p_0(r) = \frac{\int_{V'} \exp[-\beta U]\, d\vec{r}_1 \ldots d\vec{r}_N}{\int_V \exp[-\beta U]\, d\vec{r}_1 \ldots d\vec{r}_N}, \tag{5.47}$$

where V is the volume of the system, and V' is the volume outside of the cavity of radius r. Introduce the function

$$\begin{aligned} \epsilon(\vec{r}_i) &= 1, \quad |\vec{r}_i - \vec{R}| < r \\ &= 0, \quad |\vec{r}_i - \vec{R}| > r, \end{aligned} \tag{5.48}$$

where $\vec{R}$ is the center of the cavity. Hence,

$$p_0(r) = \frac{\int \prod_{i=1}^{N} [1 - \epsilon(\vec{r}_i)] \exp[-\beta U]\, d\vec{r}_1 \ldots d\vec{r}_N}{\int \exp[-\beta U]\, d\vec{r}_1 \ldots d\vec{r}_N} \tag{5.49}$$

where both integrations are over the volume V. Now

$$\prod_{i=1}^{N} [1 - \epsilon(\vec{r}_i)] = 1 - \sum_{i=1}^{N} \epsilon(\vec{r}_i) + \sum_{i<j=1}^{N} \epsilon(\vec{r}_i)\epsilon(\vec{r}_j) + \ldots\,. \tag{5.50}$$

Hence,

$$p_0(r) = 1 + \sum_{n=1}^{N} (-1)^n F_n, \tag{5.51}$$

where

$$F_1 = \frac{4}{3}\pi r^3 \rho \tag{5.52}$$

and

$$F_n = \frac{\rho^n}{n!} \int_{\text{sphere of radius } r} g_n(\vec{r}_1 \ldots \vec{r}_n)\, d\vec{r}_1 \ldots d\vec{r}_n\,. \tag{5.53}$$

Thus for $0 \leqslant r \leqslant d/2$, $p_0(r)$ is given by (5.10). For $d/2 \leqslant r \leqslant d/\sqrt{3}$, two molecule centers can lie within the sphere and

$$p_0(r) = 1 - \frac{4\pi}{3} r^3 \rho + \frac{1}{2}\rho^2 \int g(\vec{r}_1, \vec{r}_2)\, d\vec{r}_1 d\vec{r}_2. \tag{5.54}$$

Now $g(\vec{r}_1, \vec{r}_2)$ depends only upon r_{12}. Hence, we can integrate (5.54) in part to obtain

$$p_0(r) = 1 - \frac{4\pi}{3} r^3 \rho + 2\pi\rho^2 \int_0^{2r} s^2 g(s) \left[\frac{4\pi r^3}{3} \left\{1 - \frac{3}{4}\left(\frac{s}{r}\right) + \frac{1}{16}\left(\frac{s}{r}\right)^3\right\}\right] ds. \tag{5.55}$$

The term in the square parenthesis is the common volume of two spheres of radius r whose centers are a distance s apart. At $r = d/\sqrt{3}$, three molecule centers can lie within the sphere. As r increases, more centers can lie within the cavity. For example, at $r = d$, twelve molecule centers can lie within the cavity.

The function $G(r)$ for hard spheres can now be calculated from $p_0(r)$. As mentioned earlier, $g(r)$ must be known to obtain $G(r)$ for $d/2 \leqslant r \leqslant d/\sqrt{3}$. It can be verified directly from (5.55) that G and its first derivative are continuous at $r = d/2$ and are given by (5.43) and (5.44). The second derivatives at $r = d/2$ are

$$\left.\frac{d^2G}{dr^2}\right|_{r=(d/2)-0} = \frac{6\eta(4-\eta)}{d^2(1-\eta)^3} \tag{5.56}$$

and

$$\left.\frac{d^2G}{dr^2}\right|_{r=(d/2)+0} = \left.\frac{d^2G}{dr^2}\right|_{r=(d/2)-0} - \frac{48\eta}{d^2(1-\eta)} G(d), \tag{5.57}$$

where (5.45) has been used. Thus, the second derivative of G is discontinuous at $r=d/2$. At $r=d/\sqrt{3}$, the first three derivatives of G are continuous and there is a discontinuity proportional to the triplet distribution function $g(a,a,a)$ in the fourth derivative. It appears that the order of the first discontinuous derivative increases by two at each singular point.

Thus, for hard spheres $G(r)$ is nonanalytic but quite smooth and it is reasonable to assume that G can be approximated fairly closely by a suitably chosen analytic function.

The function which is chosen is

$$G(r)=\sum_{n=0}^{m} G_n r^{-n}. \tag{5.58}$$

Equation (5.57) provides an extra condition, in addition to (5.43), (5.44), and (5.46). Equation (5.45) is not independent. It is tempting to use (5.43), (5.44), (5.46), and (5.57) together with (5.58) with $m=3$. However, if this is done, poor results are obtained. At first sight this is disconcerting. However, Tully-Smith and Reiss (1970) have shown that, for hard spheres,

$$G_3=0. \tag{5.59}$$

If (5.59) were not valid, the integral

$$\int_0^r s^2G(s)ds$$

would give rise to terms in $\ln r$ which would give terms inconsistent with (5.58) in certain consistency equations obtained by Tully–Smith and Reiss. In k dimensions, G_3 in (5.59) would be replaced by G_k. They show that if (5.43), (5.44), (5.46), (5.57), and (5.59) are used with (5.58) with $m=4$, results only slightly less satisfactory than the CS equation of state are obtained.

The original form of the SPT $G(r)$ for hard spheres, Eq. (5.15), actually satisfies (5.43), (5.44), (5.46), and (5.59), if (5.58) is used with $m=4$. Tully–Smith and Reiss obtain the further condition,

$$\eta^2G(d)+\frac{1}{4}[\ln(1-\eta)+\eta]$$
$$=6\eta^2\int_{1/2}^{1}\xi^2G(\xi)d\xi-6\int_0^{\eta}zdz\int_{1/2}^{1}\xi^2G(\xi)d\xi, \tag{5.60}$$

and observe that if (5.43), (5.44), (5.46), (5.59), and (5.60) are used with (5.58) with $m=4$ that $G_4=0$ and the original form of the SPT satisfies five conditions, not three as originally thought. Because of this it is plausible to use (5.43), (5.44), (5.46), (5.57), (5.59), and $G_4=0$ together with (5.58) with $m=5$. Tully–Smith and Reiss (1970) have done this and obtain the best of their equations of state, which is almost as good as the CS equation state but lacking its empirical character.

More recently, Reiss and Tully–Smith (1971) and Vieceli and Reiss (1972a, 1972b, 1973) have investigated the statistical thermodynamics of curved surfaces and have applied these results to the SPT. They obtain two equations of state for hard spheres. The hard-sphere solid equation of state is not very accurate and, as a result, no phase transition is found. Nonetheless, the approach is very promising.

The recent work of Reiss and colleagues described above may be summarized as an attempt to obtain $G(d)$ through the extrapolation of the results of a study of large cavities. Stillinger and Cotter (1971) and Cotter and Stillinger (1972) have made a study, in part complementary to that of Reiss *et al.*, of $G(r)$ for small r for hard discs. They obtain approximate expressions for $G(r)$ for $d/2\le r\le d/\sqrt{3}$, by means of an expansion in powers of $(r-d/2)^{1/2}$, and use

$$G(r)=G_0+\frac{G_1}{r}+\frac{G_3}{(r-\lambda_3)^3}+\frac{G_4}{(r-\lambda_4)^4}, \tag{5.61}$$

where the G_n and λ_n are constants to be determined, for $r\ge d/\sqrt{3}$. The unknown constants in $G(r)$ are determined from several conditions including the continuity of $G(r)$ and its first three derivatives at $r=d/\sqrt{3}$.

Helfand and Stillinger (1962), Harris and Tully–Smith (1971), and Reiss and Casberg (1974) have attempted to use the SPT to obtain the radial distribution function of hard spheres as well as their thermodynamic properties. The work of the latter authors is the most complete. They obtain an approximate integral equation for $g(r)$ which involves the triplet distribution which they approximate. The resulting equation can be solved for $\rho d^3\lesssim 0.5$ and gives good values for $g(r)$. The thermodynamics calculated from this $g(r)$ are more accurate than the original SPT results (5.18). The accuracy of this approach at high densities is not known. Reiss and Casberg (1974) were unable to obtain solutions to their equation because of numerical difficulties.

Lebowitz and Praestgaard (1964) have obtained an integral equation for $g(r)$ by means of arguments similar to those of the SPT. The equation, which they are unable to solve, is highly nonlinear. Interestingly, under appropriate linearizations it yields several of the equations which we will consider in the next section, Sec. **VI**.

Attempts to extend the SPT to fluids with attractive forces have yielded useful information (Frisch, 1964; Reiss, 1965). The nonhard core part of the intermolecular potential is regarded as a uniform background which serves to determine the density of the liquid while the internal structure is determined by the packing of hard cores. Reiss and his collaborators were among the first to recognize this. However, these ideas are formulated more systematically in the perturbation theories considered in Sec. VII and so will not be further pursued here.

VI. CORRELATION FUNCTIONS AND INTEGRAL EQUATIONS

A. Introduction

In this section we shall examine several methods for calculating the distribution or correlation functions at high densities. At low densities, the distribution functions can be calculated by means of the density expansions considered in Sec. IV. When this procedure is used, the resulting distribution functions are exact to a given order in the density and the resulting thermodynamics are exact to some order in the density no matter what route, connecting the thermodynamic properties to the distribution functions, is used.

The methods discussed in this section are approximate and approximate distribution functions are obtained. As a result, this thermodynamic consistency is lost and differing routes to thermodynamics will give, in general, differing results.

Throughout most of this section, we assume that only pairwise-additive spherically symmetric terms contribute to the potential energy. For this situation only the pair distribution function need be specified to determine the thermodynamic properties. We shall be concerned mostly with spherical potentials. However, a few applications to nonspherical systems will be considered.

Other recent reviews of the methods we examine here have been made by Baxter (1971) and Watts (1973). Henderson and Leonard (1971), McDonald (1973), and Henderson (1974) have reviewed the application of these methods to liquid mixtures.

B. Born–Green theory

Let us differentiate (1.10) with respect to $\vec{r}_1$. If only pair potentials contribute to U_N,

$$-k_B T\vec{\nabla}_1 g(1\ldots h)=\sum_{j=2}^{h} g(1\ldots h)\vec{\nabla}_1 u(1j) +\rho\int g(1\ldots h+1)\vec{\nabla}_1(1,h+1)d\vec{r}_{h+1}, \tag{6.1}$$

where $u(ij)=u(r_{ij})$. These equations were obtained by Yvon (1935), Bogoliubov (1946), and Born and Green (1946).

In the special case $h=2$, (6.1) becomes

$$-k_B T\vec{\nabla}_1 g(12)=g(12)\vec{\nabla}_1 u(12)+\rho\int g(123)\vec{\nabla}_1 u(13)d\vec{r}_3. \tag{6.2}$$

Equation (6.2) cannot be solved for $g(12)$ unless $g(123)$ is approximated. Following Kirkwood (1935), we can assume that

$$g(123)=g(12)g(13)g(23). \tag{6.3}$$

This approximation is called the *superposition approximation* (SA). We have seen that (6.3) is valid only at low densities. Direct calculation of the correction term, $d_3'(123)$, shows that this term is not small. Thus, from (4.58) we see that the SA must be significantly in error at intermediate densities. Alder (1964) has made simulation studies of $g(123)$ for hard spheres at high densities. These calculations, although not conclusive, indicate that the SA is reasonably reliable at high densities.

In any case, if (6.3) is substituted into (6.2) we obtain the *BG equation* (Born and Green, 1946)

$$-k_B T\vec{\nabla}_1 \ln g(12)=\vec{\nabla}_1 u(12)+\rho\int g(13)g(23)\vec{\nabla}_1 u(13)d\vec{r}_3. \tag{6.4}$$

If (6.4) is expanded in powers of the density, an expansion of $g(12)$ may be obtained and the virial coefficients resulting from (6.4) may be calculated. The first two terms in the expansion of $g(r)$ are correct but the higher-order terms are approximate. In fact, the higher-order terms for $g(r)$ in the BG theory cannot be expressed in terms of integrals involving only $f(r)$, the Mayer f function. Thus, the BG equation gives B and C correctly but gives approximations to the higher-order virial coefficients. The BG equation virial coefficients for the hard-sphere potential (Hart *et al.*, 1951; Rushbrooke and Scoins, 1951; Nijboer and van Hove, 1952; Nijboer and Fieschi, 1953) are listed in Table XIII. The consistency of the pressure and compressibility virial coefficients, denoted by P and C, respectively, is poor and the agreement with the correct values is disappointing.

The BG equation has been solved numerically for the hard-sphere potential (Kirkwood *et al.*, 1950; McLellan, 1952; Levesque, 1966). The results for the equation of state are plotted in Fig. 16. The agreement with the computer simulations is good at low densities, but becomes less satisfactory as the density increases and the SA breaks down.

Perhaps the most interesting result of the application of the BG equation to a system of hard spheres is that for densities greater than about $\rho d^3\sim 0.95$ the integral of the total correlation function, $h(r)$, does not converge and the BG equation has no acceptable solutions. This has been interpreted as indicating that a system of hard spheres undergoes a transition to an ordered phase at $\rho d^3\sim 0.95$ despite the absence of any attractive forces. The existence of this phase transition was the subject of considerable discussion before its confirmation by the simulation studies. Because the BG equation has no solution for densities greater than $\rho d^3\sim 0.95$ statements to the effect the BG equation predicts a hard-sphere phase transition are frequently found in the literature. This is really an overstatement of the situation. All that happens is that the BG theory breaks down at high densities. The breakdown of a theory may be symptomatic of the onset of a phase transition but is hardly a theory of the phase transition.

Recently, Raveché and Stuart (1975) have considered (6.1) with $h=1$. They claim to have obtained "fluidlike" and "solidlike solutions" for $g(\vec{r}_1)$. The "fluidlike solutions" have the property that $g(\vec{r}_1)=1$ and the "solidlike solutions" for $g(\vec{r}_1)$ are periodic. It is difficult to determine the significance of this because, elsewhere in their paper, they claim that, in the thermodynamic limit, $g(\vec{r}_1)=1$ follows immediately, for all T and ρ, from the definition of $g(\vec{r}_1)$ (see their Eqs. A1 and A6). Presuming their latter result to be correct, the "solidlike solutions" for $g(\vec{r}_1)$ must be unphysical, introduced by differentiation, and their existence can, at most, be indicative of an instability of the fluid at high densities rather than the basis of a theory of freezing.

The results of the BG equation for more realistic potentials (Kirkwood *et al.*, 1952; Zwanzig *et al.*, 1953, 1954; Broyles, 1960, 1961a; Levesque, 1966) are no better. The BG predictions (Levesque 1966) for the critical constants of a 6–12 fluid are given in Table VII. The pressure results must be obtained by extrapolation because the pressure equation critical point lies in the region of no solution. The agreement with experiment and simulation studies is not very satisfactory.

Recently, there has been an extensive study of the BG equation for the square-well potential by Luks and collaborators (Schrodt and Luks, 1972; Kozak *et al.*, 1972; Schrodt *et al.*, 1972; Schrodt *et al.*, 1974; Lincoln *et al.*, 1974; Lincoln *et al.*, 1975a, b). It is difficult to determine whether the optimism of these authors is justified because almost all their calculations are for a cutoff of the potential at $\lambda = 1.85$, rather than 1.5σ which has been used in the simulation studies, and comparison is made with experimental results for argon. Nonetheless, there is some indication that the BG equation deals fairly satisfactorily with the nonhard core part of the potential and that the poor results for the BG equation for potentials with attractive tails is due, in part at least, to its errors in treating the hard core. We will return to this subject when we discuss perturbation theory in Sec. VII.C.5.

Born and Green (1947) and Mazo and Kirkwood (1958) have developed a quantum version of the BG equation.

The inadequacy of the SA is further illustrated by considering an integral equation obtained by Kirkwood (1935). We write the potential energy in such a manner as to include a *coupling parameter*:

$$U_N(\vec{r}_1\cdots\vec{r}_N)=\xi\sum_{j=2}^{N}u(1j)+\sum_{i<j=2}^{N}u(ij). \tag{6.5}$$

The actual situation is, of course, represented by $\xi = 1$. When $\xi = 0$, molecule 1 has been "uncoupled." Differentiating with respect to ξ yields

$$-k_BT\,\frac{\partial \ln g(12)}{\partial \xi}=u(12)+\rho\int u(13)\left[\frac{g(123)}{g(12)}-g(13)\right]d\vec{r}_3. \tag{6.6}$$

Equations (6.2) and (6.6) are exact and, therefore, equivalent. However, if the SA is used, this equivalence is lost. Substituting (6.3) into (6.6) yields the *Kirkwood equation*.

$$-k_BT\,\frac{\partial \ln g(12)}{\partial \xi}=u(12)+\rho\int u(13)g(13)[g(23)-1]d\vec{r}_3. \tag{6.7}$$

The virial coefficients and equation of state resulting from (6.7) have been calculated for the hard-sphere potential. The second and third virial coefficients are exact. The Kirkwood (K) values for D (Stell, 1962) are listed in Table XIII and are seen to be inferior to the BG values. This is true for the equation of state also (Kirkwood *et al.*, 1950).

The difference between the BG and K results is a reflection of the inadequacy of the SA. In the absence of any approximations the two methods would yield the same results.

When we say that the SA is inadequate we mean this only in relation to the integral equations we have considered. As was mentioned earlier, direct calculations of $g(123)$ for hard spheres indicate that the superposition approximation is fairly good at high densities. Thus, the poor results obtained from (6.4) and (6.7) probably result from the fact that these equations grossly magnify the errors in the SA. Other uses of the SA may yield good results. Such uses will be considered in Sec. VII.

We may write

$$g(123)=g(12)g(13)g(23)\exp\{S(123)\}, \tag{6.8}$$

where $S(123)=0$ (the low density limit) in the SA. Rice and collaborators (Rice and Lekner, 1965; Young and Rice, 1967a, b, c; Rice and Young, 1967) have approximated $S(123)$ by calculating the first two terms in the density expansion of $S(123)$ and using a Padé extrapolation to approximate $S(123)$. Good results are obtained at low densities but the equation has no solution at higher densities where the system is still fluid.

Finally, we mention the work of Lee *et al.* (1968, 1969, 1971) who have investigated the possibility of using a generalization of the SA

$$g(1234)=\frac{g(123)g(124)g(134)g(234)}{g(12)g(13)g(14)g(23)g(24)g(34)}, \tag{6.9}$$

together with (6.1), for $h=3$, to determine $g(123)$. The resulting values of $g(123)$ may then be used with (6.2) to determine $g(12)$. This procedure yields excellent results for the hard-sphere virial coefficients and for the hard-sphere $g(r)$ at low densities. However, the procedure is computationally so complex that it is unlikely to be a practical method of determining $g(r)$ at high densities.

C. Percus–Yevick theory

In Sec. I, the direct correlation function, $c(r)$, was defined by the OZ relation.

$$h(12)=c(12)+\rho\int h(13)c(23)d\vec{r}_3, \tag{6.10}$$

where $h(r)=g(r)-1$. In Sec. IV.C, the expansion

$$y(r)=\sum_{n=0}^{\infty}\rho^n y_n(r), \tag{6.11}$$

where $g(r)=e(r)y(r)$ and $e(r)=\exp\{-\beta u(r)\}$, was given. We have seen that $y_0=1$,

$$y_1(r)=c_2(r), \tag{6.12}$$

and

$$y_2(r)=d_3(r)+2d_4(r)+\frac{1}{2}\{c_2^2(r)+d_5(r)\}. \tag{6.13}$$

Substitution of (6.11) into (6.10) gives

$$c(r)=\sum_{n=0}^{\infty}\rho^n\gamma_n(r), \tag{6.14}$$

where

$$\gamma_0(r)=f(r)=f(r)y_0(r) \tag{6.15}$$

and

$$\gamma_1(r)=f(r)y_1(r). \tag{6.16}$$

Thus, *at low densities*

$$c(r)=f(r)y(r). \tag{6.17}$$

At higher densities, (6.17) is not true. For example,

$$\gamma_2(r)=f(r)y_2(r)+\frac{1}{2}\{c_2^2(r)+d_5(r)\}. \tag{6.18}$$

Thus, in general

$$c(r)=f(r)y(r)+d(r). \tag{6.19}$$

At low densities

$$d(r)=\frac{1}{2}\rho^2\int f_{13}f_{14}f_{23}f_{24}e_{34}\,d\vec{r}_3\,d\vec{r}_4+\cdots. \tag{6.20}$$

For hard spheres of diameter d, $f(r) = -1$ for $r<d$, and is zero otherwise. Thus, for hard spheres a particular configuration of molecules 1, 2, 3, and 4 makes a contribution to the integral in (6.20) only if r_{13}, r_{14}, r_{23} and r_{24} are all less than d and if r_{34} is greater than d. This is an unlikely configuration and thus we would expect $d(r)$ to be small for hard spheres. For other potentials the situation is less clear.

In any case, we can adopt (6.17) as an approximation at all densities. Equation (6.17) is the *Percus–Yevick* (PY) *approximation* (Percus and Yevick 1958). Substitution of (6.17) into (6.10) yields the PY integral equation.

$$y(12) = 1 + \rho \int f(13)y(13)[e(23)y(23) - 1]d\vec{r}_3. \tag{6.21}$$

If we substitute (6.11) into (6.21) we find that $y_0 = 1$, $y_1(r) = c_2(r)$, and

$$y_2(r) = d_3(r) + 2d_4(r). \tag{6.22}$$

Thus, as we would expect, y_0 and y_1 are exact. Hence, B and C will also be exact in the PY theory.

It is instructive to define

$$N(r_{12}) = \rho \int h(13)c(23)d\vec{r}_3. \tag{6.23}$$

$N(r)$ is the indirect part of the total correlation function, $h(r)$. From (6.10) and (6.19) we see that

$$y(r) = 1 + N(r) + d(r) \tag{6.24}$$

so that we could also state the PY approximation as

$$y(r) = 1 + N(r). \tag{6.25}$$

Baxter (1967b) has shown that, in the PY theory, the pressure, calculated from

$$\frac{pV}{Nk_BT} = 1 - 4\pi\rho \int_0^\infty r^2 c(r)dr + 2\pi\rho \int_0^\infty r^2 f(r)e(r)y^2(r)dr + \frac{1}{2\pi^2\rho}\int_0^\infty k^2\{\rho\tilde{c}(k) + \ln[1-\rho\tilde{c}(k)]\}dk, \tag{6.26}$$

where $\tilde{c}(k)$ is the Fourier transform of $c(r)$, is the same as the pressure obtained by integrating the compressibility equation.

Further, Baxter (1968a) has also shown that if $c(r) = 0$ for $r<R$, the OZ relation can be rewritten as

$$rc(r) = -Q'(r) + 2\pi\rho \int_r^R Q'(s)Q(s-r)ds, \tag{6.27}$$

and

$$rh(r) = -Q'(r) + 2\pi\rho \int_0^R (r-s)h(|r-s|)Q(s)ds, \tag{6.28}$$

for all $r>0$, where $Q(r)$ is a new function which satisfies

$$Q(r) = 0, \tag{6.29}$$

for all $r>R$, whose value can be determined by solving (6.27) and (6.28). The function $Q'(r)$ is the derivative of $Q(r)$. Baxter also showed that the compressibility equation can be written in the form

$$\frac{1}{k_BT}\left(\frac{\partial p}{\partial \rho}\right)_T = \{\tilde{Q}(0)\}^2, \tag{6.30}$$

where

$$\tilde{Q}(k) = 1 - 2\pi\rho \int \exp\{i\vec{k}\cdot\vec{r}\}Q(r)dr. \tag{6.31}$$

Note that the compressibility is always positive. If the potential has a finite range, R, the PY $c(r)$ exactly satisfies the condition $c(r) = 0$ for $r>R$.

The advantage of Baxter's formulation is that if $c(r)$ and $h(r)$ are desired in the range $0<r<R_{\max}$, then (6.27) and (6.28) need be considered only within this range whereas if (6.10) is used it is necessary to do the calculations over $0<r<2R_{\max}$. Baxter (1967a) has given an alternative formulation of the OZ equation which is valid when $c(r) = 0$ for $r>R$.

1. Solution of the PY equation for hard spheres

For hard spheres the PY theory requires that

$$c(r) = 0, \quad r>d \tag{6.32}$$

and

$$h(r) = -1, \quad r>d. \tag{6.33}$$

Thus, putting $R=d$, we have from (6.28)

$$Q'(s) = as + b \tag{6.34}$$

or

$$Q(s) = \frac{1}{2}a(s^2-1) + b(s-1), \tag{6.35}$$

where $s = r/d$. Substitution of (6.34) and (6.35) into (6.28) requires that

$$a = (1+2\eta)/(1-\eta)^2 \tag{6.36}$$

and

$$b = -3\eta/2(1-\eta)^2, \tag{6.37}$$

where $\eta = \pi\rho d^3/6$. Substitution of these results into (6.27) yields

$$-c(s) = y(s) = a^2 - 6\eta(a+b)^2 s + \frac{1}{2}\eta a^2 s^3, \quad r<d$$
$$c(s) = 0, \quad r>d. \tag{6.38}$$

Thus, in the PY approximation

$$y(d) = \frac{1+\eta/2}{(1-\eta)^2}. \tag{6.39}$$

We now have enough results to calculate the equation of state. The pressure equation yields

$$\frac{pV}{Nk_BT} = 1 + 4\eta y(d) = \frac{1+2\eta+3\eta^2}{(1-\eta)^2}, \tag{6.40}$$

while the compressibility equation yields

$$\frac{1}{k_BT}\left(\frac{\partial p}{\partial \rho}\right)_T = \{\tilde{Q}(0)\}^2 = \frac{(1+2\eta)^2}{(1-\eta)^4}. \tag{6.41}$$

Thus, the compressibility equation of state is

$$\frac{pV}{Nk_BT}=\frac{1+\eta+\eta^2}{(1-\eta)^3}\ . \tag{6.42}$$

These results were obtained earlier by Wertheim (1963, 1964) and Thiele (1963) by a direct solution of (6.21). We have seen in Sec. V.A. that (6.4) also results from the scaled-particle theory (SPT). One should not conclude that the SPT and PY theory are identical. They give different results for two-dimensional hard discs.

As may be seen in Fig. 16, Eqs. (6.40) and (6.42) are in good agreement with the simulation results. This is particularly true for the compressibility equation of state.

The virial coefficients which result from (6.40) and (6.42) are listed in Table XIII. As we have pointed out already, B and C are exact. The agreement of the higher virial coefficients is good.

Equations (6.40) and (6.42) may be integrated to obtain the free energy. The result is

$$\frac{A}{Nk_BT}=3\ln\lambda-1+\ln\rho+2\ln(1-\eta)+\frac{6\eta}{(1-\eta)}\ , \tag{6.43}$$

for the pressure equation of state, and

$$\frac{A}{Nk_BT}=3\ln\lambda-1+\ln\rho-\ln(1-\eta)+\frac{3}{2}\eta\frac{2-\eta}{(1-\eta)^2}\ , \tag{6.44}$$

for the compressibility equation of state. In (6.43) and (6.44)

$$\lambda=h/(2\pi mkT)^{1/2}\ . \tag{6.45}$$

It is worth noting that the CS equation of state (Carnahan and Starling, 1969), which was mentioned in Sec. V.A., can be obtained from

$$\left(\frac{pV}{Nk_BT}\right)_{\rm CS}=\frac{1}{3}\left(\frac{pV}{NkT}\right)_p+\frac{2}{3}\left(\frac{pV}{NkT}\right)_c\ , \tag{6.46}$$

where the subscripts p and c indicate that the PY pressure and compressibility hard sphere equations of state are used.

We can solve (6.28) for hard spheres by letting $f(s) = sy(s)$ and changing variables in the first integral on the right-hand side. Thus, for $1\leq s\leq 2$,

$$f(s)=s+12\eta\int_1^s f(t)Q(s-t)dt-12\eta\int_0^1(s-t)Q(t)dt\ . \tag{6.47}$$

Equation (6.47) may be solved by differentiating three times to obtain the linear third-order ordinary differential equation

$$f'''(s)+\frac{6\eta}{1-\eta}f''(s)+\frac{18\eta^2}{(1-\eta)^2}f'(s)-\frac{12\eta(1+2\eta)}{(1-\eta)^2}f(s)=0. \tag{6.48}$$

The solution of (6.48), for $1\leq s\leq 2$, is

$$sg(s)=sy(s)=\sum_{l=0}^{2}A_l\exp\{m_l s\}\ , \tag{6.49}$$

where the m_l are the three solutions of the cubic equation,

$$m^3+\frac{6\eta}{1-\eta}m^2+\frac{18\eta^2}{(1-\eta)^2}m-\frac{12\eta(1+2\eta)}{(1-\eta)^2}=0\ , \tag{6.50}$$

which may be solved analytically. It is straightforward to show that $y(r)$ and its first two derivatives are continuous at $r=d$. These conditions may be used to determine the A_l.

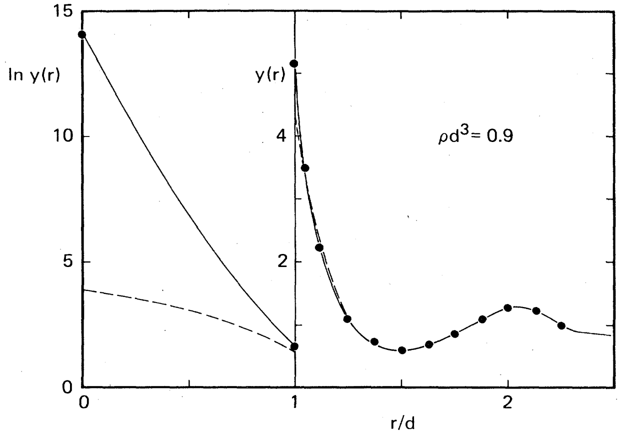

FIG. 17. $y(r)$ of hard spheres at $\rho d^3=0.9$. The points give the simulation results of Barker and Henderson (1971a, 1972) and the solid line gives the semiempirical results of Verlet and Weis (1972a) and Grundke and Henderson (1972) and the broken curve gives the PY results.

Wertheim (1963, 1964), Chen *et al.* (1965), and Smith and Henderson (1970) have obtained these results by a different method. Smith and Henderson have obtained $y(r)$ analytically for $0\leq r\leq 5d$. Throop and Bearman (1965) have given numerical results for $g(r)$. Recently, Perram (1975) has developed an efficient numerical method for calculating $g(r)$, based upon differential equations similar to (6.48), which works for arbitrarily large r.

The PY values of $y(r)$, $g(r)$, and $c(r)$ for hard spheres are plotted in Figs. 17 and 18. The PY values of $g(r)$ are in good agreement with the simulation results except near $r=d$ where they are somewhat low. There are no machine simulations for $c(r)$ or for $y(r)$ for $r<d$. However, the PY results can be compared with accurate semiempirical expressions which will be discussed in

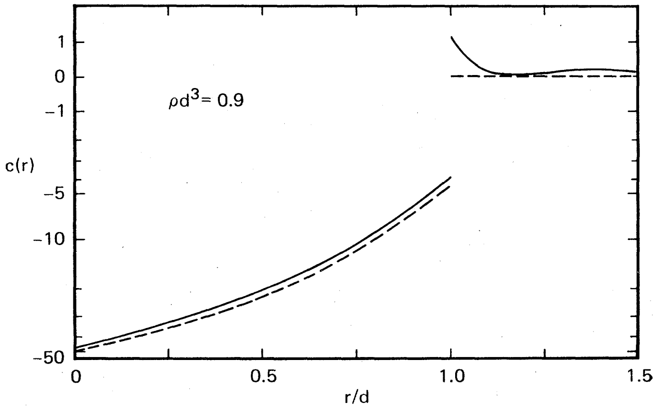

FIG. 18. Direct correlation function of hard spheres at $\rho d^3=0.9$. The solid curve gives the semiempirical results of Grundke and Henderson (1972) and the broken curve gives the PY results. The curve is plotted on a $\sinh^{-1}$ scale. This pseudologarithmic scale combines the advantages of a logarithmic scale with the ability to display zero and negative quantities.

Sec. VI.C.4 The PY expression for $c(r)$ is quite good but is everywhere too negative. The PY expression for $y(r)$ for $r<d$, and hence $d(r)$, is exceedingly poor (Henderson and Grundke, 1975). Stell (1963) has examined the PY theory for one-dimensional hard rods. He found that the PY results for $g(r)$ and $c(r)$, and, hence, the thermodynamics, were exact but that the PY result for $y(r)$ for $r<d$ and for $d(r)$ were poor.

The fact that $c(r)$ does not equal the PY expression for $r<d$ is of interest because it is not uncommon to read the statement that the PY $c(r)$ is exact for hard spheres for $r<d$ [see, for example, Eq. (2) of Croxton (1974a)]. Although the PY $c(r)$ is a good approximation in this region, the statement is false. Indeed, Stell (1963) has shown that if $c(r)$ were equal to the PY expression inside the core but were not zero outside the core, the radial distribution function (RDF) generated by the Ornstein–Zernike equation would not be zero inside the core. The point is that although the diagrams in $d(r)$ are cancelled by diagrams in $y(r)$ when $r<d$, there still remain diagrams in $y(r)$, which are not of the PY-type, and which contribute inside the core. These diagrams are convolutions involving diagrams which appear in $d(r)$.

The PY $g(r)$ becomes negative for $\rho d^3 \gtrsim 1.18$ so that the PY results for fluid hard spheres are physically unacceptable for densities greater than this. It is clear that the PY theory is unphysical at high densities because (6.40) and (6.42) predict a fluid phase at densities greater than close-packing. If we wished, we could regard this as an indication of the solid–fluid phase transition, but it is not a theory of the phase transition any more than the breakdown of the BG theory is a theory of this transition.

Lebowitz (1964) has solved the PY equations for hard-sphere mixtures. For the compressibility equation, he obtains the same result as that obtained from the SPT, Eq. (5.28). Again an accurate equation of state for hard-sphere mixtures can be obtained from (6.46). Leonard *et al.* (1971) have obtained results for the RDF's of a binary hard-sphere mixture and Perram (1975) has developed a numerical method for obtaining the RDF of a hard-sphere mixture with more than two components.

The PY theory has been applied to nonadditive hard-sphere mixtures where $d_{12} \neq (d_{11}+d_{22})/2$ (Lebowitz and Zomick, 1971; Penrose and Lebowitz, 1972; Ahn and Lebowitz, 1973, 1974; Melnyk *et al.*, 1972; Guerrero *et al.*, 1974). This problem is not as esoteric as one might think. The solution to this problem might be of interest for the perturbation theories discussed in Sec. VII. The particular case $d_{11}=d_{22}=0$, $d_{12}\neq 0$ is also of interest because it is isomorphic with a model of the critical point (Widom and Rowlinson, 1970).

2. Results for other systems

The PY theory has been applied to the square-well potential, with a cutoff at $\lambda=1.5$, by Levesque (1966), Verlet and Levesque (1967), Tago (1973a,b, 1974), and Smith *et al.* (1974). Although this potential is not very realistic, it is a very useful model potential. It is a relatively short-range potential and, as we see in Sec. VII, such potentials tend to expose defects in theories.

The PY $g(r)$ for the SW potential is plotted in Fig. 19 for $\rho^*=0.8$ and $\beta\epsilon=0$ and 1.5. At $\beta\epsilon=0$ (high temperatures), the PY $g(r)$ for the SW potential is just the PY hard-sphere $g(r)$, and is in reasonably good agreement with the simulation results. At $\beta\epsilon=1.5$ (in the liquid

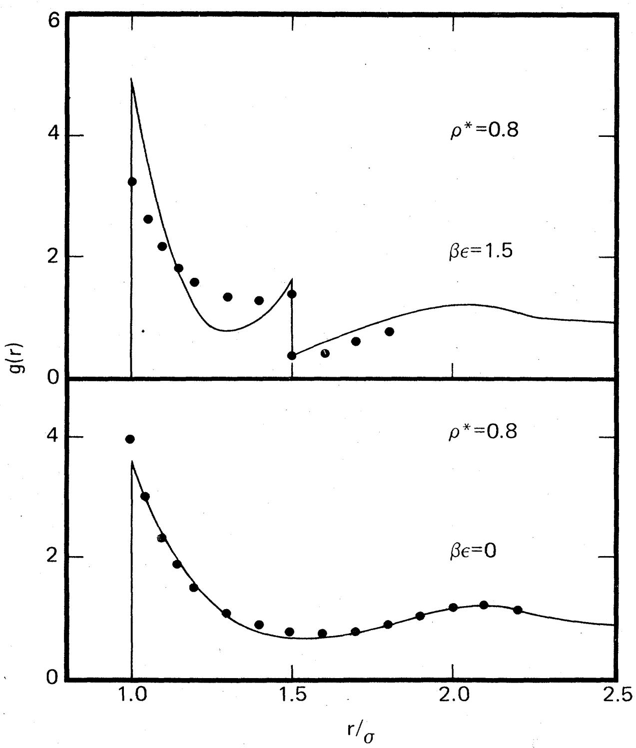

FIG. 19. RDF of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.8$. The points give the MC results of Barker and Henderson (1971a, 1972) and Henderson, Madden, and Fitts (1976) for the square-well fluid at $\beta\epsilon=0$ (hard spheres) and $\beta\epsilon=1.5$, respectively. The curves give the PY results of Smith *et al.* (1974).

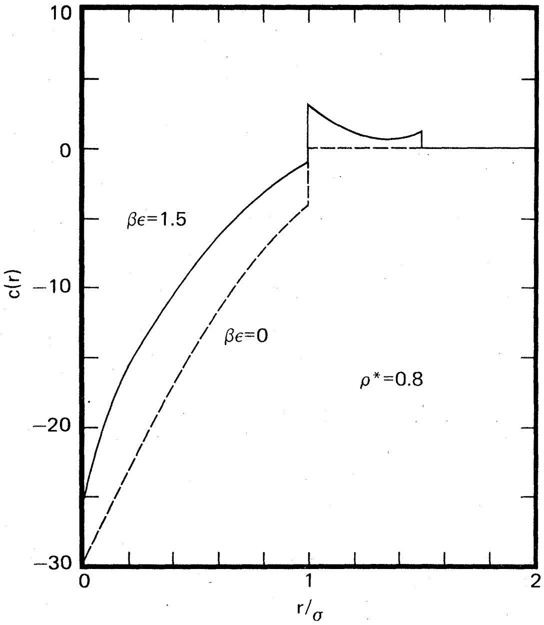

FIG. 20. Direct correlation function of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.8$ calculated from the PY theory by Smith *et al.* (1974).

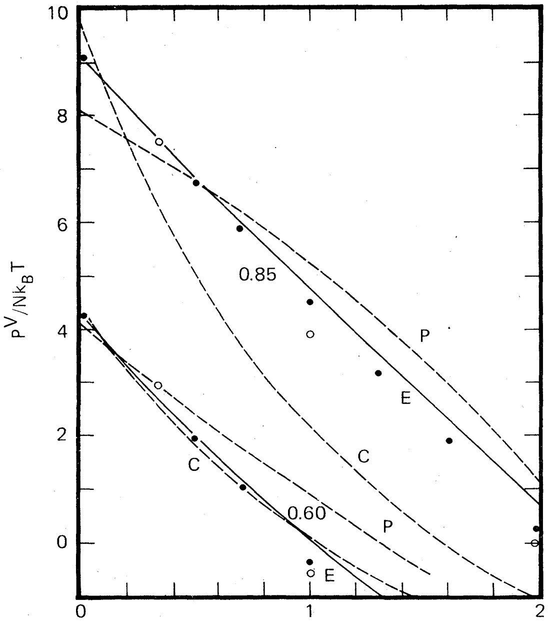

FIG. 21. Equation of state of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.6$ and 0.85. The points, denoted by ○ and ●, give the simulation results of Rotenberg (1965) and Alder *et al*. (1972), respectively, and the curves give the PY results calculated by Smith *et al*. (1974). The letters *P*, *C*, and *E* indicate, respectively, that the isochore was calculated using the pressure, compressibility, or energy equation.

region, near the triple point), the PY $g(r)$ is quite poor for $r<1.5\sigma$. The PY $c(r)$ is plotted for the same states in Fig. 20. There are no simulation results for comparison. However, we would expect the PY $c(r)$ to be appreciably in error at the lower temperature. The thermodynamic properties are plotted for $\rho^*=0.60$ and 0.85 in Figs. 21–24. The pressure and compressibility equation results are not satisfactory at the low temperatures and high densities characteristic of the liquid state. On the other hand, the energy and, to a lesser extent, the heat capacity, calculated by differentiating the energy, are reasonably satisfactory. This is partly due to the fact that the pressure and compressibility, calculated from the pressure and compressibility equa-

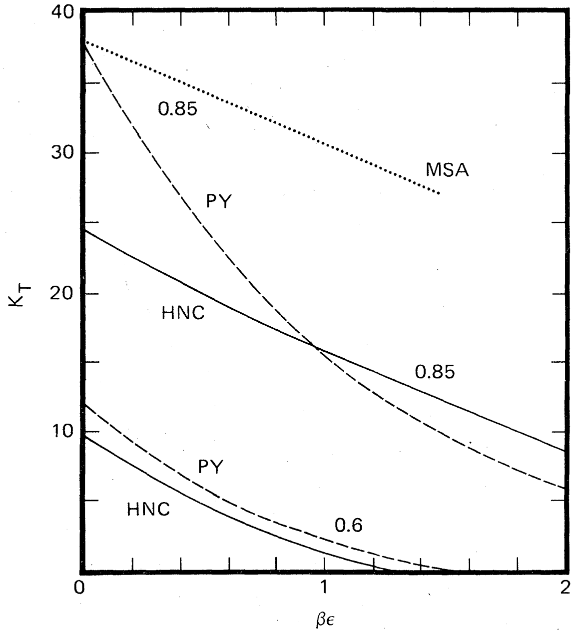

FIG. 22. Compressibility of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.6$ and 0.85. The PY, MSA, and HNC results were calculated by Smith *et al*. (1974), Smith *et al*. (1976), and Henderson, Madden, and Fitts (1976).

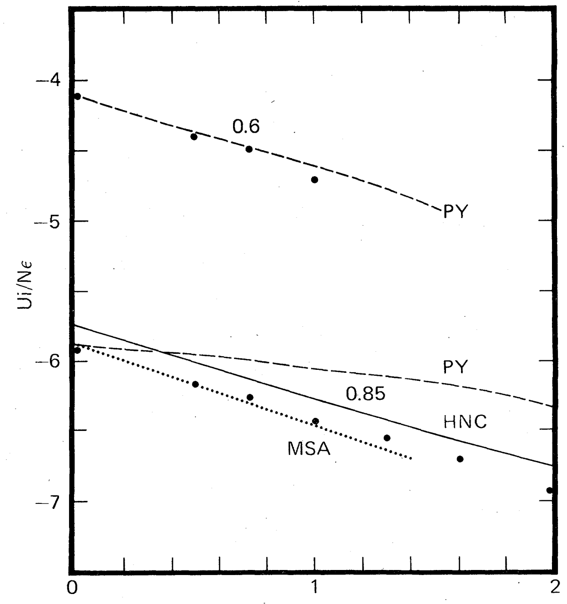

FIG. 23. Internal energy of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.6$ and 0.85. The points give the MD results of Alder *et al*. (1972) and the curves give the theoretical results calculated by the same authors as cited in the caption of Fig. 22.

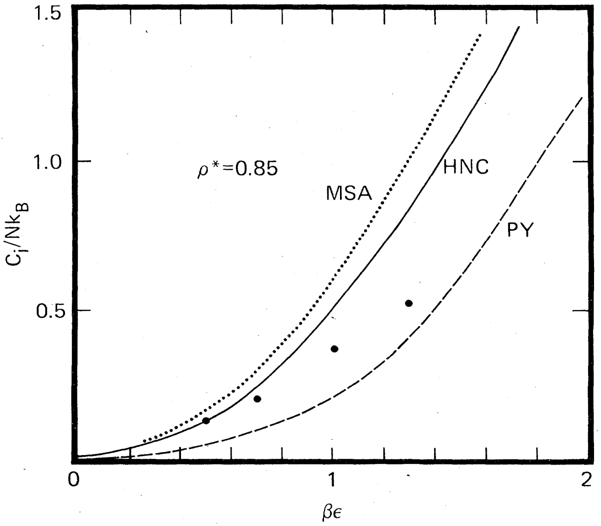

FIG. 24. Internal heat capacity of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.85$. The points give the MD results of Alder *et al*. (1972) and the curves give the theoretical results calculated by the same authors as cited in the caption of Fig. 22.

tions, respectively, are small residues remaining after the cancellation of much larger positive and negative contributions. In contrast, there is much less cancellation in obtaining the energy from the energy equation. Because of the relatively satisfactory results for the energy, it is not surprising that the energy equation values of the pressure are better than the pressure and compressibility equation values.

The PY theory has been applied to the 6–12 potential by several authors (Broyles, 1961b; Broyles *et al.*, 1962; Verlet, 1964; Verlet and Levesque, 1967; Levesque, 1966; Throop and Bearman, 1966a; Mandel and Bearman, 1968; Mandel *et al.*, 1970; Bearman *et al.*, 1970; Theeuwes and Bearman, 1970; Watts, 1968, 1969a, c, d; Barker *et al.*, 1970; Henderson *et al.*, 1970; Henderson and Murphy, 1972). Only the last three references include the energy equation of state results. The RDF is plotted in Fig. 25. The agreement with the simulation results is fairly good except in the neighborhood of the first peak. This error in the neighborhood of the first peak produces large errors in the pressure and compressibilty equations of state. However, the energy equation of state is quite good. The PY results for the equation of state at $\rho^* = 0.85$ are plotted in Fig. 26. The PY energy equation of state results are listed in Tables VI to IX. The agreement with the simulation value is good for the energy equation. The critical density is fairly low. Thus, it is not surprising that the agreement with simulation results is good even if the PY pressure and compressibility equations of state are used.

Throop and Bearman (1966b, 1967) and Grundke, Henderson, and Murphy (1971, 1973) have solved the PY equations for a mixture of 6–12 fluids. The calculations of Grundke *et al.* show that good results for the thermodynamic properties are obtained if the energy equation is used.

The PY theory works well for hard spheres. However, the effect of attractive forces on the RDF at high densities is not satisfactorily described by the PY theory. The use of the energy equation minimizes these problems for potentials like the square-well and 6–12 potentials. However, it is important to note that the energy equation will not always be the preferred route (Watts, 1971).

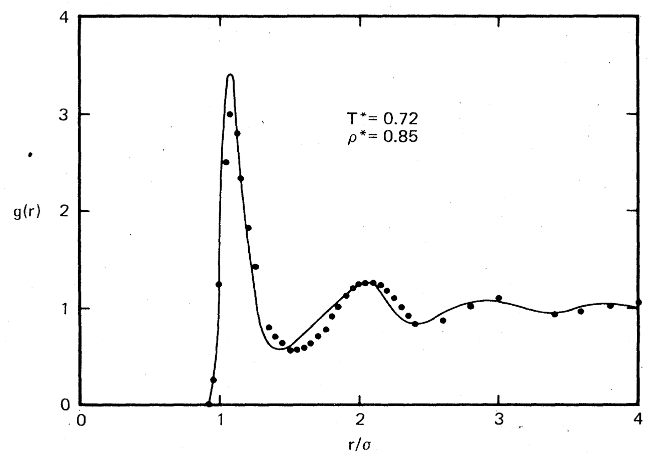

FIG. 25. RDF of the 6–12 fluid near its triple point. The points give the MD results of Verlet (1968), and the curve gives the PY results of Henderson *et al*. (1970).

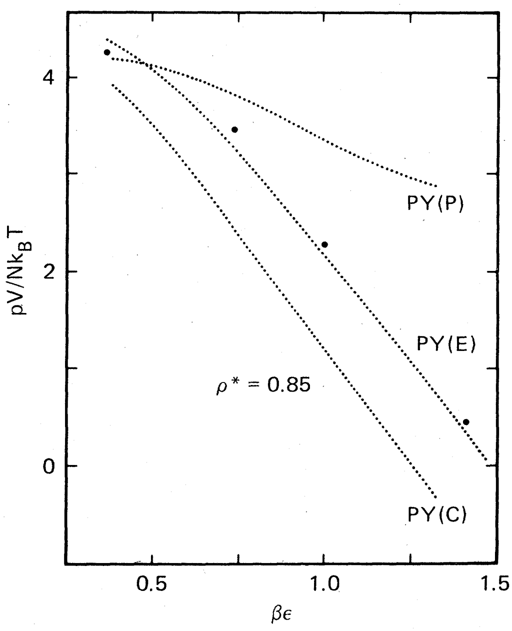

FIG. 26. Equation of state of the 6–12 fluid. The points give the simulation results (Verlet and Levesque, 1967; Verlet, 1967; Levesque and Verlet, 1969). The three curves labeled C, P, and E give the PY results calculated by Henderson *et al*. (1970) using the compressibility, pressure, and energy equations, respectively.

For molecular fluids with non-spherical interactions, the PY equation results from the substitution of the PY approximation,

$$c(r_{12}, \Omega_1, \Omega_2) = f(r_{12}, \Omega_1, \Omega_2)\, y(r_{12}, \Omega_1, \Omega_2)\,, \tag{6.51}$$

into the Ornstein–Zernike equation

$$h(r_{12}, \Omega_1, \Omega_2) = c(r_{12}, \Omega_1, \Omega_2) + \rho \int h(r_{13}, \Omega_1, \Omega_3) c(r_{23}, \Omega_2, \Omega_3) d\vec{r}_3 d\Omega_3\,. \tag{6.52}$$

Ben-Naim (1970) has proposed an *approximate* form of the PY equation for molecular fluids and has applied it to water. He approximates the function $y(r_{12}, \Omega_1, \Omega_2)$, where Ω_1 and Ω_2 are the orientation variables, by

$$y(r_{12}, \Omega_1, \Omega_2) = y(r_{12}) \tag{6.53}$$

so that

$$g(r_{12}, \Omega_1, \Omega_2) = \exp\{-\beta u(r_{12}, \Omega_1, \Omega_2)\}\, y(r_{12})\,. \tag{6.54}$$

Equation (6.53) can be expected to be valid only at low densities or for systems in which the non-spherical interaction is weak. It is unlikely to be of use for more general situations. At low densities the density expansions are available. We shall see in Sec. VII.E.3 that perturbation expansions are available for weak interactions. Thus, (6.53) is probably not of major value.

Chen and Steele (1969, 1970, 1971) have applied to PY equation to diatomic fused hard spheres. They expanded $g(r_{12}, \Omega_1, \Omega_2)$ in spherical harmonics and obtained a set of coupled integral equations which can be solved if the harmonic expansion is truncated. The results of the thermodynamic functions of fused diatomic hard spheres are almost indistinguishable from the PY hard-sphere results when plotted as functions of $\eta = \rho v_m$, where v_m is the volume of a molecule. There are no simulation results for comparison. However, inspection of the virial coefficients in Table XV and reasoning by analogy with the prolate spherocylinder SPT results in Sec. V.B, leads one to expect that, at constant η, pV/NkT increases as l/σ increases, where l is the separation of the centers of the two spheres whose diameter is σ. Thus, it seems plausible that the results of Chen and Steele become increasingly in error as l/σ increases. Whether this is a feature of the PY theory or their method of solution is not known.

Chandler and Andersen (1972) and Chandler (1973) have developed an integral equation for the correlation functions of a fluid whose molecules are composed of several (not necessarily linear) interaction sites, usually taken to be fused hard spheres. Chandler and Andersen focus their attention on the site–site radial distribution functions. The derivation of their equation is based on arguments similar to those used in obtaining the PY theory. In fact, it is just the PY equation when applied to central potentials. They call their model the *reference interaction site model* (RISM). Lowden and Chandler (1973, 1974) have applied the RISM to several systems of fused hard spheres. For diatomic fused hard spheres, the theory seems less satisfactory than is the PY theory for hard spheres. For the values of l/σ which they consider, the difference between the pressure and compressibility equations of state increases as l/σ increases. More seriously, although the compressibility value of pV/NkT at constant η, increases as l/σ increases (as one expects), the pressure value of pV/NkT at constant η, decreases as l/σ increases, at least for the values of l/σ considered by Lowden and Chandler. This seems to imply that although the compressibility equation of state remains accurate as l/σ increases, the pressure equation result becomes increasingly in error. In terms of the correlation functions, this may mean that, although the area under the RDF is given reasonably accurately in the RISM, the pair correlation function as a whole becomes less reliable as l/σ increases. Even if these comments prove valid, the RISM is the only theory that has been applied to complex molecules composed of fused hard spheres and is a valuable contribution to the theory of molecular fluids.

As mentioned earlier, almost all work on the PY theory, and theories of this nature, has been based on the assumption of pairwise additivity. However, Rushbrooke and Silbert (1967), Rowlinson (1967), Casanova *et al.* (1970), and Dulla *et al.* (1971) have discussed the incorporation of three-body interactions into the PY theory. They seek an effective pair-potential which will give the correct RDF. Barker and Henderson (1972) discuss this approach in detail and point out that this effective pair-potential may be very difficult to calculate theoretically. Probably it is better to use Eq. (4.61) together with the superposition approximation.

Chihara (1973) has recently formulated a quantum version of the PY equation. In addition, there have been several applications of the PY equation in variational studies of the ground state of liquid helium. Murphy and Watts (1970) give a useful summary of such calculations.

3. Extensions of the PY theory

The PY theory works quite well for hard spheres. However, as attractive forces become important the PY theory becomes less accurate. We have seen that, in general

$$c(r) = f(r)y(r) + d(r)\,. \tag{6.55}$$

If $d(r)$ is known, an integral equation can be obtained by substituting (6.55) into the OZ equation. Thus

$$y(12) = 1 + d(12) + \rho \int [\,f(13)y(13) + d(13)\,][\,e(23)y(23) - 1\,]\,d\mathbf{r}_3\,. \tag{6.56}$$

If an exact expression for $d(r)$ were available, the resulting integral equation would be exact.

In the PY theory, $d(r) = 0$. Since this PY approximation to $d(r)$ is valid in the limit of low densities, we might expect that (6.20) might be useful (Stell 1963). We could even generate more elaborate approximations by replacing the f_{ij} by h_{ij} or c_{ij} or some of the f_{ij} by h_{ij} and others by c_{ij} (Stell, 1963; Verlet, 1965; Rowlinson, 1966). Green (1965) and Francis *et al.* (1970) have suggested combining this type of approach with the further approximation of neglecting $d(13)$ in the integral in (6.56). Any of these approximations would yield the correct $y_2(r)$ and D. However, thus far none of them has been of much value at high densities.

Percus (1962) has obtained the Percus–Yevick theory by means of a functional Taylor series expansion truncated at first order. In principle, this method provides a systematic scheme for extending the Percus–Yevick or for generating other approximations. Verlet (1964) has taken the Taylor expansion to second order and obtained a new set of integral equations, which he calls the PY 2 equations. The PY 2 theory is not a fully systematic extension of the PY theory. An approximation for $g(123)$ must be introduced. Usually, an approximation to $g(123)$ which has the unappealing property of being asymmetric in r_{12}, r_{13}, and r_{23} is used. In any case, the PY 2 theory gives $y_2(r)$ and D correctly. For hard spheres, the PY 2 theory gives results which are better than the PY results (Verlet and Levesque, 1967). However for systems with attractive forces, the improvement over the PY results at high densities does not appear worth the extra computational effort involved in the PY 2 equations.

Allnatt (1966), Wertheim (1967), and Lux and Münster (1967, 1968) have proposed other extensions of the PY theory. Most of these theories give improved results for hard spheres (although there are exceptions). However, it is doubtful that any of these methods will be useful for the 6–12 or realistic potentials because of the lengthy computations involved.

Recently, Croxton (1972, 1973, 1974a, b, c) has proposed an extension of the PY theory which he claims provides a theory of the solid-fluid phase transition for hard spheres. We find Croxton's arguments *ad hoc* and hard to follow. However, it appears that he approximates $d(r)$ by an infinite sum of integrals of the form of (6.20). The factor of 1/2 in (6.20) is missing from Croxton's expression and the factors which Croxton assigns to the higher-order terms in his series are not justified clearly. However, let us ignore this. Croxton then replaces the integrals in his series by integrals only involving the field points. For hard spheres this is justified if the integration variables are restricted to the common volume of two spheres of diameter d which are separated by a distance r_{12}. Croxton does not do this, but instead uses a spherical region of radius R. Clearly, R should be a function of r_{12}. However, for simplicity, Croxton assumes R to be independent of r_{12}. This may not be unreasonable as the PY theory can be obtained from the assumption that $R=d$, independent of the value of r_{12}. Croxton finds that if he makes a particular (but approximate) choice of the diagrams which are included in his expression for $d(r)$ that he can sum the series. Further, he assumes, incorrectly, that for hard spheres, $c(r)$ is equal to the PY expression for $r<d$. On this basis he finds that $\partial p/\partial \rho$ can equal zero and that it is possible to choose R so as to make his predicted "phase transition" occur at the correct density. In view of the many approximations and unclear arguments in this approach, this cannot be regarded as a theory of the hard-sphere phase transition. However, it is indicative. The approach might be worth pursuing and refining.

4. Semiempirical expressions for the hard-sphere correlation functions

Verlet and Weis (1972a) have used the PY $g(r)$ as the basis of a parameterization of the simulation $g(r)$. They write

$$\begin{aligned} g(r/d, \rho d^3) &= 0, \quad r<d \\ &= g_{\mathrm{PY}}(r/d', \rho d'^3) \\ &\quad + (A/r)\exp\{m(r-d)\}\cos\{m(r-d)\}, \quad r>d\,. \end{aligned} \tag{6.57}$$

The purpose of the various terms is quite simple. The purpose of A is to raise the value of $g(r)$ at contact. The PY and simulation $g(r)$ are quite close for large r and hence the correction term is exponentially damped. The correction must change sign and be negative for $r \sim 1.2d$ and, therefore, the cosine is included. Presumably, the purpose of the r^{-1} term is to aid in the computation of the Fourier transform. The purpose of $d'<d$ is to compensate for the fact that the PY $g(r)$ is slightly out of phase with the simulation $g(r)$ at large r. Verlet and Weis find that

$$\left(\frac{d'}{d}\right)^3 = 1 - \frac{\eta}{16} \tag{6.58}$$

is satisfactory. Thus, A and m, respectively, are chosen to make the pressure and compressibility equation results agree with the CS equation of state. Verlet and Weis (VW) give analytic approximations for A and m. However, it is no more difficult to make the agreement with the CS equation of state exact and obtain numerical values for A and m. The resulting $g(r)$ is plotted in Fig. 17 and is seen to be in close agreement with simulation RDF.

Although this parametrization is very convenient, it should not be thought of as a substitute for the simulation studies of the RDF. Verlet and Weis state that the above $g(r)$ differs from the simulation $g(r)$ by at most 0.03. This is about three times the statistical error in the simulation results and may lead to errors in some applications.

Grundke and Henderson (1972) have used the VW $g(r)$ to compute the Fourier transforms $\tilde{h}(k)$ and $\tilde{c}(k)$. Their results, almost entirely analytic, are given in Henderson and Grundke (1975). The direct correlation function can be obtained from $\tilde{c}(k)$. The resulting $c(r)$ is compared with PY $c(r)$ in Fig. 18. The more accurate Grundke–Henderson (GH) $c(r)$ is everywhere more positive than the PY $c(r)$.

In addition, Grundke and Henderson (1972) have approximated $y(r)$ for $0 \leq r \leq d$ by making use of the relations, valid only for hard spheres,

$$\ln y(0) = \beta\mu - \ln \rho\lambda^3\,, \tag{6.59}$$

where μ is the chemical potential and $\lambda = h/(2\pi mkT)^{1/2}$, and

$$\left.\frac{\partial \ln y(r)}{\partial r}\right|_{r=0} = -6\eta y(d)\,. \tag{6.60}$$

Equations (6.59) and (6.60) are due to Hoover and Poirier (1962) and Meeron and Siegert (1968), respectively. Grundke and Henderson (1972) give generalizations of (6.59) and (6.60) for hard-sphere mixtures. The procedure of GH is to approximate $\ln y(r)$, for $r \leq d$, as a cubic polynomial which is fit to (6.59) and (6.60) and to the values of $y(d)$ and $y'(d)$ computed from the WV $g(r)$. Their results for $y(r)$, for $r \leq d$, are compared with the PY results in Fig. 17. The PY $y(r)$ is enormously in error for $r \leq d$. The low values of the PY $g(r)$ at contact are the early symptoms of this failure. Normally, only $r \geq d$ is of interest and these errors are of no consequence. However, if Eqs. (6.59) or (6.60) were used to compute the hard-sphere equation of state, very poor results would be obtained. In addition, we shall see in Sec. VII.D.3 that some perturbation theories require the hard-sphere $y(r)$ for $r \leq d$, so that reliable results are essential.

These more reliable values of $y(r)$ and $c(r)$ can be used to compute $d(r)$ for hard spheres. The GH $d(r)$ plotted in Fig. 27. The PY approximation, $d(r)=0$, is very poor inside the core. The reason why the PY theory works so well for hard spheres, despite the fact that $d(r)=0$ is a poor approximation, is due to the fact that the large errors in $d(r)$ for small r and high densities almost exactly cancel the large error in $y(r)$ so that reasonable values of $c(r)$ and, thus $g(r)$, result. Although one prefers an approximation to $d(r)$ which is reliable for all r, it is only essential, for hard spheres at least, that the approximation be valid in the region $r \sim \sigma$. For this region $d(r)=0$ is a fairly good approximation for hard spheres.

Henderson and Grundke (1975) have obtained approximate, but accurate, expressions for the hard-sphere $d(r)$ and $d'(r)$ at $r=0$ and accurate *ad hoc* expressions

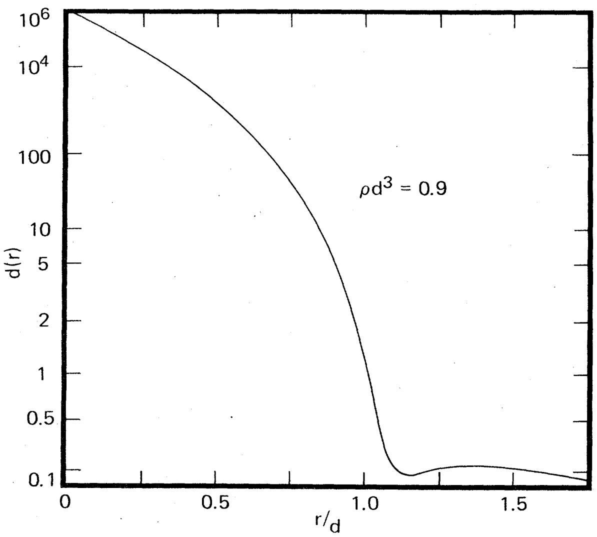

FIG. 27. The function $d(r)$ for hard spheres at $\rho d^3 = 0.9$. The constant d [not to be confused with the function $d(r)$] is the hard-sphere diameter. The curve gives the semiempirical results of Grundke and Henderson (1972). The curve is plotted on a $\sinh^{-1} \sinh^{-1}$ scale.

for $d(r)$ and $d'(r)$ for hard spheres at contact. They approximate $\ln d(r)$ by a cubic polynomial and fit the coefficients to these expressions to obtain a useful parametrization of $d(r)$ for hard spheres.

Waisman (1973a) has obtained an analytic solution of the mean spherical approximation for the Yukawa potential. His result could be used to parametrize the hard-sphere $c(r)$. We shall discuss his result in the next section.

D. Mean spherical approximation

We recall that (6.17) is the PY approximation. For large r, (6.17) becomes

$$c(r) = -\beta u(r) . \tag{6.61}$$

Lebowitz and Percus (1966) have suggested using (6.61), not just for large r, but for all r in the region where the potential is attractive. This approximation, called the *mean spherical approximation* (MSA), has been applied almost exclusively to potentials with a hard core of diameter σ. For such potentials, the MSA is specified by

$$h(r) = -1, \quad r < \sigma$$

and (6.62)

$$c(r) = -\beta u(r), \quad r > \sigma ,$$

together with the OZ equation. The coefficients in the MSA density expansion cannot be expressed in terms of integrals involving the Mayer f function. Moreover, the MSA does not become exact in the limit of low densities, and so does not even given B exactly.

One advantage of the MSA is that it can be solved analytically for a fairly wide variety of systems. If $u(r) = 0$ for $r > R$, the Baxter (1968a) form of the OZ equation can be used with the MSA without additional approximation. For hard spheres, the MSA is just the PY approximation. Waisman and Lebowitz (1970, 1972a, b) have solved the MSA for changed hard spheres. Waisman (1973a) has solved the MSA for hard spheres with a Yukawa tail. Waisman's solution involves six parameters which must be determined by solving six simultaneous equations and so his solution is not immediately useful. Henderson *et al.* (1975) have obtained series expansion of Waisman's solution in powers of both ρ and $\beta\epsilon$. Høye and Stell (1975a) have simplified Waisman's solution. Recently, the MSA has been solved for a mixture of hard spheres with Yukawa tails (Waisman, 1973b) and for hard spheres with a tail consisting of two Yukawa tails (Waisman, 1974).

We will not attempt to review these applications of the MSA. Instead, we will examine the application of the MSA to the square-well potential and to dipolar hard spheres as illustrative examples of the application of the MSA to spherical and nonspherical potentials.

1. Results for square-well potential

Smith *et al.* (1976) have solved the MSA for the square-well potential with $\lambda = 1.5$. The MSA $g(r)$ for the SW potential is plotted in Fig. 28 for $\rho^* = 0.8$ and $\beta\epsilon = 0$ and 1.5. At $\beta\epsilon = 0$ (high temperatures), the MSA $g(r)$ is just the PY hard-sphere $g(r)$. It is in reasonably good agreement with the simulation results. At $\beta\epsilon = 1.5$, which is a liquid state near the triple point, the MSA $g(r)$ is quite good for $r < 1.5\sigma$. To some extent, this good agreement is due to a cancellation of errors because the hard-sphere MSA (or PY) $g(r)$ is too low near contact. Thus, the MSA correction to the hard-sphere $g(r)$ due to the attractive forces is underestimated for $r \sim \sigma$. Even so, the results are better than the corresponding PY results in Fig. 19. The MSA $c(r)$ values are plotted in

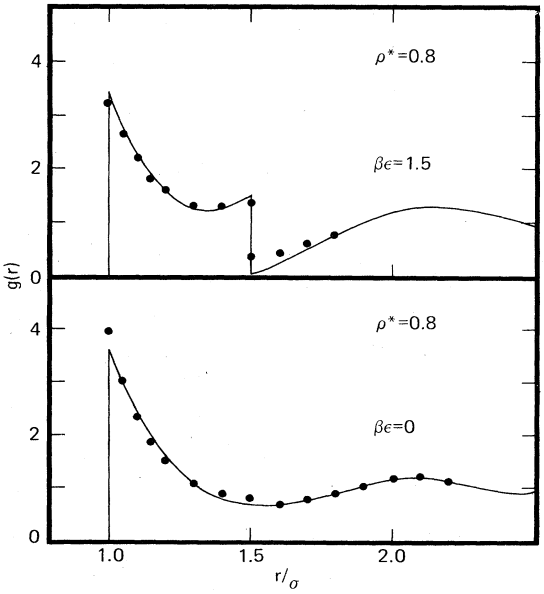

FIG. 28. RDF of the square-well fluid, with $\lambda = 1.5$, at $\rho\sigma^3 = 0.8$. The points give the MC results of Barker and Henderson (1971a, 1972) and Henderson, Madden and Fitts (1976) for the square-well fluid at $\beta\epsilon = 0$ (hard spheres) and $\beta\epsilon = 1.5$, respectively. The curves give the MSA results of Smith *et al*. (1976).

Fig. 29. There are no simulation results for comparison. However, the MSA $c(r)$ should be reasonably good. Some MSA values for the thermodynamic properties are plotted for $\rho^* = 0.60$ and 0.85 in Figs. 22–24. With the exception of the heat capacity, the MSA results are superior to the PY results where simulation results are available for comparison. The simulation results for the heat capacity are harder to obtain accurately than are the other results, and may well have appreciable errors. Although there are no simulation results for comparison, we believe the MSA values for the compressibility in Fig. 22 to be quite good. Thermodynamic properties calculated from the energy equation should be better than those calculated from the other routes. However, at the time of writing, pressures calculated from the energy equation are not available so that this conjecture cannot be tested.

2. Solution of the MSA for dipolar hard spheres

Wertheim (1971) has solved the MSA for dipolar hard spheres, for which

$$u(r_{12}, \Omega_1, \Omega_2) = \infty, \quad r_{12} < \sigma$$
$$= -(\mu^2/r_{12}^3)D(1,2), \quad r_{12} > \sigma, \tag{6.63}$$

where μ is the dipole moment, and

$$D(1,2) = 3(\hat{\mu}_1 \cdot \hat{\mathbf{r}}_{12})(\hat{\mu}_2 \cdot \hat{\mathbf{r}}_{12}) - \hat{\mu}_1 \cdot \hat{\mu}_2 \tag{6.64}$$

and $\hat{\mu}_1$ and $\hat{\mathbf{r}}_{12}$ are unit vectors. If $h(1,2) = h(r_{12}, \Omega_1, \Omega_2)$ is the total correlation function, where Ω_1 and Ω_2 are the angular coordinates specifying the orientation of the dipoles, we may define the projections

$$h_S(r_{12}) = \int h(1,2)\,d\Omega_1 d\Omega_2, \tag{6.65}$$

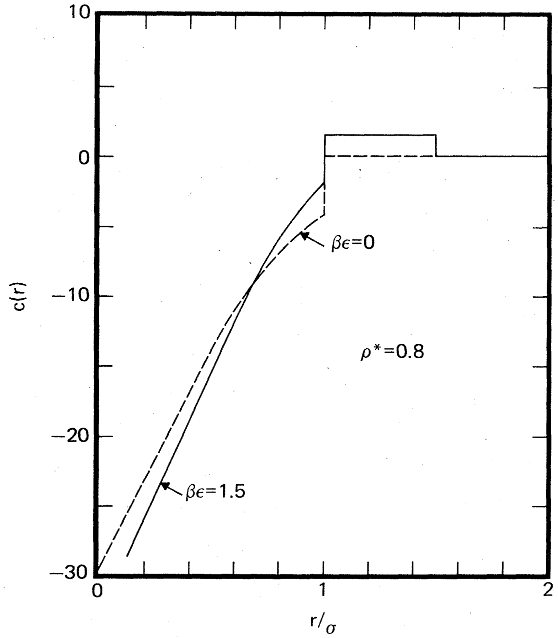

FIG. 29. Direct correlation function of the square-well fluid, with $\lambda = 1.5$, at $\rho\sigma^3 = 0.8$ calculated from the MSA by Smith *et al*. (1976).

$$h_D(r_{12}) = \frac{3}{2} \int D(1,2) h(1,2)\,d\Omega_1 d\Omega_2, \tag{6.66}$$

and

$$h_\Delta(r_{12}) = 3 \int \Delta(1,2) h(1,2)\,d\Omega_1 d\Omega_2, \tag{6.67}$$

where

$$\Delta(1,2) = \hat{\mu}_1 \cdot \hat{\mu}_2 . \tag{6.68}$$

The functions $D(1,2)$ and $\Delta(1,2)$ have the property that

$$\int D(1,2)\,d\Omega_1\, d\Omega_2 = 0, \tag{6.69}$$

$$\int D^2(1,2)\,d\Omega_1 d\Omega_2 = \frac{2}{3}, \tag{6.70}$$

$$\int \Delta(1,2)\,d\Omega_1 d\Omega_2 = 0, \tag{6.71}$$

and

$$\int \Delta^2(1,2)\,d\Omega_1 d\Omega_2 = 1/3 . \tag{6.72}$$

Further $D(1,2)$ and $\Delta(1,2)$ are orthogonal, i.e.,

$$\int D(1,2)\Delta(1,2)\,d\Omega_1 d\Omega_2 . \tag{6.73}$$

Wertheim (1971) showed that, in the MSA,

$$h(1,2) = h_S(r_{12}) + h_D(1,2)D(1,2) + h_\Delta(1,2)\Delta(1,2), \tag{6.74}$$

where $h_S(r_{12})$ is just the PY hard-sphere result and $h_D(1,2)$ and $h_\Delta(1,2)$ can be calculated easily from $h_S(r_{12})$. In contrast to h_S, h_D and h_Δ are functions of $\beta\mu^2$ as well as r.

The thermodynamic properties can then be calculated from

$$\frac{pV}{Nk_BT} = 1 + 4\eta y_S(\sigma) - \frac{1}{3} N\rho\mu^2 \int r^{-3} h_D(r)\,d\vec{\mathbf{r}}, \tag{6.75}$$

$$k_BT\left(\frac{\partial\rho}{\partial p}\right)_T = 1 + \rho \int h_S(r)\,d\vec{\mathbf{r}}, \tag{6.76}$$

or

$$U_i = -\frac{1}{3} N\rho\,\mu^2 \int r^{-3} h_D(r, \beta\mu^2)\,d\vec{\mathbf{r}} . \tag{6.77}$$

Thus, in the MSA the compressibility equation results for dipolar hard spheres are equal to the PY hard-sphere compressibility results. The difference in the pressure or energy equation results from the hard-sphere results are determined by $h_D(1,2)$. On the other hand, the dielectric constant, ϵ, is determined by $h_\Delta(1,2)$, through

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = yg_k , \tag{6.78}$$

where

$$y = (4\pi/9)\rho\beta\mu^2 , \tag{6.79}$$

$$g_k = 1 + \frac{1}{3}\rho \int h_\Delta(r, \beta\mu^2)\,d\vec{\mathbf{r}} . \tag{6.80}$$

Patey and Valleau (1973, 1974, 1976) and Verlet and

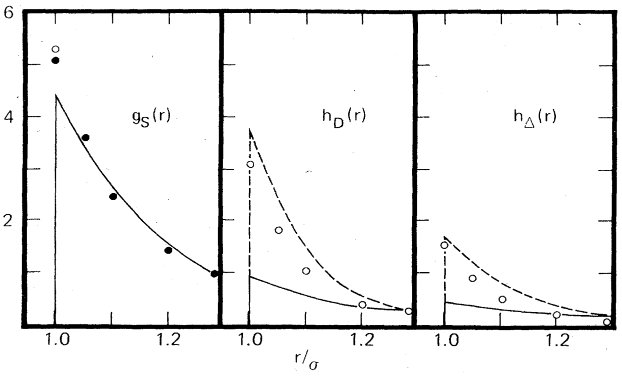

FIG. 30. Pair distribution functions of dipolar hard spheres at $\rho\sigma^3=0.9$. The points given by ● and ○ give the results of Barker and Henderson (1971a, 1972) and Verlet and Weis (1974) for $\beta\mu^2=0$ (hard spheres) and $\beta\mu^2=1$, respectively. The solid and broken curves give the MSA and LEXP results, respectively, for $\beta\mu^2=1$. For $g_s(r)$, the MSA and LEXP results are identical.

Weis (1974) have made computer simulations of the dipolar hard-sphere system. They find that the MSA thermodynamic properties are poor. This is because the MSA results for $h_S(r)$, $h_D(r, \beta\mu^2)$, and $h_\Delta(r, \beta\mu^2)$ are unsatisfactory. This may be seen in Fig. 30. Although $h_S(r, \beta\mu^2)$ is very nearly independent of $\beta\mu^2$, it does vary with $\beta\mu^2$—otherwise the compressibility equation of state would have no $\beta\mu^2$ dependence. Most of the error in the MSA $g_S(r)=h_S(r)+1$ is the error in the PY hard-sphere result. The MSA results for $h_D(r, \beta\mu^2)$ and $h_\Delta(r, \beta\mu^2)$ are too small at contact. Just as for the SW potential, the MSA underestimates the correction to the hard sphere $h(1,2)$.

For the dielectric constant, Wertheim (1971) obtained

$$\epsilon=\frac{(1+4\xi)(1+\xi)^4}{(1-2\xi)^6}\,, \tag{6.81}$$

where ξ is determined from

$$y=\frac{1}{3}\left[\frac{(1+4\xi)^2}{(1-2\xi)^4}-\frac{(1-2\xi)^2}{(1+\xi)^4}\right]. \tag{6.82}$$

The parameter ξ must be less (usually much less) than 1/2. Equation (6.81) is an improvement upon the Clausius–Mossotti result

$$(\epsilon-1)/(\epsilon+2)=y\,, \tag{6.83}$$

which has an incorrect singularity at $y=1$, and the Onsager (1936) result

$$(\epsilon-1)(2\epsilon+1)/9\epsilon=y \tag{6.84}$$

which, as seen from (6.78) corresponds to $g_k=1$ or $h_\Delta(r, \beta\mu^2)=0$. Expanding, the MSA result for small y, gives

$$\frac{\epsilon-1}{\epsilon+2}=y-\frac{15}{16}\,y^3+\ldots, \tag{6.85}$$

whereas the Onsager result gives

$$\frac{\epsilon-1}{\epsilon+2}=y-2y^3+\ldots\,. \tag{6.86}$$

The coefficient 15/16 is known to be correct (Jepson, 1966).

Recently, the MSA has been solved for mixtures of dipolar hard spheres (Adelman and Deutch, 1973; Sutherland *et al.*, 1974; Isbister and Bearman, 1974). The work of the latter authors is the most general since, in this work, both the hard-sphere diameters and the dipole moments of the components are unrestricted.

Blum and Torruella (1972) and Blum (1972, 1973, 1974) have applied the MSA to systems of hard spheres with more general charge distributions. The system of quadrupolar hard spheres is of some interest because quadrupoles appear to have much larger effects on the thermodynamic properties and structure than do comparable dipoles (Patey and Valleau, 1975).

3. Extensions

The MSA is identical to the PY approximation when $\beta=0$. Andersen and Chandler (1970, 1972) and Andersen *et al.* (1972) have suggested replacing (6.61) by

$$c(r)=c_{\mathrm{HS}}(r)-\beta u(r)\,, \tag{6.87}$$

for $r>\sigma$. In (6.87) $c_{\mathrm{HS}}(r)$ is the hard-sphere direct correlation function. If $c_{\mathrm{HS}}(r)=0$ for $r>\sigma$, then (6.87) is just (6.61). However, if an accurate result for $c_{\mathrm{HS}}(r)$ is used, (6.87) will give very accurate results when $\beta=0$. Andersen *et al.* refer to (6.87) as the *optimized random phase approximation* (ORPA).

If we define

$$\begin{aligned}\mathcal{C}(1,2)&=g(1,2)-g_{\mathrm{HS}}(1,2)\\&=-\beta\psi(1,2)\,,\end{aligned} \tag{6.88}$$

where $g_{\mathrm{HS}}(1,2)$ is the hard-sphere result, we can obtain a good approximation to the ORPA results by adding the MSA value for $\mathcal{C}(1,2)$ to the correct hard-sphere RDF. In the limit of low densities, $\mathcal{C}(1,2)=-\beta u(1,2)$, for $r>\sigma$, and so $\psi(1,2)$ can be regarded as a *renormalized potential* for $r>\sigma$. For $r<\sigma$, $\psi(1,2)=0$, of course. We shall return to this idea of a renormalized potential in Sec. VII.B and C. The resulting RDF for the square-well potential, with $\lambda=1.5$, is plotted in Fig. 31. At $\beta\epsilon=1.5$, the ORPA $g(r)$ is slightly worse at contact than the MSA result because of the fortuitous cancellation of errors in the latter. Note that the ORPA $g(r)$ retains the errors in the MSA result for $r\sim1.5\sigma$.

Andersen and Chandler (1972) have suggested the *exponential* (EXP) *approximation*

$$g(1,2)=g_{\mathrm{HS}}(r)\exp\{\mathcal{C}(r)\}\,. \tag{6.89}$$

Equation (6.89) seems very attractive. In contrast to the MSA, the EXP approximation is exact in the limit of low densities and will produce the exact B.

The EXP result for the RDF for the SW potential with cutoff at 1.5σ is plotted in Fig. 31. For $\beta\epsilon=1.5$, the EXP approximation is an improvement over the ORPA results for $r>1.5$. For $r\lesssim1.5\sigma$, the EXP results are somewhat worse than the MSA or ORPA results. On the other hand, the EXP results are an improvement at contact.

Even better results can be obtained if a linearized version of the exponential approximation, suggested by Verlet and Weis (1974), is used. This approximation, which we will call the LEXP approximation, is

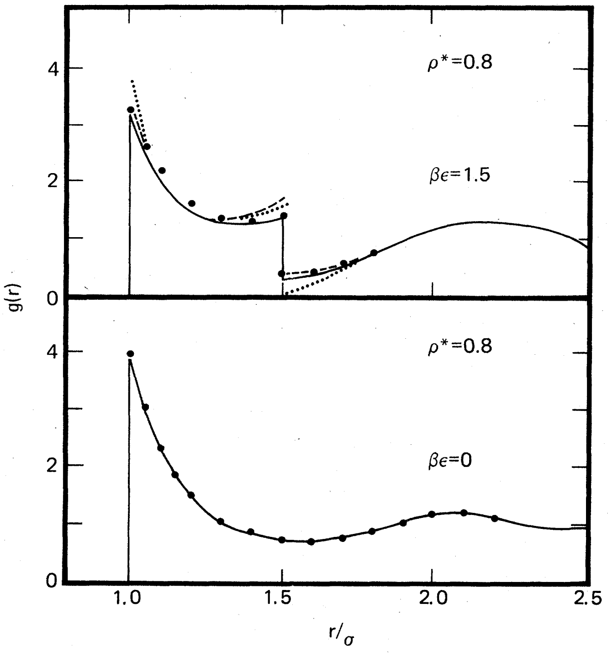

FIG. 31. RDF of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.8$. The points give the MC results of Barker and Henderson (1971a, 1972) and Henderson, Madden, and Fitts (1976) for the square-well fluid at $\beta\epsilon=0$ (hard spheres) and $\beta\epsilon=1.5$, respectively. The dotted, broken, and solid curves, respectively, give the ORPA, EXP, and LEXP results (Smith *et al.*, 1976). For $\beta\epsilon=0$ all three approximations give the same result.

$$g(1,2)=g_{\mathrm{HS}}(r)\{1+\mathcal{C}(1,2)\}. \tag{6.90}$$

Equation (6.90) will not produce the correct results in the limit of low densities but, as may be seen in Fig. 31, is an improvement over the MSA, ORPA, or EXP approximations at high densities.

Verlet and Weis (1974) have found that the EXP approximation is very poor for dipolar hard spheres. However, they found the LEXP approximation to be quite good for this system. From Fig. 30 we see that, although the LEXP $g_S(r)$ is not improved over the MSA result, the LEXP $h_D(r)$ and $h_\Delta(r)$ are a considerable improvement.

All of the applications of the MSA or its extensions which have been considered thus far in this section have been to potentials with a hard core. Blum and Narten (1972), Narten *et al.* (1974), and Watts *et al.* (1972) have considered extensions to systems with soft cores. Aspects of the perturbation theory of Andersen *et al.* (1972), which will be discussed in Secs. VII.C.6 and VII.D.3 can be regarded as an extension of the MSA to systems with soft cores.

Finally, we mention the *generalized mean spherical approximation* (GMSA). The term was coined by Høye *et al.* (1974). However, the earliest work of this type was that of Waisman (1973a) who solved the MSA for hard spheres with a Yukawa tail and applied the solution to the hard-sphere system. In the GMSA, the Yukawa tail is not a pair potential but rather the assumed form for the direct correlation function outside the core. The parameters in the Yukawa tail are chosen to give thermodynamic consistency between the pressure and compressibility equations.

Høye *et al.* (1974) have applied the GMSA to charged hard spheres and dipolar hard spheres by solving the MSA for charged hard spheres and dipolar hard spheres with a Yukawa tail and adjusting the parameters of the Yukawa to give reasonable and consistent results for charged or dipolar hard spheres from the energy, pressure, and compressibility equations.

E. Hyper-netted chain approximation

If the function $N(r)$, defined in Eq. (6.23), is expanded in powers of the density, it is found that

$$N(r)=\rho c_2(r)+\rho^2[d_3(r)+2d_4(r)]+\dots\,. \tag{6.91}$$

Comparison with (4.44) and (4.45) shows that in lowest order (6.25) is valid. If we assume (6.25) to be valid in all densities we are led to the PY theory. However, we can compare $\ln y(r)$, as well as $y(r)$, with $N(r)$. Comparison of (6.91) with (4.47) and (4.48) shows that, in lowest order

$$\ln y(r)=N(r)\,. \tag{6.92}$$

Let us assume (6.92) to be valid at all densities. Equation (6.92) is called the *hyper-netted chain* (HNC) *approximation* or, less frequently, the convolution approximation. Substitution of (6.92) and the definition of $h(r)$ into the OZ equation gives the alternative statement of the HNC approximation

$$c(r)=f(r)y(r)+y(r)-1-\ln y(r)\,. \tag{6.93}$$

Thus, in the HNC approximation

$$d(r)=y(r)-1-\ln y(r)\,. \tag{6.94}$$

It is of some interest to note that $d(r)$ given by (6.94) can never be negative. Substitution of (6.93) into the OZ equation gives the HNC integral equation

$$\ln y(12)=\rho\int[f(13)y(13)+y(13)-1-\ln y(13)]\times[e(23)y(23)-1]d\vec{r}_3\,. \tag{6.95}$$

The HNC theory has been developed by several authors (Morita, 1958, 1960; Van Leeuwen *et al.*, 1958; Morita and Hiroike, 1960, 1961; Meeron, 1960a, b, c; Rushbrooke, 1960; Verlet, 1960).

It is important to note that, even if $u(r)=0$ for $r>R$, $c(r)$ will not vanish for $r>R$ in the HNC approximation and the Baxter (1968a) form of the OZ equation cannot be used except as an additional approximation.

Expansion of (6.95) in powers of the density gives $y_0=1$

$$y_1(r)=c_2(r)\,, \tag{6.96}$$

and

$$y_2(r)=d_3(r)+2d_4(r)+\tfrac{1}{2}\,c_2^2(r)\,. \tag{6.97}$$

Thus, y_0 and y_1, and hence B and C, are exact in the HNC theory. The expansion of $c(r)$ is given by (6.14) where γ_0 and $\gamma_1(r)$ are given by (6.15) and (6.16) and

$$\gamma_2(r)=f(r)y_2(r)+\tfrac{1}{2}\,c_2^2(r)\,. \tag{6.98}$$

The HNC theory includes more diagrams than does the PY theory. On the other hand, we have argued that for hard spheres, $c_2^2(r)$ and d_5 nearly cancel so that including more diagrams is not necessarily an improvement. It turns out that, for hard spheres, although the PY theory negects more diagrams than does the HNC theory, the PY theory does a better job of eliminating groups of diagrams whose contributions cancel. For systems with attractive forces, this cancellation is not so complete and, in many applications, the HNC is more satisfactory than the PY theory.

Diagrams of the form of $c_2(r)$ and $d_3(r)$ are often called *simple chains* and diagrams of the form of $d_4(r)$ are often called *netted chains*. Diagrams such as $c_2^2(r)$ and $f(r)c_2(r)$ are often called *bundles*. The name hypernetted chain theory reflects the fact that this theory includes the contribution to $y(r)$ of the bundles as well as the chains. In fact, the HNC theory includes the contributions to $y(r)$ or $c(r)$ of all of the chains and bundles. The chains and bundles can be formed by repeated convolutions of Mayer f functions. They are the complete class of such diagrams. The name convolution theory reflects this fact. Because the HNC theory includes the complete class of such diagrams, the HNC energy equation results are, apart from a constant of integration, identical to the pressure equation results. The remaining class of diagrams not included in the HNC theory are the most complex diagrams and are called, somewhat amusingly, *elementary diagrams*. An example of an elementary diagram is $d_5(r)$.

Rushbrooke and Hutchinson (1961) and Hutchinson and Rushbrooke (1963) have calculated the B through F for hard spheres from the HNC theory. Their results are listed in Table XIII. The agreement with the exact hard-sphere results is less satisfactory than was the case for the PY theory. Klein (1963), Levesque (1966), and Henderson, Madden, and Fitts (1976) have solved the HNC equation for hard spheres. The HNC $g(r)$ for hard spheres is plotted in Fig. 32. It is not as satisfactory as the PY $g(r)$ for hard spheres. The HNC equation of state for hard spheres is plotted in Fig. 16. It is less satisfactory than the PY result but is better than the BGY result.

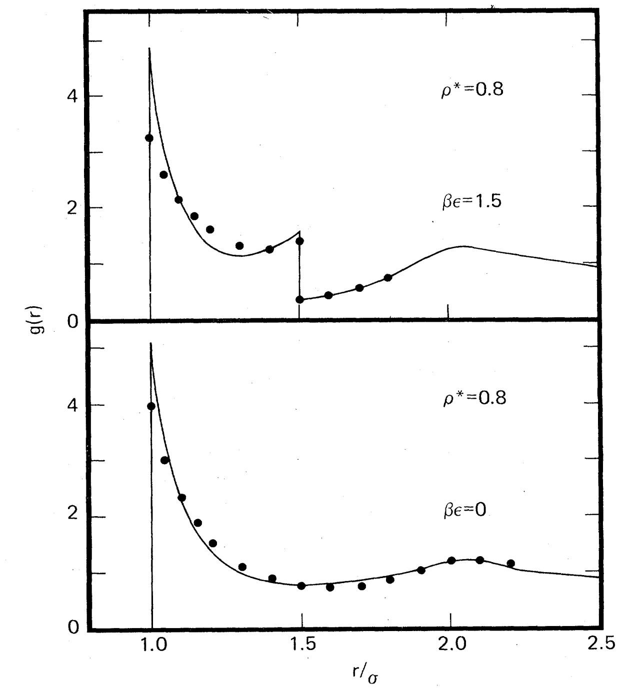

FIG. 32. RDF of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.8$. The points give the MC results of Barker and Henderson (1971a, 1972) and Henderson, Madden, and Fitts (1976) for the square-well fluid at $\beta\epsilon=0$ (hard spheres) and $\beta\epsilon=1.5$, respectively. The curve gives the HNC results of Henderson, Madden, and Fitts (1976).

The general consensus has been that the HNC theory is inferior to the PY theory for other systems also. However, the recent HNC calculations of Henderson, Madden, and Fitts (1976) for the square-well potential (with $\lambda=1.5$) have shown this to be an oversimplification. The square-well $g(r)$ and $c(r)$, calculated from the HNC theory, are plotted in Figs. 32 and 33. The hard-sphere case is $\beta\epsilon=0$. The results at $\beta\epsilon=1.5$ are not too good although they are better than the PY results shown in Fig. 19. However, close inspection shows the errors in these results to be, to a good approximation, the same as for the hard-sphere case. In other words, we could write

$$g(r,\beta\epsilon)=g(r,0)+g_{\mathrm{HNC}}(r,\beta\epsilon)-g_{\mathrm{HNC}}(r,0)\,, \qquad (6.99)$$

where $g(r,0)$ and $g_{\mathrm{HNC}}(r,0)$ are the exact and HNC hard-sphere $g(r)$, respectively. Although Eq. (6.99) has been introduced here as an *ad hoc* approximation, it can be placed on a systematic basis by means of the perturbation theories discussed in Sec. VII and we will defer detailed discussion until Sec. VII.C.5.

The HNC thermodynamic properties for the square-well fluid are plotted in Figs. 22 to 24 and 34. The HNC energy equation of state is identical to the HNC pressure equation of state except for a constant of integra-

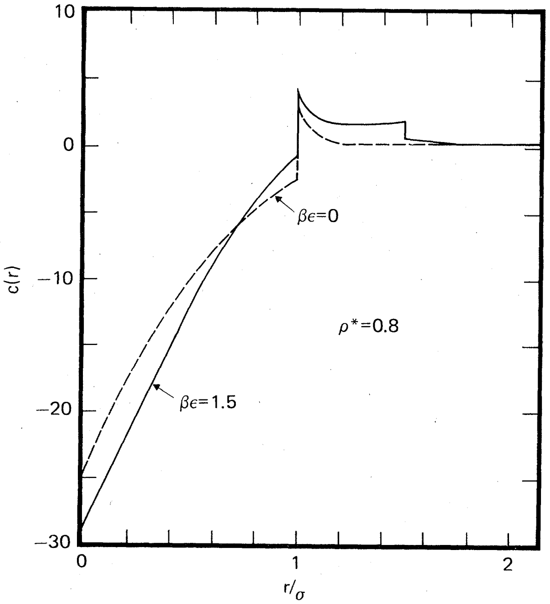

FIG. 33. Direct correlation function of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.8$ calculated from the HNC theory by Henderson, Madden, and Fitts (1976).

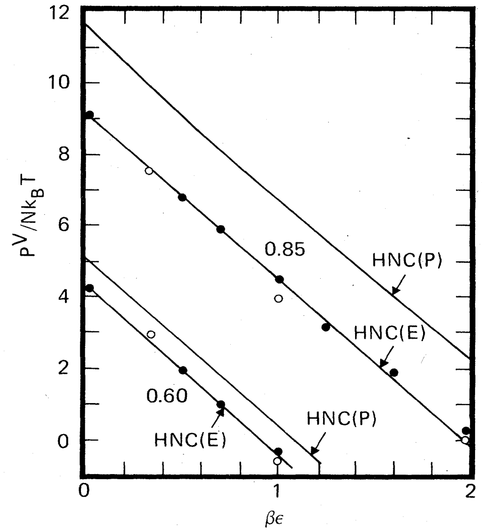

FIG. 34. Equation of state of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.6$ and 0.85. The points given by ○ and ● give the simulation results of Rotenberg (1965) and Alder *et al*. (1972), respectively, and the curves give the HNC pressure and energy equation results calculated by Henderson, Madden, and Fitts (1976). The HNC energy equation results are identical to the HNC pressure equation results except for a constant of integration.

tion (Morita and Horoike, 1960). If this constant of integration is chosen so that the hard-sphere ($\beta\epsilon=0$) results are given correctly, the energy equation of state is in very close agreement with the simulation results. The HNC value of the energy is in close agreement with the simulation results. It is surprising that the HNC values of the heat capacity, determined by differentiating the energy, show appreciable differences with the simulation results. As we have already commented, the simulation results for the square-well heat capacity may have a significant error.

The thermodynamic properties which result from (6.99) can be obtained from the HNC values by shifting the curves so that the hard-sphere ($\beta\epsilon=0$) value coincides with the correct hard-sphere result. This will not affect the heat capacity. However, the pressure and energy are improved. Although there are no simulation values of the compressibility for comparison, the HNC compressibilities are brought into good agreement with the MSA results and, presumably, are improved.

The HNC theory has been applied to the 6–12 potential by Broyles *et al.* (1962), Verlet and Levesque (1962), Klein and Green (1963), de Boer *et al.* (1964), Levesque (1966), and Watts (1969b). The results were not very encouraging and, as a result, the HNC equation has received less attention for this system than has the PY equation. Most of these calculations were carried out at high temperatures. Recently, Madden and Fitts (1974b) obtained encouraging results for $g(r)$ for the 6–12 fluid at low temperatures using the HNC equation. Thus, the problem with the HNC equation lies with the treatment of the repulsive part of the potential. Madden and Fitts (1975) have found that approximations such as (6.99) give improved results for the 6–12 potential. The HNC values for the 6–12 critical constants are given in Table VII.

Rushbrooke and Silbert (1967) have discussed the incorporation of three-body interactions into the HNC by means of an effective potential. There are difficulties with this approach. Equation (4.61) probably provides a better method.

Chihara (1973) has recently formulated a quantum version of the HNC theory. Murphy and Watts (1970) give a summary of applications of the HNC theory in variational studies of the ground state of liquid helium.

For hard spheres, the HNC expression overestimates $d(r)$. It has been popular (Rowlinson, 1965; Carley and Lado, 1965) to use the approximation

$$d(r)=\phi\{y(r)-1-\ln y(r)\}, \qquad (6.100)$$

where ϕ is a parameter, independent of r but depending on the thermodynamic variables, which is chosen so that the pressure and compressibility equations give the same result. As we have seen in Fig. 27, $d(r)$ is always positive for hard spheres (at least in the range where $d(r)$ is non-negligible). Thus, it is not surprising that a value of ϕ, between 0 and 1, which is independent of r should lead to reasonable results for hard spheres because the quantity in parenthesis in (6.100) is also always positive. However, for many potentials with attractive tails, $d(r)$, although positive for $r<\sigma$, is negative at low densities for $r\sim\sigma$. There is every reason to believe that $d(r)$ can change sign at high densities also. Hence if ϕ is independent of r, $d(r)$ given by (6.100) must always have the sign of ϕ. Thus, (6.100) cannot be a satisfactory approximation to $d(r)$. Therefore, it is no surprise that (6.100) has not been found useful for such potentials.

Henderson and Grundke (1975) have considered (6.100) when ϕ is a function of r. Their procedure is probably too cumbersome to be used for anything other than hard spheres. However, they do make the interesting observation that (6.94) or (6.100) can give rise to the correct asymptotic behavior of the correlation functions when r becomes large.

Another approximation, which will give the correct hard-sphere results and which would probably give good results for other temperatures, is

$$d(r,\beta\epsilon)=d(r,0)+d_{\rm HNC}(r,\beta\epsilon)-d_{\rm HNC}(r,0), \qquad (6.101)$$

where $d_{\rm HNC}(r,0)$ and $d(r,0)$ are the HNC and exact expressions for the hard sphere $d(r)$. In contrast to the HNC expression, (6.101) can have negative values. No calculations, based on (6.101), have been made.

Percus (1962) has shown that the HNC theory can be obtained by means of a first-order functional Taylor series. Verlet (1964) has taken this series to second-order and obtained a new set of integral equations, which he calls the HNC 2 equations. Again Verlet introduces an unsymmetric approximation for $g(123)$. The HNC 2 theory has not been as fully tested as the PY 2 because of the belief (probably mistaken for systems other than hard spheres) that the PY theory is a better starting point that the HNC theory. Even so, for systems with attractive forces, the improvement over the HNC results probably does not justify the extra computational effort involved in the HNC 2 equations.

Wertheim (1967) and Baxter (1968b) have proposed other extensions of the HNC theory.

F. Kirkwood–Salsburg equation

Kirkwood and Salsburg (1953) derived a set of integral relations between distribution functions of the form

$$g(1\cdots n) = \exp\left\{\beta\left[\mu_e - \sum_{k=2}^{n} u(1k)\right]\right\} \times\left\{g(2\cdots n) + \sum_{s=1}^{\nu}\frac{1}{s!}\rho^s \int K_s(1;n+1,\cdots,n+s) \times g(2\cdots n+s)d\vec{r}_{n+1}\ldots d\vec{r}_{n+s}\right\}, \tag{6.102}$$

where μ_e is the excess chemical potential given by

$$\exp[-\beta\mu_e] = 1 + \sum_{s=1}^{\nu}\frac{1}{Vs!}\rho^s \int K_s(1;\ 2\cdots s+1) \times g(2\cdots s+1)d\vec{r}_1\cdots d\vec{r}_{s+1}, \tag{6.103}$$

and

$$K_s(1;n+1,\ldots,n+s) = \prod_{m=n+1}^{n+s}\{\exp[-\beta u(1m)] - 1\}. \tag{6.104}$$

For potentials with finite range and hard cores the upper limit ν in the summations is *finite* and equal to the maximum number of molecules which can be packed into a sphere whose radius is equal to the range of the potential (since the integrands vanish when s is greater than this value). Potentially this is an attractive feature. However in practice ν is a relatively large number (of the order of 13 even for hard spheres). Hence these equations have been more useful in formal theoretical developments (Lebowitz and Percus, 1963b; Squire and Salsburg, 1964; Cheng and Kozak, 1973; Klein, 1973) than in actual numerical calculations. However Chung and Espenscheid (1968) used these equations with the superposition approximation to calculate virial coefficients for hard spheres; the virial coefficients up to the *fourth* were given exactly, and reasonable values for the fifth were obtained (better than HNC but worse than PY). However, Chung (1969) found for the 6–12 potential that unsatisfactory values for the fifth virial coefficient were obtained at low temperatures. Sabry (1971) used the equations to derive approximate integral equations for hard spheres; the equations actually solved led to unsatisfactory results except at quite low densities.

G. Some remarks about integral equations for the correlation functions

In Sec. VI we have examined in detail four theories for the correlation functions. For hard spheres, the PY theory is the most satisfactory. However, the PY theory seems to be satisfactory for hard spheres and nothing else. We have seen that the PY theory does not work well for systems with attractive forces. However even for repulsive soft spheres, the PY theory is not satisfactory (Watts, 1971). The HNC theory, and possibly the BG theory also, seems to be the complement of the PY theory. It is unsatisfactory for hard spheres but appears to account satisfactorily for the effect of the attractive forces and nonhard core forces. Modification of the HNC theory through (6.99) or (6.101) should lead to good results for hard spheres and systems with attractive forces. The MSA seems to combine the virtues of the PY and HNC theories. It is identical to the PY theory for hard spheres and gives good results for systems with attractive forces-especially when used in the LEXP version. The lack of a systematic extension to nonhard-sphere systems is the main weakness of this approach.

Generally speaking, the energy equation leads to the best thermodynamic properties. In fact for the square-well and 6–12 systems, this route is insensitive to the defects in the PY correlation functions and gives good thermodynamic properties. For the PY theory, the compressibility equation is generally to be preferred over the pressure equation. However, for the HNC theory the pressure equation is, apart from a constant of integration, the same as the energy equation and is often to be preferred over the compressibility equation.

Finally, there seems to be a widespread feeling that further study of integral equations may be unrewarding. Despite our close association with perturbation theory which has, to some extent, displaced the integral equation approaches, we feel that the integral equations are still of great value. They can provide information unavailable from other sources. For example, the integral equations give results for $y(r)$ inside the core. Recently, Henderson, Abraham, and Barker (1976) have been able to obtain the density profile of a fluid near a surface by using integral equations.

VII. PERTURBATION THEORIES

A. Introduction

In this section we shall examine some of the perturbation theories which have been developed and have received much attention in the past few years. The methods which we will discuss are quite general and can be applied to any system which is, in some sense, slightly perturbed from some reference system whose properties are known. In practice, the reference system is usually taken to be the hard-sphere system. This is both because hard spheres are a good reference fluid for many liquids of interest and because there is so much data available from machine simulations for the RDF and thermodynamic properties of hard spheres.

As was the case in Sec. VI, the methods developed here are approximate and thermodynamic consistency is lost. Almost without exception, the energy equation is used to relate the thermodynamic properties to the RDF. However, we note that one advantage of perturbation theory is that the thermodynamic properties can be calculated without reference to the RDF of the system.

Throughout most of this section we will be interested mainly in pairwise additive forces. We will also be mainly interested in spherical potentials. However, a few applications to systems with three-body forces or with nonspherical potentials will be considered.

The reason for the success of the perturbation theory of liquids is that the structure of a simple liquid is determined primarily by the hard-core part of the potential and that the main effect of the nonhard-core part of the potential is to provide a uniform background potential in which the molecules move.

This concept has been used for some time. It is the basis of the equation of state of van der Waals (1873). If, following van der Waals (vdW), we assume the molecules to have a hard core, i.e.,

$$\begin{aligned} u(r) &= \infty, \quad r<\sigma \\ &= u_1(r), \quad r>\sigma, \end{aligned} \tag{7.1}$$

then, using this concept, the Helmholtz free energy A of the liquid is the same as that of a system of hard spheres of diameter σ, except that the free energy is lowered because of the background potential field. Thus,

$$A = A_0 + \tfrac{1}{2} N\psi , \tag{7.2}$$

where A_0 is the free energy of the hard-sphere gas, and

$$\psi = 4\pi\rho \int_0^\infty u_1(r) g_0(r) r^2 dr . \tag{7.3}$$

The factor of 1/2 in (7.2) arises because the energy ψ is shared by two molecules, and hence would be counted twice if this factor were not inserted. Since $g(r)$ is the RDF, $\rho g(r) 4\pi r^2$ is the average number of molecules in a spherical shell of thickness dr and radius r surrounding a molecule at the origin and (7.3) follows immediately. A subscript zero has been placed on $g(r)$ in (7.3) to emphasize that, as a result of our assumptions, the RDF is the same as that of hard-sphere gas.

Van der Waals made the further assumption that the molecules are randomly distributed, i.e., $g_0(r)=1$. Thus

$$\psi = -2\rho a, \tag{7.4}$$

where

$$a = -2\pi \int_\sigma^\infty u_1(r) r^2 dr . \tag{7.5}$$

Until recently the properties of hard spheres were not known. Thus vdW had to approximate A_0 by assuming it to be the free energy of a perfect gas with V replaced by a smaller "free volume," V_f, because the molecules themselves occupy a finite volume. Therefore,

$$A_0/Nk_BT = 3\ln\lambda - 1 - \ln V_f + \ln N , \tag{7.6}$$

where

$$V_f = V - Nb , \tag{7.7}$$

and $b = 2\pi\sigma^3/3$. The factor b has this form because, when two molecules collide, the center of mass of one of the molecules is excluded from a volume of $4\pi\sigma^3/3$. This excluded volume is divided by 2 because it is shared by two molecules.

Combining (7.2) and (7.4)–(7.7) and differentiating with respect to V yields the van der Waals equation of site

$$(p + N^2a/V^2)(V - Nb) = Nk_BT . \tag{7.8}$$

Equation (7.8) gives results which are in poor agreement with experimental data. This is particularly true if a is calculated from (7.5). The situation can be improved somewhat by regarding a as a parameter chosen to fit some experimental data. However, even in this case, the results are unsatisfactory.

On the other hand, applications of the SPT to fluids with attractive forces indicated that liquids could be regarded as hard spheres in a uniform background potential (Reiss 1965). Also, Longuet-Higgins and Widom (1964) and Guggenheim (1965a) have shown that the main defect in the van der Waals theory lies in the use of (7.6) and (7.7) for the hard-sphere free energy. Thus, if (7.8) is replaced by

$$p = p_0 - N^2a/V^2 \tag{7.9}$$

and some more reliable expression for p_0 is used, then good agreement with experimental results for argon is obtained. For example, the PY or CS expressions could be used. However, the Longuet-Higgins and Widom (LHW) equation of state is fairly insensitive to the precise form of p_0. In fact, Guggenheim (1965b) showed that good results could be obtained by replacing the vdW expression

$$p_0V/Nk_BT = (1-4\eta)^{-1} \tag{7.10}$$

by the simple and more accurate expression

$$p_0V/Nk_BT = (1-\eta)^{-4} . \tag{7.11}$$

It is to be borne in mind that, in the LHW equation of state, a is a parameter. The value of a which results from (7.5) is quite different from that which is required to fit experimental data.

It is interesting to note that (7.9) has been obtained regorously for a weak, long-range potential (Kac *et al.*, 1963; Uhlenbeck *et al.*, 1963; Hemmer *et al.*, 1964; Hemmer, 1964). This result may be seen intuitively from (7.3). If $u(r)$ is extremely long ranged, then the major contribution to the integral comes from large values of r where $g_0(r)$ is unity. We shall refer to this limit of a weak, long-range potential as the vdW limit.

The first influential modern use of perturbation theory was that of Longuet-Higgins (1951) who used it to develop the conformal theory of solutions.

Zwanzig (1954) obtained Eqs. (7.2) and (7.3) by assuming that the intermolecular potential can be written as the sum of the hard-sphere potential and a perturbation potential

$$u(r) = u_0(r) + u_1(r) , \tag{7.12}$$

where $u_0(r)$ is the hard-sphere potential for spheres of diameter d. If the partition function, and thus the free energy, are expanded in powers of β, then, to first order, Eqs. (7.2) and (7.3) follow. Zwanzig, and later Smith and Alder (1959), calculated the equation of state using the 6–12 potential and the BG results (which at the time were the best available) for A_0 and $g_0(r)$. More recently, Frisch *et al.* (1966) made similar calculations using the PY results for A_0 and $g_0(r)$. The results of these calculations are in quite reasonable agreement with experiment at high temperatures. However, these results are very sensitive to the choice of d, for which no satisfactory criterion is provided.

An alternative approach has been given by Rowlinson

(1964b, c) for repulsive potentials. He expanded the free energy of a system of molecules with pair potential

$$u(r)=c_1r^{-n}-c_2r^{-n/2} \tag{7.13}$$

in powers of n^{-1}. The reference system ($n=\infty$) is the hard-sphere gas. If this expansion is taken to first order, and n is set equal to 12 to give the 6–12 potential, good results are obtained for the equation of state of gases at high temperatures (T^* above 12).

McQuarrie and Katz (1966) combined the Zwanzig and Rowlinson techniques by treating the attractive term in (7.13) as a perturbation on the repulsive term and treating the repulsive term by means of the n^{-1} expansion. This procedure yields a satisfactory equation of state for T^* above 3.

Thus, the situation in 1967 was that much of the evidence indicated that perturbation theories appeared to work only at high temperatures. However, the work of LHW and the work of Reiss and others on the SPT indicated that the hard-sphere fluid was an excellent reference system for the properties of liquids, even at the lowest temperatures, although firm conclusions could not be reached because of the presence of adjustable parameters in these approaches.

It is clearly important to determine whether the supposed failure of the Zwanzig approach at low temperatures is due to the perturbation approach itself or to the inadequate treatment of the finite steepness of the repulsive potential. For this reason we devote some time to an examination of perturbation theory for potentials with a hard core. In such potentials, the effect of the attractive forces is not complicated by the "softness" of the repulsive part of the potential.

The potential with a hard core which we chose is the square-well potential with cutoff at $\lambda=1.5$. This is partly because this system has been thoroughly studied both by the machine simulation methods and by the integral equation approaches of Sec. VI but also because, with $\lambda=1.5$, the square-well potential is relatively short-ranged and the perturbation expansion converges relatively slowly. As a result, we can examine the relative merits of various approaches which generally give the correct first-order term but gives differing approximations to the higher-order terms. Other potentials with a hard core, such as the triangle-well and Yukawa potentials (for which simulation results are available), when their parameters are adjusted to give as good a representation of argon as they are able, are relatively long-ranged and close to the vdW limit. As a result, almost any approach gives good agreement with the simulation results and little is learned about the higher-order terms.

For this reason we commence with a study of perturbation theory for the square-well fluid. In later sections we apply the theory to systems in which the repulsive potential has a finite steepness, and to systems with quantum effects, three-body interactions, and nonspherical potentials.

Henderson and Barker (1971) and Smith (1973) have reviewed perturbation theories of liquids. In addition, Henderson and Leonard (1971), McDonald (1973), and Henderson (1974) have reviewed the application of perturbation theory to the theory of liquid mixtures.

B. Second-order perturbation theory for potentials with a hard core

1. Formal expressions for first- and second-order terms

There is considerable flexibility in perturbation theory. Both the function to be expanded and expansion parameter may differ from application to application. Since there are many combinations, we cannot hope to review more than a few possibilities. However, we will try to be as general as possible.

Consider a system of molecules with a pairwise additive potential such that $e(r)=\exp\{-\beta u(r)\}$ depends on a parameter γ

$$e(r)=e(\gamma;r)\,. \tag{7.14}$$

We may then obtain a perturbation series, similar to (7.2) by expanding the free energy in powers of γ

$$A=A_0+\gamma\left(\frac{\partial A}{\partial\gamma}\right)_{\gamma=0}+\frac{1}{2}\gamma^2\left(\frac{\partial^2A}{\partial\gamma^2}\right)_{\gamma=0}+\cdots\,. \tag{7.15}$$

Usually γ is equal to unity for the physical system under consideration. This is essentially the method used by Zwanzig (1954), who assumed the particular form

$$u(r)=u_0(r)+\gamma u_1(r)\,. \tag{7.16}$$

We will use (7.14) for generality.

Assuming pairwise additivity, the free energy is given by

$$A=-k_BT\ln\int\prod_{i<j=1}^{N}e(r_{ij})d\vec{r}_1\cdots d\vec{r}_N\,, \tag{7.17}$$

where terms independent of γ have been dropped. Therefore,

$$\beta\frac{\partial A}{\partial\gamma}=-\frac{1}{2}\rho^2\int g(12)e_\gamma(12)d\vec{r}_1d\vec{r}_2 \tag{7.18}$$

and

$$\begin{aligned}\beta\frac{\partial^2A}{\partial\gamma^2}=&-\frac{1}{2}\rho^2\int g(12)e_{\gamma\gamma}(12)d\vec{r}_1d\vec{r}_2\\&-\rho^3\int g(123)e_\gamma(12)e_\gamma(23)d\vec{r}_1d\vec{r}_2d\vec{r}_3\\&-\frac{1}{4}\rho^4\int[g(1234)-g(12)g(34)]\\&\qquad\times e_\gamma(12)e_\gamma(34)d\vec{r}_1d\vec{r}_2d\vec{r}_3d\vec{r}_4\,,\end{aligned} \tag{7.19}$$

where

$$e_\gamma=e^{-1}\partial e/\partial\gamma\,, \tag{7.20}$$

and

$$e_{\gamma\gamma}=e^{-1}\partial^2e/\partial\gamma^2\,. \tag{7.21}$$

Essentially, this is Zwanzig's result. Although formally correct, it is not useful for numerical computation because it has been obtained in the canonical ensemble and is valid only for a *finite* system. To obtain results which are useful, we must take the *thermodynamic limit* ($N\to\infty$, N/V fixed). The only term which poses any difficulty in the thermodynamic limit is the last term in (7.19).

Lebowitz and Percus (1961) and Hiroike (1972) have shown that, when molecules $1,\ldots,m$ and $m+1,\ldots,$

$m+n$ are widely separated, asymptotically

$$\rho^{m+n}g(1\cdots m+n)$$

$$=\rho^{m+n}g(1\cdots n)g(m+1,\ldots,m+n)$$

$$-\frac{\rho^2}{\beta N}\left(\frac{\partial\rho}{\partial p}\right)_T\left\{\frac{\partial[\rho^m g(1\cdots m)]}{\partial\rho}\right\}\left\{\frac{\partial[\rho^n g(m+1,\ldots,m+n)]}{\partial\rho}\right\}$$

$$+O\left(\frac{1}{N^2}\right). \tag{7.22}$$

The second term on the RHS of (7.22) makes a contribution to the last integral in (7.19). Although of order N^{-1} it makes a finite contribution when integrated over all space. If $e(ij)$, $e_\gamma(ij)$, $e_{\gamma\gamma}(ij)$, etc., are central, then we can integrate over $\vec{r}_1$ to obtain V. Thus,

$$\beta\left(\frac{\partial A}{\partial\gamma}\right)_{\gamma=0}=-\frac{1}{2}N\rho\int g_0(12)e_\gamma(12)d\vec{r}_2 \tag{7.23}$$

and

$$\beta\left(\frac{\partial^2 A}{\partial\gamma^2}\right)_{\gamma=0}=-\frac{1}{2}N\rho\int g_0(12)e_{\gamma\gamma}(12)d\vec{r}_2$$

$$-N\rho^2\int g_0(123)e_\gamma(12)e_\gamma(23)d\vec{r}_2 d\vec{r}_3$$

$$-\frac{1}{4}N\rho^3\int[g_0(1234)-g_0(12)g_0(34)]$$

$$\times e_\gamma(12)e_\gamma(34)d\vec{r}_2 d\vec{r}_3 d\vec{r}_4$$

$$+N\beta^{-1}\left(\frac{\partial\rho}{\partial p_0}\right)_T\left[\frac{\partial}{\partial\rho}\left\{\frac{1}{2}\rho^2\int g_0(12)e_\gamma(12)d\vec{r}_2\right\}\right]^2, \tag{7.24}$$

where e_γ and $e_{\gamma\gamma}$ are to be evaluated in the limit $\gamma\to 0$ and $g_0(12)$, etc., are the distribution functions of the reference fluid. Similar expressions can be written for the higher-order derivatives. The procedure is straightforward. However, we do not give any results here because of the length of the expressions.

As we have seen in Sec. VII.A, to first-order in the free energy, the structure of the fluid is the same as that of the reference fluid and the first-order term in the free energy gives the average contribution of $e_\gamma(r)$. This first-order term is often called the *mean-field term* and perturbation expansions which are truncated at first-order in A are often called *mean-field theories*.

Similarly

$$\left(\frac{\partial g(12)}{\partial\gamma}\right)_{\gamma=0}$$

$$=g_0(12)e_\gamma(12)+2\rho\int g_0(123)e_\gamma(23)d\vec{r}_3$$

$$+\frac{1}{2}\rho^2\int[g_0(1234)-g_0(12)g_0(34)]e_\gamma(34)d\vec{r}_3 d\vec{r}_4$$

$$-2(\rho\beta)^{-1}\left(\frac{\partial\rho}{\partial p_0}\right)_T\left\{\frac{1}{2}\rho^2 g_0(12)\right\}\frac{\partial}{\partial\rho}\left(\frac{1}{2}\rho^2\int g_0(34)e_\gamma(34)d\vec{r}_4\right). \tag{7.25}$$

Equations (7.24) and (7.25) are suitable for numerical calculations because in the thermodynamic limit $g(1234)-g(12)g(34)$ approaches zero *exactly* when the pairs (12) and (34) are widely separated. These equations have been obtained earlier using the grand-canonical ensemble (Barker and Henderson, 1968; Henderson and Barker, 1971). Henderson *et al.* (1972) have generalized (7.23) and (7.24) for mixtures. Similar results can be found in the earlier papers of Buff and Brout (1955) and Buff and Schindler (1958). Equations (7.24) and (7.25) could be put into an alternative form by using the well-known result (Baxter, 1964a, b; Schofield, 1966)

$$\left(\frac{\partial\rho}{\partial p}\right)_T\frac{\partial}{\partial\rho}[\rho^2 g(12)]=2\beta\rho g(12)+\beta\rho^2\int[g(123)-g(12)]d\vec{r}_3. \tag{7.26}$$

In Zwanzig's expansion

$$e(\gamma;r)=\exp\{-\beta[u_0(r)+\gamma u_1(r)]\}. \tag{7.27}$$

If the potential has a hard core, $u_0(r)$ would be the hard-sphere potential. Using (7.27)

$$e_\gamma(r)=-\beta u_1(r) \tag{7.28}$$

and

$$e_{\gamma\gamma}(r)=\beta[u_1(r)]^2. \tag{7.29}$$

In the Zwanzig or $u_1(r)$ expansion

$$A=\sum_{n=0}^{\infty}(\beta\epsilon)^n A_n, \tag{7.30}$$

where ϵ is some parameter measuring the strength of the potential, usually the depth, and

$$g(r)=\sum_{n=0}^{\infty}(\beta\epsilon)^n g_n(r). \tag{7.31}$$

If the energy equation is used to obtain thermodynamic functions from $g(r)$,

$$\frac{A_n}{Nk_BT}=\frac{1}{2n}\rho\int u_1^*(r)g_{n-1}(r)d\vec{r}, \tag{7.32}$$

where $u_1^*(r)=u_1(r)/\epsilon$. For $n=1$, (7.32) is a special case of (7.23). For $n=2$, (7.32) could also be obtained from (7.24) and (7.25).

If the pressure or compressibility equation is used to relate thermodynamics to $g(r)$, then A_n depends upon $g_n(r)$ whereas, in the case of the energy equation, A_n depends upon $g_{n-1}(r)$. Thus, we would expect that a truncated expansion for $g(r)$ would yield best results when used with the energy equation.

However, it is important to point out that although the free energy expansion can be obtained from the expansion of $g(r)$ using these familiar routes to thermodynamics, Eq. (7.15) is more general than this. Equation (7.15) can be applied to systems with multi-body forces or quantum effects without reference to the question of how $g(r)$ is affected.

The $u_1(r)$ expansion is useful when $u_1(r)$ is *small* compared to k_BT. In addition, it is often useful at high densities even if $u_1(r)\sim k_BT$. In the $u_1(r)$ expansion, the second- and higher-order terms in $g(r)$ are fluctuation terms reflecting the changes in the structure of the fluid because of the presence of $u_1(r)$. This will be made more clear when we use the discrete representation in the following section. If the potential, $u(r)$, is strongly repulsive at small r as is the case if the potential has a hard core, it is to be expected that such changes in structure will become less likely as the density increases. Thus, the higher-order terms, although important at low densities, become less important at high densities. Hence, the more useful criterion for the convergence of the $u_1(r)$ expansion is that the effect of $u_1(r)$ on the structure should be small.

At low densities $g_1(r) = -u_1^*(r)g_0(r)$. Thus, $\psi(r) = -\epsilon \times g_1(r)/g_0(r)$ can be regarded as a *renormalized* potential, similar to that used in the ORPA which is equal to $u_1(r)$ at low densities but which is damped at high densities.

An obvious generalization of (7.27) is

$$e(\gamma; r) = \exp[-\beta u(\gamma; r)]. \tag{7.33}$$

In this case

$$e_\gamma(r) = -\beta u_1(r), \tag{7.34}$$

where

$$u_1(r) = \partial u(r)/\partial\gamma, \tag{7.35}$$

and

$$e_{\gamma\gamma}(r) = \beta^2[u_1(r)]^2 - \beta\partial u_1(r)/\partial\gamma. \tag{7.36}$$

In some applications, the perturbation energy

$$u_1(r) = u(r) - u_0(r) \tag{7.37}$$

may be large and positive. Clearly, the $u_1(r)$ expansion, (7.28), is inappropriate for this case. However, following Barker (1957) we can write

$$e(\gamma; r) = e_0(r) + \gamma e_0(r) f_1(r), \tag{7.38}$$

where $e_0(r) = \exp\{-\beta u_0(r)\}$ and

$$f_1(r) = \exp\{-\beta u_1(r)\} - 1. \tag{7.39}$$

For this case

$$e_\gamma = f_1(r) \tag{7.40}$$

and $e_{\gamma\gamma} = 0$. In principle, this approach can be used with negative perturbation potentials, $u_1(r)$, also. However, in this case this expansion is generally less useful. If $u_1(r)$ is small $f_1(r) \simeq -\beta u_1(r)$ and the approach has no advantages over the $u_1(r)$ expansion. If $u_1(r)$ is large and negative $\exp\{-\beta u_1(r)\} \gg -\beta u_1(r)$ and at high densities this exponential expansion usually converges more slowly than the $u_1(r)$ expansion. On the other hand, in the limit of low densities, this exponential expansion becomes exact. For example, the mean-field term gives the contributions of $u_1(r)$ to order ρ exactly. Thus, at low densities the exponential expansion may be the preferred expansion.

Occasionally, it is convenient (or even necessary) to combine $e^{-1}(r)$ and $g(1\ldots h)$. In this case, the first-order term corresponding to (7.38) is

$$\beta\left(\frac{\partial A}{\partial\gamma}\right)_{\gamma=0} = -\frac{1}{2}N\rho\int y_0(r)e_1(r)d\vec{\mathbf{r}}, \tag{7.41}$$

where

$$\begin{aligned} e_1(r) &= e_0(r)f_1(r), \\ &= e(r) - e_0(r). \end{aligned} \tag{7.42}$$

Lastly, we have the general case where the γ dependence of $e(\gamma; r)$ is not linear and not confined to the argument of the exponential. For such cases, it is usually convenient to combine $e^{-1}(r)$ and $g(1\ldots h)$. Thus, the first-order term is (7.41) with $e_1(r)$ replaced by $\partial e(r)/\partial\gamma$. Henderson and Barker (1968a) have used this type of exponential expansion in the theory of mixtures of hard spheres.

Instead of, or in addition to, the expansion of $g(r)$ one could expand $y(r)$. The first-order term in this expansion is just (7.25) with the first term on the RHS missing and the remaining terms multiplied by $e_0^{-1}(12)$. This expansion arises naturally in the exponential expansions. However in the $u_1(r)$ expansions, this expansion does not arise naturally and generally converges slower than the $g(r)$ expansion at high densities. On the other hand, at low densities, the $y(r)$ series converges faster than the $g(r)$ series, even in the $u_1(r)$ expansion, and can be useful. For example, $y(r) = y_0(r)$ is exact in the limit of low densities.

Finally, we mention the possibility of the expansion of $\ln g(r)$. The first-order term in this expansion is just $-\psi^*(r) = g_1(r)/g_0(r)$. Thus, the first-order $\ln g(r)$ and $g(r)$ series bear the same relationship to each other as the EXP and LEXP approximations discussed in Sec. VI.D. In the $u_1(r)$ expansion, the $\ln g(r)$ series gives results which are slightly less satisfactory in the few applications of the $\ln g(r)$ series which have been made so far at high densities. Despite this, the $\ln g(r)$ series is of interest. It gives exact results in the limit of low densities even when truncated at first order. This is not surprising because the $\ln g(r)$ and $\ln y(r)$ series differ only by $e_\gamma(r)$ and so have similar convergence properties.

Equations (7.24) and (7.25) are not very useful for computation because of the complexity of the three- and four-body distribution functions. However, if the superposition approximations

$$g_0(1234) = g_0(12)g_0(13)g_0(14)g_0(23)g_0(24)g_0(34) \tag{7.43}$$

$$g_0(123) = g_0(12)g_0(13)g_0(23) \tag{7.44}$$

are substituted into (7.24) and (7.25) and all *reducible* cluster integrals are omitted, then we obtain the more easily used *approximate* expressions of Barker and Henderson (1968)

$$\begin{aligned} \beta\left(\frac{\partial^2 A}{\partial\gamma^2}\right)_{\gamma=0} = {} & -\frac{1}{2}N\rho\int g_0(12)e_{\gamma\gamma}(12)d\vec{\mathbf{r}}_2 - N\rho^2\int g_0(12)g_0(23)e_\gamma(12)e_\gamma(23)h_0(13)d\vec{\mathbf{r}}_2 d\vec{\mathbf{r}}_3 \\ & -\frac{1}{4}N\rho^3\int g_0(12)g_0(34)e_\gamma(12)e_\gamma(34)[2h_0(13)h_0(24) + 4h_0(13)h_0(14)h_0(24) + h_0(13)h_0(14)h_0(23)h_0(24)]d\vec{\mathbf{r}}_2 d\vec{\mathbf{r}}_3 d\vec{\mathbf{r}}_4 \end{aligned} \tag{7.45}$$

and

$$\left(\frac{\partial g(12)}{\partial \gamma}\right)_{\gamma=0}=g_0(12)\Big\{e_\gamma(12)+2\rho\int g_0(123)e_\gamma(23)h_0(13)d\vec{r}_3$$

$$+\frac{1}{2}\rho^2\int g_0(34)e_\gamma(34)\Big[2h_0(13)h_0(24)+4h_0(13)h_0(14)h_0(24)+h_0(13)h_0(14)h_0(23)h_0(24)\Big]d\vec{r}_3 d\vec{r}_4\Big\}. \qquad (7.46)$$

We shall refer to (7.45) and (7.46) as the superposition approximations (SA) to $\partial^2 A/\partial\gamma^2$ and $\partial g/\partial\gamma$.

Although simpler to use than the exact expressions, the SA is not very useful. It is possible to calculate $\partial^2 A/\partial\gamma^2$ and $\partial g/\partial\gamma$ from the exact expressions so that the SA is not needed for these terms. On the other hand, the SA expressions for the higher-order terms are too complex for useful calculations.

2. Discrete representation

An alternative formulation of perturbation theory which is more suitable for numerical work has been given by Barker and Henderson (1967a). We refer to this formulation as the *discrete representation*. The range of intermolecular distances is divided into intervals $(r_0, r_1), \ldots (r_i, r_{i+1}), \ldots,$ etc. By taking the limit as the interval widths tend to zero, the continuous description is recovered. However, the discussion is simpler in terms of discrete divisions. If $p(N_1, N_2, \ldots)$ is the probability that the system has N_i intermolecular distances in the interval (r_i, r_{i+1}), then

$$\langle N_i\rangle=\sum_{N_1, N_2,\ldots} N_i p(N_1, \ldots), \qquad (7.47)$$

etc. If $u(r)$ can be regarded as having the constant value $u(r_i)$ in the interval (r_i, r_{i+1}), then

$$p(N_1, N_2, \ldots)=\int_R \exp(-\beta U_N)d\vec{r}_1\cdots d\vec{r}_N\Big/Q_N, \qquad (7.48)$$

where R is the region of configuration space for which there are N_i intermolecular distances in the interval (r_i, r_{i+1}), Q_N is the configurational partition function of the system and

$$U_N=\sum_i N_i u(r_i) \qquad (7.49)$$

is the potential energy.

We now proceed to obtain the perturbation expansion for the specific case when (7.16) is valid. Results appropriate to the exponential expansion can be obtained easily from the results given here. The partition function can be written

$$Z_N=Z_0\sum_{N_1 N_2\ldots} p_0(N_1, \ldots)\exp\Big[-\beta\sum_i N_i u_1(r_i)\Big]$$

$$=Z_0\left\langle\exp\Big\{-\beta\sum_i N_i u_1(r_i)\Big\}\right\rangle_0, \qquad (7.50)$$

where Z_0 is the partition function of the reference system, $p_0(N_1, \ldots)$ is the probability that the *reference* system has N_i intermolecular distances in the interval (r_i, r_{i+1}), and $u_1(r)$ is the perturbation energy defined by (7.16) (with $\gamma=1$). The subscript zero on the angular brackets means that the average is over the reference system.

Expanding the exponential in (7.50) yields

$$Z_N=Z_0\Big\{1-\beta\sum_i\langle N_i\rangle_0 u_1(r_i)$$

$$+\frac{1}{2}\beta^2\sum\langle N_i N_j\rangle u_1(r_i)u_1(r_j)+\cdots\Big\}. \qquad (7.51)$$

Hence,

$$(A-A_0)/k_B T=\beta\sum_i\langle N_i\rangle_0 u_1(r_i)$$

$$-\frac{1}{2}\beta^2\sum_{ij}\{\langle N_i N_j\rangle_0-\langle N_i\rangle_0\langle N_j\rangle_0\}u_1(r_i)u_1(r_j)$$

$$+\cdots. \qquad (7.52)$$

Thus,

$$A_1/k_B T=\sum_i\langle N_i\rangle_0 u_1^*(r_i) \qquad (7.53)$$

and

$$A_2/k_B T=-\frac{1}{2}\sum_{ij}\{\langle N_i N_j\rangle_0-\langle N_i\rangle_0\langle N_j\rangle_0\}u_1^*(r_i)u_1^*(r_j). \qquad (7.54)$$

Similarly, it is easy to show that

$$A_3/k_B T=\frac{1}{6}\sum_{ijk}\{\langle N_i N_j N_k\rangle_0-3\langle N_i N_j\rangle_0\langle N_k\rangle_0$$

$$+2\langle N_i\rangle_0\langle N_i\rangle_0\langle N_k\rangle_0\}u_1^*(r_i)u_1^*(r_j)u_1^*(r_k) \qquad (7.55)$$

with increasingly more complex expressions for the higher-order A_n. The terms, such as $\langle N_i\rangle$ and $\langle N_i N_j\rangle-\langle N_i\rangle\langle N_j\rangle$, which appear in the expressions for the A_n are called *cumulants* and the terms such as $\langle N_i\rangle$ and $\langle N_i N_j\rangle$ which appear in the expansion of the partition function are called *moments*. The particular term $\langle N_i N_j\rangle-\langle N_i\rangle\langle N_j\rangle$ is called a *covariance*.

Barker and Henderson (1967a) have observed that to obtain these results it is not necessary to assume that the potential is pairwise additive. All that is required is that the perturbation be pairwise additive.

The $\langle N_i\rangle_0$ are of course related to the radial distribution function. Thus,

$$\langle N_i\rangle_0=2\pi N\rho\int_{r_i}^{r_{i+1}} r^2 g_0(r)dr. \qquad (7.56)$$

Hence, (7.53) is equivalent to (7.23).

If the potential has a hard core, $u_0(r)$ would be the hard-sphere potential. In this case the first-order term makes no contribution to the entropy. Hence, in first-order the structure of the fluid is unaffected and the only effect of the attractive forces is to provide a background or mean field in which the molecules move as hard spheres. As is seen from (7.54) and (7.55), the higher-order A_n are fluctuations in the energy which represent the effect of the attractive potential on the structure of the fluid in compressing the molecules into energetically favorable regions. We would expect these higher-order terms to be least important at high densities, where the fluid is nearly incompressible and changes in structure are difficult. Thus, the u_1 expansion should be most useful at high densities.

Expressions for $g_0(r)$ and $g_1(r)$ can be obtained in the discrete representation also. Substitution of (7.48) and (7.50) into (7.47) gives

$$\langle N_i\rangle = \sum_{N_1\cdots} N_i \times \int_R \exp(-\beta U_0)\exp(-\beta U_1)d\vec{r}_1\cdots d\vec{r}_N \Big/ \{Q_0\langle\exp(-\beta U_1)\rangle_0\}, \tag{7.57}$$

where

$$U_0 = \sum_{i<j} u_0(r_{ij}), \quad = \sum_i N_i u_0(r_i), \tag{7.58}$$

and similarly for U_1. Now

$$p_0(N_1,\ldots) = \int_R \exp(-\beta U_0)\, d\vec{r}_1\cdots d\vec{r}_N \Big/ Q_0 . \tag{7.59}$$

Hence,

$$\langle N_i\rangle = \sum_{N_1\cdots} N_i \exp(-\beta U_1) p_0(N_1\ldots)\Big/\langle\exp(-\beta U_1)\rangle_0 = \langle N_i\exp(-\beta U_1)\rangle_0/\langle\exp(-\beta U_1)\rangle_0. \tag{7.60}$$

Expanding (7.60) yields

$$\langle N_i\rangle = \langle N_i\rangle_0 - \beta\epsilon\sum_j\{\langle N_iN_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0\}u_1^*(r_j). \tag{7.61}$$

Hence,

$$g_0(r_i) = 3\{N_i\}_0/2\pi N\rho(r_i^3 - r_{i-1}^3) \tag{7.62}$$

and

$$g_1(r_i) = -\frac{3\sum_j\{\langle N_iN_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0\}u_1^*(r_j)}{2\pi N\rho(r_i^3 - r_{i-1}^3)} . \tag{7.63}$$

Barker and Henderson (1968, 1972) and Henderson and Barker (1971) have made a Monte Carlo calculation of $\langle N_i\rangle_0$ and $\langle N_iN_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0$ for a hard-sphere reference system for arbitrary hard-sphere diameter. In their calculation, the small intervals were chosen to be given by $r_\lambda = (1+0.07\lambda)^{1/2}d$, where d is the hard-sphere diameter and $\lambda = 1,\ldots, 60$. Their calculations can be applied to any perturbation potential. Barker and Henderson (1971a, 1972) have used these values of $\langle N_i\rangle_0$ to obtain extensive tables of $g_0(r)$ for hard spheres.

In addition, Barker and Henderson (1972) have written (7.54) in the form

$$A_2/Nk_BT = -\pi\rho d^3\int_1^\infty g_0(r)[u_1^*(rd)]^2r^2dr + \int_1^\infty\int_1^\infty F(r_1, r_2)u_1^*(r_1d)u_1^*(r_2d)dr_1dr_2, \tag{7.64}$$

where r is the distance divided by d, and

$$F_0(r_i, r_j) = \lim_{\Delta r_i\to 0\,\Delta r_j\to 0}[\langle N_iN_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0 - \delta_{ij}\langle N_i\rangle_0]/2N\Delta r_i\,\Delta r_j \tag{7.65}$$

is a continuous function. They fitted $F_0(r_1, r_2)$ to an expression of the form

$$F_0(r_1, r_2) = \sum_{m,n=1}^{9} A_{mn}\phi_m(r_1)\phi_n(r_2), \tag{7.66}$$

where A_{mn} is symmetric, and

$$r^4\phi_1(r) = 1, \tag{7.67}$$

$$r^4\phi_2(r) = r - 1, \tag{7.68}$$

$$r^4\phi_m(r) = \sin[(\pi/\alpha)(l-2)(r-1)],\quad 3\leqslant m\leqslant 9, \tag{7.69}$$

and $\alpha = (5.2)^{1/2} - 1$. This value of α was used because $(5.2)^{1/2}$ was the largest value of r for which $\langle N_iN_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0$ had been calculated. Thus, Eq. (7.66) should be used only in the specified region for which it is intended. It is assumed that the perturbation $u_1^*(rd)$ can be neglected for $r > (5.2)^{1/2}$ in computing the second integral in (7.64). However, in calculating A_1 and the first integral in (7.64) the contributions of $u_1^*(r)$ for all values of r must be included.

Thus,

$$A_2/Nk_BT = -\pi\rho d^3\int_1^\infty g_0(r)[u_1^*(rd)]^2r^2dr + \sum_{m,n=1} A_{mn}I_mI_n, \tag{7.70}$$

where

$$I_n = \int_1^{1+\alpha} u_1^*(rd)\phi_n(r)dr. \tag{7.71}$$

A table of the A_{mn} has been given by Barker and Henderson (1972).

This parametrization of the $\langle N_iN_j\rangle_0$ can be used to calculate $g_1(r)$. Thus,

$$g_1(r) = -u_1^*(rd)g_0(r) + \frac{1}{\pi\rho r^2d^3}\sum_{m,n=1}^{9} A_{mn}I_m\phi_n(r), \tag{7.72}$$

where again r is the distance divided by d.

There is considerable cancellation between the first and second terms in (7.70) or (7.72). To preserve this it is preferable to use the MC values of $g_0(r)$ of Barker and Henderson (1971a, 1972) which were used in the fit of the A_{mn} in evaluating the first term.

Because of the factorized form of (7.70) it is possible to calculate A_2 and $g_1(r)$ with little labor. In most applications it is probably better to use (7.70) and (7.72) rather than the original MC data for $\langle N_iN_j\rangle_0$ since the fit of the A_{mn} has introduced some smoothing into A_2 and $g_1(r)$.

3. Lattice gas

The simplest application of the above results is to the case of the lattice gas where the N molecules have no kinetic energy and their positions are restricted to L lattice sites. Further, the intermolecular potential is

$$\begin{aligned} u(r) &= \infty, \quad r=0 \\ &= -\epsilon, \quad r \text{ is the nnd} \\ &= 0 \text{ otherwise}, \end{aligned} \tag{7.73}$$

where nnd means nearest-neighbor distance. This system is of interest because it is simple enough so that exact results may be obtained. We will obtain results for the u_1 expansion.

For the unperturbed system a lattice gas of noninteracting molecules, subject to the restriction that only one molecule can occupy a lattice site, can be used. Thus,

$$\frac{A_0}{Nk_BT} = \ln x + \frac{1-x}{x}\ln(1-x), \tag{7.74}$$

where $x=N/L$ plays the role of the density. In applying (7.18) and (7.24) we must replace cluster integrals by cluster sums. The $g_0(1\ldots h)$ are equal to unity when all the molecules occupy different sites and are zero otherwise. Hence, the use of the superposition approximation for the $g_0(1\ldots h)$ introduces no error. However, it should be noted that the $g(1\ldots h)$ of the perturbed system will not in general satisfy the superposition approximation. Thus, $h_0(12)$ is zero unless molecules 1 and 2 are on the same site; and $u_1^*(12)g_0(12)$ is zero unless molecules 1 and 2 are nearest neighbors.

Hence, if z is the number of nearest neighbors

$$A_1/Nk_BT = -\tfrac{1}{2}xz. \tag{7.75}$$

Let us write

$$A_2/Nk_BT = -\tfrac{1}{4}xI_1 - \tfrac{1}{2}x^2I_2 - \tfrac{1}{8}x^3(2I_3+4I_4+I_5), \tag{7.76}$$

where the I_n are the cluster sums in (7.45). We see that

$$I_1 = -I_2 = I_3 = -z \tag{7.77}$$

and

$$I_4 = I_5 = 0. \tag{7.78}$$

Thus,

$$A_2/Nk_BT = -\tfrac{1}{4}x(1-x^2)z. \tag{7.79}$$

The higher-order terms can also be evaluated. For example,

$$A_3/Nk_BT = -\tfrac{1}{12}x(1-x)^2(1-2x)^2z - \tfrac{1}{6}x^2(1-x)^3\xi, \tag{7.80}$$

where ξ is the total number of triangles of nearest neighbors that can be formed on the lattice divided by N. Equations (7.75) and (7.79) were obtained first by Kirkwood (1938).

We can also determine $g_1(r)$. Making use of the fact that $-u_1^*(12)g_0(12)$ is unity when molecules 1 and 2 are nearest neighbors and zero otherwise, we obtain

$$\begin{aligned} g(r) &= 0, \quad r=0 \\ &= g_0(r)[1+\beta\epsilon(1-x)^2+\cdots], \quad r \text{ is the nnd} \\ &= g_0(r), \quad \text{otherwise}. \end{aligned} \tag{7.81}$$

4. Results for square-well potential

To calculate the thermodynamics of the square-well potential, we need know only N_1, the number of intermolecular distances in the range of the attractive well of the potential which we take here to be $\sigma \leq r \leq 3\sigma/2$. Thus,

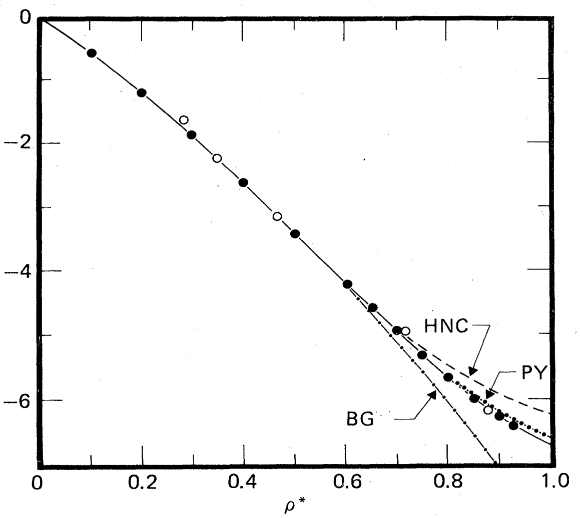

FIG. 35. A_1 for the square-well potential with $\lambda=1.5$. The solid and open points give the simulation results of Barker and Henderson (1968, 1972) and Alder *et al.* (1972), respectively, and the solid curve gives the results obtained from (7.84). The curves marked ····, ---, and —•— give the results obtained using (7.23) with the PY, HNC, and BG $g_0(r)$, respectively.

$$A_1/Nk_BT = -\langle N_1\rangle_0/N, \tag{7.82}$$

and

$$A_2/Nk_BT = -\tfrac{1}{2}[\langle N_1^2\rangle_0 - \langle N_1\rangle_0^2]/N. \tag{7.83}$$

The MC values of A_1 and A_2 of Barker and Henderson (1968, 1972) are plotted in Figs. 35 and 36, respectively. The A_1 curve is quite smooth. However, there is some scatter in the MC values of A_2 indicating, as one would expect, that it is much harder to calculate the difference $\langle N_iN_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0$ than the $\langle N_i\rangle_0$.

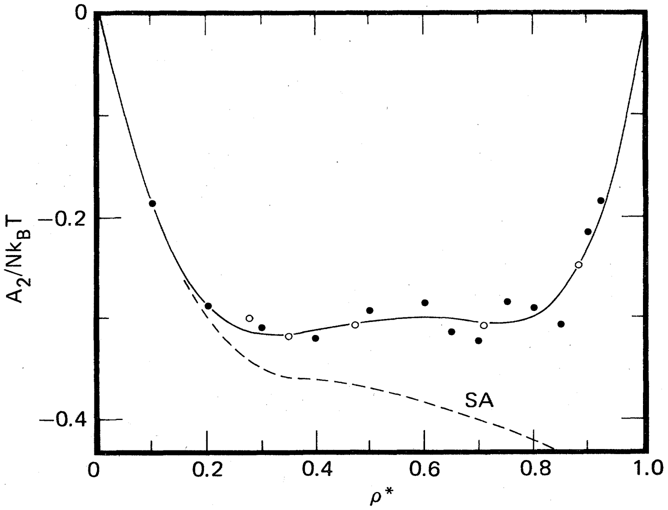

FIG. 36. A_2 for the square-well potential with $\lambda=1.5$. The solid and open points and the solid curve have the same meaning as in Fig. 35. The broken curve, marked SA, gives the results, obtained by Smith *et al.* (1970, 1971), from (7.45) using the PY $g_0(r)$.

TABLE XVI. Parameters used in the Fit of A_n for the square-well potential with $\lambda = 1.5\sigma$.

n	α_n	β_n	C_n	P_n	Q_n
1	1.5	$\sqrt{2}$	−8.460 822	−4.974 192	−2.427 216
2	2.75	$\sqrt{2}$	7.956 887	−2.487 096	9.919 624

It is interesting to note that A_1 is roughly a linear function of the density. Recall that one of the assumptions of the van der Waals and Longuet-Huggins and Widom theories was that A_1 was proportional to the density. In contrast to A_1, A_2 becomes small at high densities. Alder *et al.* (1972) have made MD calculations of A_1 and A_2 for the square-well potential and obtained identical results. They have also estimated A_3 and A_4 for this system. These quantities are even more difficult than A_2 to obtain numerically. As a result, their values are probably only qualitative. However, it is of interest to note that their calculations confirm that A_3 and A_4 rapidly go to zero at high densities.

We have fit the MC results to the function

$$A_n/Nk_BT = C_n\{1 - \exp[-\alpha_n\rho/(\beta_n - \rho)] - \alpha_n\rho/\beta_n\} + P_n\rho + Q_n\rho^2, \quad (7.84)$$

for $n = 1$ and 2. We chose $\beta_n = \sqrt{2}$ (i.e., the close-packed density) and forced the P_n to give the correct contribution of order ρ, which can be calculated from (7.23) and (7.24). The remaining coefficients were chosen by the least squares criterion. The resulting values of the parameters are given in Table XVI. The values of A_1 and A_2 which result from (7.84) are plotted in Figs. 35 and 36.

The thermodynamic functions can now be calculated from the series

$$A = A_0 + \beta\epsilon A_1 + (\beta\epsilon)^2 A_2, \quad (7.85)$$

where A_0 is given by the CS expression, Eq. (5.24). The equation of state of the sqaure-well fluid, calculated from (7.85), is plotted in Fig. 37. The agreement with the machine simulations (Alder *et al.*, 1972) is good even if the series is truncated after A_1 and is excellent if A_2 is included.

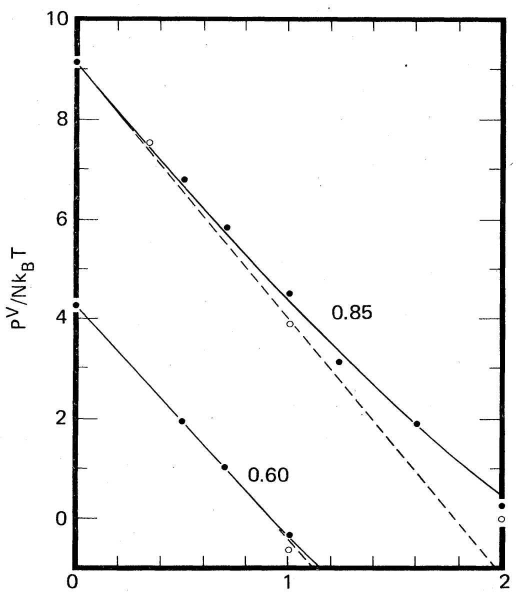

FIG. 37. Equation of state of the square-well fluid, with $\lambda = 1.5$, at $\rho\sigma^3 = 0.6$ and 0.85. The points denoted by ○ and ● give the simulation results of Rotenberg (1965) and Alder *et al.* (1972), respectively. The broken and solid curves give the results of first- and second-order perturbation theory, respectively.

In as much as A_2 makes a significant contribution to the thermodynamics, one might argue that the good agreement in Fig. 37 is fortuitous and that if the perturbation expansion were truncated after A_3 or some higher-order term less satisfactory agreement would be obtained. However, truncation after A_2 is not as arbitrary as one might think at first. As Barker and Henderson (1967a) have pointed out, if $p_0(N_1, \ldots)$ were a multivariate *normal* distribution, the series would terminate exactly with A_2. The distribution cannot be exactly normal, if only because the N_i must be positive. However, at high densities the values of N_i near zero are unimportant and the distribution may be approximately normal. As we have mentioned the estimates of A_3 and A_4 of Alder *et al.* (1972) indicate that these terms are near zero at high densities, confirming that $p_0(N_1, \ldots)$ is approximately normal at high densities.

The internal energy, U_i, and the internal heat capacity, C_i, are more sensitive than the free energy to the higher-order terms as may be seen from

$$\frac{U_i}{N\epsilon} = \sum_{n=1}^{\infty} n(\beta\epsilon)^{n-1} \frac{A_n}{Nk_BT} \quad (7.86)$$

and

$$\frac{C_i}{Nk_B} = -\sum_{n=2}^{\infty} n(n-1)(\beta\epsilon)^n \frac{A_n}{Nk_BT}. \quad (7.87)$$

These functions, calculated from (7.86) and (7.87) with the series terminated at A_2, are plotted in Figs. 38 and

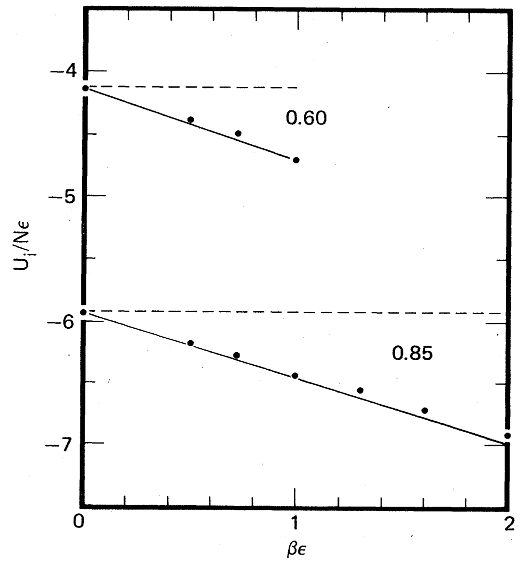

FIG. 38. Internal energy of the square-well fluid, with $\lambda = 1.5$, at $\rho\sigma^3 = 0.6$ and 0.85. The points and curves have the same meaning as in Fig. 37.

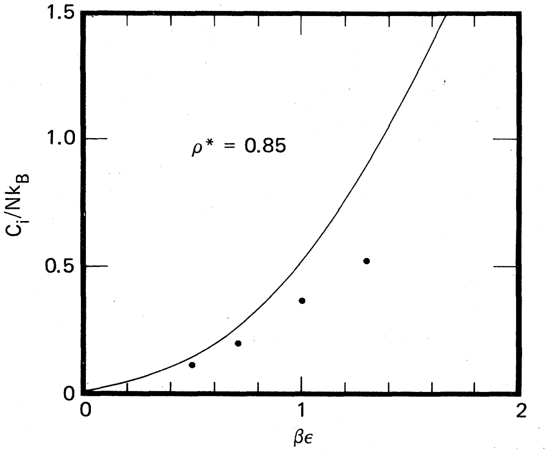

FIG. 39. Internal heat capacity of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.85$. The points and curves have the same meaning as in Fig. 38.

39. The agreement of the second-order perturbation theory values of U_i with the simulation results (Alder *et al.*, 1972) is quite good. On the other hand, except at low temperatures, the second-order perturbation theory results for C_i are significantly different from the simulation results (Alder *et al.*, 1972). This is not too worrisome because the simulation results for C_i are probably less accurate than the results for U_i. The simulation results for U_i and C_i both indicate that A_3 or possible some of the higher-order A_n are positive at high densities.

Smith *et al.* (1971) have calculated $g_1(r)$ for the square-well potential using (7.63) and have given an extensive tabulation. With the exception of $g_1(\sigma)$ at high densities, the results in this tabulation are very accurate. The fact that the values of the Smith *et al.* (1971) $g_1(\sigma)$ are slightly in error at high densities can be seen from Fig. 40 where the tabulated values of $g_1(\sigma)$ are compared with those calculated from

$$g_1(\sigma)=(p_1V/NkT)/4\eta+\lambda^3 g_0(\lambda\sigma), \qquad (7.88)$$

where p_1 is calculated from (7.84), $\eta=\pi\rho\sigma^3/6$ and $\lambda=3/2$ for the usual choice of the width of the attractive well. The values of $g_1(\sigma)$ which are obtained from (7.88) are the more accurate because they are obtained entirely from the $\langle N_i\rangle_0$ whereas the tabulated values are obtained by extrapolation of results obtained from $\langle N_iN_j\rangle_0-\langle N_i\rangle_0\langle N_j\rangle_0$. These more accurate values have been tabulated by Henderson, Barker, and Smith (1976). Values of $g_1(\sigma)$, calculated from (7.72), are generally closer to those obtained from (7.88) than to the tabulated values. This is because some smoothing of the MC data for $\langle N_i N_j\rangle_0$ has occurred in the fit of the A_{mn}. Just as $g_1(\sigma)$ can be obtained from (7.88) we can obtain an estimate of $g_2(\sigma)$ from

$$g_2(\sigma)=\left(\frac{p_2V}{Nk_BT}\right)\Big/4\eta+\lambda^3\left[g_1(\lambda\sigma^+)+\frac{1}{2}g_0(\lambda\sigma)\right]. \qquad (7.89)$$

The values of $g_2(\sigma)$ which result from (7.89) are plotted in Fig. 40. They are considerably smaller than the corresponding values of $g_1(\sigma)$ indicative of the rapid convergence of the expansion of the RDF.

Values of $g_0(r)$ and $g_1(r)$ are plotted in Fig. 41 for $\rho\sigma^3=0.7$. The results of (7.72) and the tabulated results are in agreement for values of r other than σ. It is seen that $g_1(r)$ is smaller than $g_0(r)$. Again this is indicative of the satisfactory convergence of the series for $g(r)$. The renormalized potential $\psi^*(r)=-g_1(r)/g_0(r)$ is plotted in Fig. 42 for $\rho^*=0$ and $\rho^*=0.8$. It is seen that $\psi(r)$ is damped at high densities, as expected.

The first-order perturbation theory results for $g(r)$ are plotted in Fig. 43. For $\beta\epsilon=0$ the agreement with the simulation results (Barker and Henderson, 1971a, 1972) is exact because an exact $g_0(r)$ is used. The agreement with the simulation results (Henderson, Madden, and

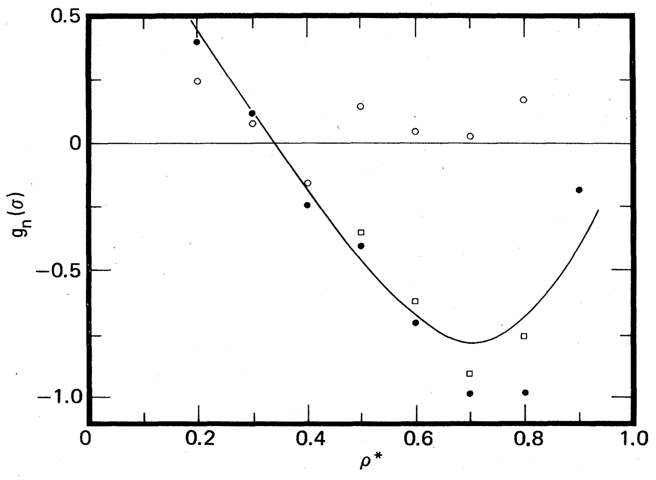

FIG. 40. Values of $g_n(\sigma)$ for the square-well potential with $\lambda=1.5$. The points denoted by ● and □ give the tabulated results for $g_1(\sigma)$ of Smith *et al*. (1971) and the results obtained from (7.72), respectively, and the curve gives the value of $g_1(\sigma)$ calculated from (7.88). The points denoted by ○ give the values for $g_2(\sigma)$ calculated from (7.89).

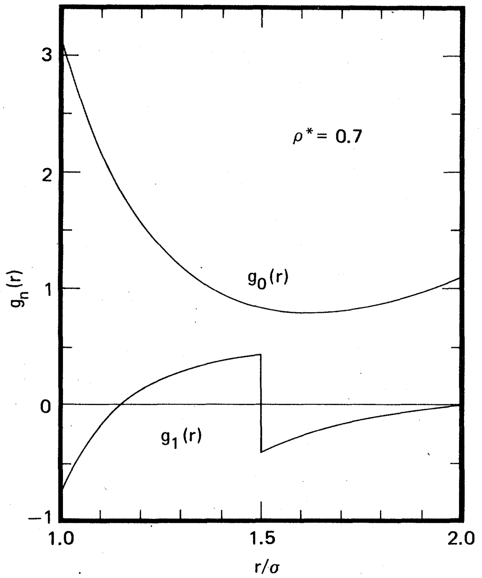

FIG. 41. Values of $g_n(r)$ for the square-well potential with $\lambda=1.5$. The values of $g_0(r)$ are the tabulated value of Barker and Henderson (1971a, 1972) and the values of $g_1(r)$ are the tabulated values of Smith *et al*. (1971) except at $r=\sigma$ where $g_1(\sigma)$ calculated from (7.88) is used.

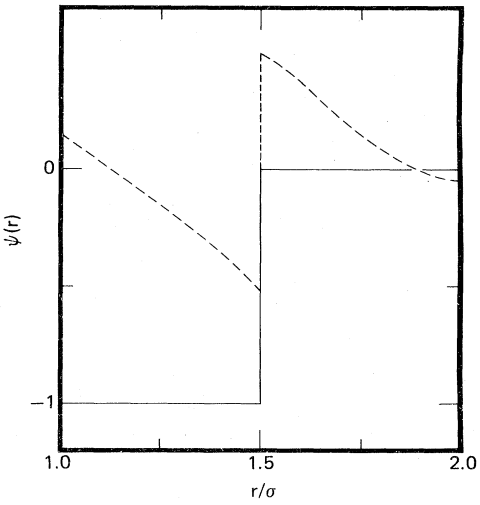

FIG. 42. Values of the renormalized potential $\psi^*(r)=g_1(r)/g_0(r)$ for the square-well potential with $\lambda=1.5$. The solid curve gives $u_1^*(r)$ which is equal to $\psi^*(r)$ at $\rho\sigma^{*3}=0$ and the broken curve gives the values for $\rho\sigma^3=0.8$.

Fitts, 1976) is very good.

In addition, the tabulation of Smith *et al.* (1971) or Eq. (7.72) can be used to obtain a first-order perturbation expansion for $y(r)$. At high densities this leads to values of $y(r)$ which are negative for some r. Thus, this y expansion is not promising. Another possibility is to use a $\ln g(r)$ or, equivalently, a $\ln y(r)$ expansion. To first-order this leads to

$$g(r)=g_0(r)\exp[\beta\epsilon g_1(r)/g_0(r)]. \tag{7.90}$$

It is to be noted that the renormalized potential appears in the exponential. At high densities, Eq. (7.90) leads to results which are slightly worse than those obtained from first-order perturbation theory for $g(r)$. As may be seen from Fig. 43, the value of $g(r)$ at $r=\sigma$, obtained from (7.90), is increased which is good. However, the value of $g(r)$ at $r\lesssim 3\sigma/2$ is increased by too large an amount. Although from this point of view Eq. (7.90) is disappointing, it does have the virtue of being exact in the limit of low densities.

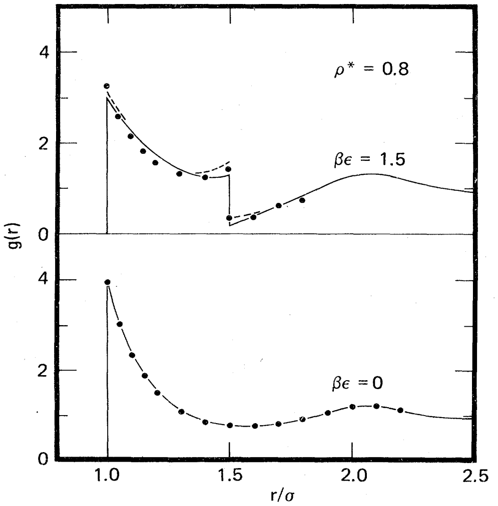

FIG. 43. RDF of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.8$. The points give the MC values of Barker and Henderson (1971a, 1972) and Henderson, Madden, and Fitts (1976) for the square-well fluid at $\beta\epsilon=0$ (hard spheres) and $\beta\epsilon=1.5$, respectively. The solid and broken curves give the results of first-order perturbation theory for $g(r)$ and $\ln g(r)$, respectively.

C. Approximate calculation of second- and higher-order terms

We have seen that it is possible to obtain machine simulation values of the terms through second-order in the perturbation expansion of the free energy and through first-order in the perturbation expansion of the RDF. Although these terms are sufficient to give good agreement with experiment at high densities, it is desirable to approximate the higher-order terms if for no other reason than to obtain completely satisfactory results at low densities. In this section we will outline some of the methods which have been proposed. Where appropriate we will test these schemes by examining their predictions for A_1, A_2, $g_0(r)$, and $g_1(r)$ for the square-well potential.

One such scheme has been discussed already. It is the use of the superposition approximation (SA) to obtain (7.45) and (7.46). Smith *et al.* (1970, 1971) have calculated A_2 and $g_1(r)$ from (7.45) and (7.46) using the square-well potential and obtained only fair agreement with the MC results as may be seen in Fig. 36. Thus, the method is not very promising. In addition, it is difficult to use the method to obtain the higher-order perturbation terms. Smith (1973) has used this method to obtain A_3 at low densities for the square-well potential. Beyond that nothing has been done. Thus, we will not consider this method further.

In this section we will consider several approximate methods for calculating higher-order perturbation terms. Some of these methods are of specialized interest. Readers not interested in these methods should pass directly to Sec. VII.D.

1. Compressibility and related approximations

We have seen that the higher-order perturbation terms are related to the cumulants of $p_0(N_1,\ldots)$. The N_i can be regarded as representing the number of molecules in spherical shells surrounding other central molecules. If these shells were large macroscopic volumes, the numbers of molecules in *different* shells would be uncorrelated:

$$\langle N_i N_j\rangle-\langle N_i\rangle\langle N_j\rangle=0,\quad i\neq j, \tag{7.91}$$

and the fluctuation of the number in a given shell would be given by

$$\langle N_i^2\rangle-\langle N_i\rangle^2=\langle N_i\rangle k_BT(\partial\rho/\partial p). \tag{7.92}$$

If these expressions can be applied to the microscopic N_i, then following Barker and Henderson (1967a)

$$\frac{A_2}{Nk_BT}=-\frac{1}{4}\rho k_BT\left(\frac{\partial p}{\partial\rho}\right)_0\int[u_1^*(r)]^2g_0(r)d\vec{r}, \tag{7.93}$$

where $(\partial p/\partial\rho)_0$ is the derivative of p with respect to ρ of reference fluid. Equation (7.93) is called the *macroscopic compressibility* (mc) *approximation*. Since

$k_BT(\partial\rho/\partial p)_0$ approaches unity at low densities and zero at high densities, the above expression is exact a low densities and has the desirable property of being small at high densities. Inasmuch as the second-order term represents the effect of the attractive potential in compressing the molecules into energetically favorable regions, it seems reasonable that this effect should be proportional to the compressibility.

The mc approximation can be used to approximate $g_1(r)$. Substituting (7.91) and (7.92) into (7.63) gives

$$g_1(r)=-k_BT(\partial\rho/\partial p)_0u_1^*(r)g_0(r). \tag{7.94}$$

Equation (7.94) is not very promising since it predicts, incorrectly, that $g_1(r)=0$ outside the range of $u_1(r)$. The mc approximation can be used to obtain the higher-order A_n. For macroscopic volumes, Münster (1969) shows that

$$\langle(N_i-\langle N_i\rangle)^{n+1}\rangle=k_BT\frac{\partial}{\partial\mu}\langle(N_i-\langle N_i\rangle)^n\rangle +n\langle(N_i-\langle N_i\rangle)^{n-1}\rangle k_BT\frac{\partial\langle N_i\rangle}{\partial\mu}, \tag{7.95}$$

where μ is the chemical potential. Thus,

$$\frac{A_3}{Nk_BT}=\frac{1}{12}\rho(k_BT)^2\left(\frac{\partial\rho}{\partial p}\right)_0\left[\frac{\partial}{\partial\rho}\left(\rho\frac{\partial\rho}{\partial p}\right)_0\right]\int[u_1^*(r)]^3g_0(r)d\vec{r}. \tag{7.96}$$

Similar expressions can be obtained for the higher-order terms.

Despite its intuitive appeal, the mc approximation has not been overly successful. For the lattice gas, $k_BT(\partial\rho/\partial p)_0=1-x$ so that the mc approximation does not yield (7.79). More seriously, as may be seen in Fig. 44, A_2 calculated from (7.93) using the square-well potential $\lambda=1.5$ is too small at intermediate and high densities. This is true for the 6–12 potential also. The third-order term, given by (7.96) is smaller, for the square-well potential, than the machine simulation estimates.

Barker and Henderson (1967a) have suggested that, since the shells containing the N_i are microscopic volumes, the relevant quantity is the *local* compressibility, $\partial[\rho g(r)]/\partial p$. Thus, one might expect better results by replacing $(\partial\rho/\partial p)_0g_0(r)$ in (7.93) by $(\partial[\rho g_0(r)]/\partial p)_0$. This gives the *local compressibility* (lc) *approximation*:

$$\frac{A_2}{Nk_BT}=-\frac{1}{4}\rho\int[u_1^*(r)]^2k_BT\left(\frac{\partial[\rho g_0(r)]}{\partial p}\right)_0d\vec{r}. \tag{7.97}$$

For the lattice gas, (7.97) is identical to (7.93). As is seen from Fig. 44, (7.94) is only slightly better for the square-well potential with $\lambda=1.5\sigma$ than (7.93). For the 6–12 potential, (7.94) underestimates A_2 at high densities also.

Praestgaard and Toxvaerd (1970) have obtained expressions for the higher-order A_n in the lc approximation and summed the A_n to obtain the free energy in closed form. They found that this approximation did not contribute significantly to the free energy except at low densities.

The semimacroscopic arguments upon which (7.93) and (7.97) are based are similar to those used in the derivation of the vdW and LHW equations of state and, hence, should be best for long range potentials. That this is the case can be seen from the calculations of Smith *et al.* (1975) for the triangle-well potential. For the case of the parameters used in their study, this potential is long ranged. The A_2 for this potential, calculated from (7.54), is very similar to that given by (7.93) and (7.97).

One possible generalization of (7.93) and (7.96) would be to use these expressions with $k_BT(\partial\rho/\partial p)_0$ replaced by

$$\alpha=-\frac{4A_2/Nk_BT}{\rho\int[u_1^*(r)^2g_0(r)d\vec{r}}. \tag{7.98}$$

This would give A_2 exactly. For the particular case of the square-well potential $\alpha=2A_2/A_1$.

Another possible generalization is to use the result (Fisher, 1964; Henderson and Davison, 1967), valid for microscopic volumes,

$$\langle N_iN_j\rangle-\langle N_i\rangle\langle N_j\rangle=\langle N_i\rangle\delta_{ij}+\rho^2\int h(r_{ij})d\vec{r}_id\vec{r}_j. \tag{7.99}$$

If the volumes are small enough that $h(r_{ij})$ is constant, then

$$\langle N_iN_j\rangle-\langle N_i\rangle\langle N_j\rangle=\langle N_i\rangle\delta_{ij}+\rho^2h(r_{ij})\Delta\vec{r}_i\Delta\vec{r}_j. \tag{7.100}$$

In our case (7.100) is an approximation because in (7.54) and (7.63) the N_i are numbers of pairs of molecules with one molecule at r_i and the other at the origin whereas in (7.100) the N_i and N_j are the number of molecules in Δr_i and Δr_j with no account taken of the third molecule at the origin.

We can attempt to correct for this assumption by multiplying the second term by the probabilities of there being pairs of molecules (with one molecule at the origin) at r_i and r_j. Thus,

$$\langle N_iN_j\rangle-\langle N_i\rangle\langle N_j\rangle=\langle N_i\rangle\delta_{ij}+\rho^2g(r_i)g(r_j)h(r_{ij})\Delta\vec{r}_i\Delta\vec{r}_j. \tag{7.101}$$

If we use (7.101), we obtain the first two terms in the SA approximations, (7.45) and (7.46). Such an approxima-

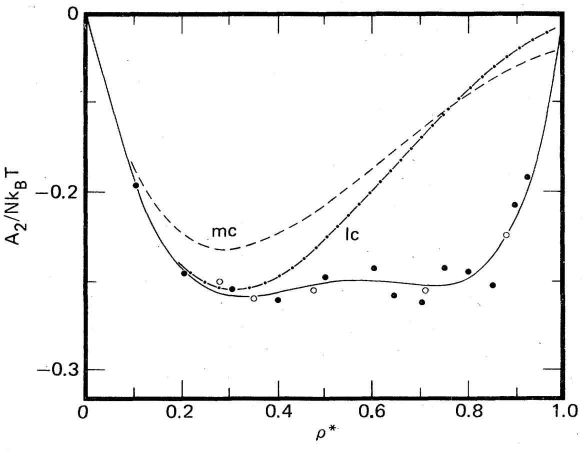

FIG. 44. A_2 for the square-well potential with $\lambda=1.5$. The solid and open points and the solid curve have the same meaning as in Fig. 35. The curves given by ---- and —•— give, respectively, the mc and lc results.

tion to A_2 will be less successful than the SA because of the cancellation will be lost. However, it is interesting to see how generalizations of (7.92) and (7.93) relate to earlier approximations.

Stell (1970) has suggested an approximation similar to the mc approximation. He observes that asymptotically

$$h(r) \sim -[k_B T(\partial \rho/\partial p)]^2 \beta u(r), \tag{7.102}$$

for large r. If the (long-range) perturbation is weak, we can replace $\partial\rho/\partial p$ by $(\partial\rho/\partial p)_0$. Thus, an approximation for $g(r)$, suggested by (7.102), is

$$\begin{aligned} g(r) &= 0, \quad r < \sigma \\ &= g_0(r) - \beta\psi(r), \quad r > \sigma, \end{aligned} \tag{7.103}$$

where

$$\psi(r) = [k_B T(\partial\rho/\partial p)]_0^2 u_1(r). \tag{7.104}$$

The function $\psi(r)$ can be regarded as a *renormalized potential* which is equal to $u_1(r)$ at low densities but is damped at high densities. It plays the same role as the renormalized potential, $-g_1(r)/g_0(r)$, or the ORPA renormalized potential but is easier to compute. In addition to (7.103) the EXP and LEXP versions of Stell's approximation can be found in a manner similar to (6.88) and (6.90). It is to be noted that all of these versions share the deficiency of predicting that $g(r) = g_0(r)$ outside the range of potential.

As we have mentioned $k_B T(\partial\rho/\partial p)_0 = 1 - x$ for the lattice gas. Thus, (7.103) and (7.104) will give the exact A_2 for the lattice gas. However, for other systems, the A_2 which results from (7.103) and (7.104) will be damped even faster than was the case for the mc approximation and so will be even further from the simulation values for A_2 than was the mc approximation.

Stell has extended (7.103) and (7.104) by forming the chain sum

$$\begin{aligned} \rho^2 \mathcal{C}(r_{12}) &= \alpha^2 \Phi(r_{12}) + \alpha^3 \int \Phi(r_{13})\Phi(r_{23}) d\vec{r}_3 \\ &\quad + \alpha^4 \int \Phi(r_{13})\Phi(r_{24})\Phi(r_{34}) d\vec{r}_3\, d\vec{r}_4 + \cdots, \end{aligned} \tag{7.105}$$

where $\alpha = \rho k_B T(\partial\rho/\partial p)_0$ and $\Phi(r) = -\beta u_1(r)$. The chain sum given above is just the sum of repeated convolutions of $\Phi(r)$ with α as a vertex function. Taking the Fourier transform of (7.105), summing, and inverting yields

$$\mathcal{C}(r) = \left(k_B T \frac{\partial\rho}{\partial p}\right)_0^2 \frac{1}{(2\pi)^3} \int e^{i\vec{k}\cdot\vec{r}} \frac{\hat{\Phi}(k)}{1 - \alpha\hat{\Phi}(k)} d\vec{k}, \tag{7.106}$$

where $\hat{\Phi}(k)$ is the Fourier transform of $\Phi(r)$. If $\alpha\hat{\Phi}(k)$ is neglected in the denominator of (7.106),

$$\mathcal{C}(r) = -\left(k_B T \frac{\partial\rho}{\partial p}\right)_0^2 \beta u_1(r). \tag{7.107}$$

Thus, we could use (7.103) or the EXP or LEXP versions of (7.103) but with $\psi(r)$ defined by

$$\psi(r) = -k_B T \mathcal{C}(r), \tag{7.108}$$

with $\mathcal{C}(r)$ defined by (7.106) for $r > \sigma$ and $\mathcal{C}(r) = 0$ for $r < \sigma$, instead of (7.104).

Equation (7.108) has not been tested. However, $\psi(r)$ defined by (7.108) will be damped less rapidly than $\psi(r)$ defined by (7.104).

2. Approximations based on the lattice gas

We have seen that for the lattice gas

$$A_1/Nk_B T = -\tfrac{1}{2} z x \tag{7.109}$$

and

$$A_2/Nk_B T = -\tfrac{1}{4} x(1-x)^2 z. \tag{7.110}$$

Expressions for the higher-order A_n can be obtained. One could use these expressions to obtain approximations for the higher-order A_n by replacing xz in A_n by

$$\rho \int \{u_1^*(r)\}^n g_0(r) d\vec{r}$$

and choosing x to equal ρ or better to give A_2 exactly. This procedure is not very satisfactory for the square-well potential. More seriously when applied to $g(r)$, this type of approximation gives no contribution to $g(r)$ outside the range of $u_1(r)$.

3. Padé approximants

We could use a Padé approximant for the free energy. Since A_1 and A_2 are known, we could write

$$\frac{(A - A_0)}{Nk_B T} = \beta\epsilon \frac{A_1/Nk_B T}{1 - \beta\epsilon(A_2/A_1)}. \tag{7.111}$$

This approximation gives

$$A_n = A_1 \left(\frac{A_2}{A_1}\right)^{n-1}. \tag{7.112}$$

Since A_2 is considerably smaller than A_1 at high densities, Eq. (7.112) predicts that the higher-order A_n are small at high densities. This is certainly attractive. On the negative side, (7.112) is incorrect at low densities. Furthermore since A_1 and A_2 are negative, all the A_n given by (7.112) will be negative. We have commented that, for the square-well potential at least, A_3 is probably positive at high densities.

We have tested (7.111) for the square-well potential with $\lambda = 1.5$. For this potential

$$A_n = \frac{1}{n!} A_1 + \cdots \tag{7.113}$$

at low densities, whereas (7.112) gives, at low densities

$$A_n = \frac{1}{2^{n-1}} A_1 + \cdots. \tag{7.114}$$

Thus, (7.111) overestimates the magnitude of the higher-order A_n at low densities. Our calculations indicate that (7.111) gives estimates of the higher-order A_n which are too negative at high densities also.

A Padé approximant based on the expansion of $g(r)$ could be formed. However, this also would be in error at low densities and there is no reason to believe that it would be useful at high densities.

4. Approximations for the distribution $p_0(N_1, \ldots)$

We have seen that if we known $p_0(N_1, \ldots)$ we can calculate the $\langle N_i \rangle_0$, $\langle N_i N_j \rangle_0$, etc., and from these, the thermodynamic functions and the RDF. Furthermore, we have seen that the use of second-order perturbation theory can be interpreted as the assumption that $p_0(N_1, \ldots)$ is a multivariate normal distribution. The distribution cannot be normal if only because the N_i are positive. A possible improvement would be to assume the distribution to be a multivariate log normal distribution for which the N_i are positive.

For simplicity in testing the usefulness of the log normal distribution, let us restrict ourselves to the square-well potential where, to obtain the thermodynamic properties, we need only consider one set of intermolecular distances, N_1. For the square-well potential, we have

$$p_0(N_1) = C \exp\{-N(\ln N_1 - \ln N_m)^2/\alpha^2\}, \tag{7.115}$$

where C is determined by normalization and N_m and α are determined from A_1 and A_2. Using (7.115) it is easy to show that

$$\langle N_1^{k-1}\rangle = N_m^{k-1} \exp\{\alpha^2(k^2-1)/4N\}. \tag{7.116}$$

This leads to

$$A_3 = 2A_1(A_2/A_1)^2. \tag{7.117}$$

Thus, the log normal distribution shares the defects of the Padé approximant (7.112) and is numerically much worse.

At low densities

$$p_0(N_1) = \exp(-x) \sum_{n=0}^{\infty} \frac{x^n}{n!} \delta(N_1 - n). \tag{7.118}$$

Instead of (7.118) let us try

$$p_0(N_1) = \exp(-x^\alpha) \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(n/\alpha+1)} \delta(N_1 - n), \tag{7.119}$$

where x and α are to be determined from A_1 and A_2. If $\alpha \to 1$ at low densities, (119) will give correct results in this limit. From (7.50) we have, for the square-well potential,

$$Z_N = Z_0 \sum_{N_1} p_0(N_1) \exp(\beta\epsilon N_1). \tag{7.120}$$

Replacing the sum by an integral and substituting (7.119) into (7.120) gives

$$Z_N = Z_0 \exp(-x^\alpha) \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(n/\alpha+1)} \exp(n\beta\epsilon). \tag{7.121}$$

In the thermodynamic limit, the distribution will be very strongly peaked at its maximum. Hence, replace the sum by its largest term. Thus, employing Stirling's approximation,

$$\ln Z_N = \ln Z_0 - x^\alpha + n \ln x - (n/\alpha)\ln(n/\alpha) + n/\alpha + n\beta\epsilon. \tag{7.122}$$

Differentiating to determine the value of n corresponding to the largest term in (7.122) gives

$$n = \alpha x^\alpha \exp(\alpha\beta\epsilon). \tag{7.123}$$

Hence,

$$\ln Z_N = \ln Z_0 + x^\alpha[\exp(\alpha\beta\epsilon) - 1]. \tag{7.124}$$

If x and α are chosen so as to given the correct value of A_1 and A_2

$$\frac{A}{NkT} = \frac{A_0}{NkT} - \left(\frac{A_1}{NkT}\right) \frac{\exp(\alpha\beta\epsilon) - 1}{\alpha}, \tag{7.125}$$

where

$$\alpha = 2A_2/A_1. \tag{7.126}$$

We note that $\alpha = 1$ at low densities so that, in this limit, (7.119) reduces to (7.118). From (7.125) we have

$$A_n = \frac{1}{n!} A_1(2A_2/A_1)^{n-1}. \tag{7.127}$$

Thus, this approximation gives A_n which are similar to those given by the Padé approximant and the log normal distribution but which are correct in the limit of low densities. On the other hand, the A_n, given by Eq. (7.127), are negative for all densities whereas for the square-well potential, at least, A_3 is probably positive at high densities. Thus, (7.125) is an improvement over second-order perturbation theory. However, at high densities (7.125) gives results which, although still very good, are very slightly inferior to those given by second-order perturbation theory.

In order to calculate $g(r)$ for the SW potential or to apply the technique to more general potentials, (7.118) must be generalized to multivariate distribution. The simplest generalization is

$$p_0(N_1, \ldots) = \prod_i \exp(-x_i^{\alpha_i}) \sum_{n_i=0}^{\infty} \frac{x_i^{n_i}}{\Gamma(n_i/\alpha_i+1)} \delta(N_i - n_i). \tag{7.128}$$

Equation (7.128) is not the most satisfactory generalization of (7.119). A more satisfactory generalization, involving some matrix of parameters, could make use of all the information contained in $\langle N_i N_j\rangle_0$. However, (7.128) is sufficient to indicate the possibilities. Using (7.128), we get in place of (7.124)

$$\ln Z_N = \ln Z_0 + \sum_i x_i^{\alpha_i}[\exp\{-\alpha_i\beta u_1(r_i)\} - 1]. \tag{7.129}$$

If we require that the first-order perturbation term in the free energy be given correctly, (7.129) leads to

$$\frac{A}{NkT} = \frac{A_0}{NkT} - \frac{1}{2}\rho \int g_0(r)\left[\frac{\exp\{-\alpha(r)\beta u_i(r)\} - 1}{\alpha(r)}\right] d\vec{r}. \tag{7.130}$$

The simplest assumption would be that α is independent of r. Requiring that A_2 be given correctly gives

$$\alpha = -\frac{4A_2/NkT}{\rho \int [u_1^*(r)]^2 g_0(r)\, d\vec{r}}. \tag{7.131}$$

Hence, the A_n are given by

$$A_n/NkT = \frac{1}{2n!}\rho(-\alpha)^{n-1} \int [u_1^*(r)]^n g_0(r)\, d\vec{r}. \tag{7.132}$$

Thus, the higher-order A_n are exact at low densities and are small and negative at high densities. Equation (7.130) has not been tested.

A second possibility is

$$\alpha(r) = -\frac{g_1(r)}{u_1(r) g_0(r)}. \tag{7.133}$$

It is easy to see that this is equivalent to

$$g(r) = g_0(r)\exp[\beta\epsilon g_1(r)/g_0(r)]. \tag{7.134}$$

That is, (7.133) is equivalent to the use of a truncated $\ln g(r)$ expansion. Equation (7.134) is exact in the limit of low densities. Expansion of (7.134) gives

$$g_n(r) = (1/n!)g_0(r)[g_1(r)/g_0(r)]^n, \tag{7.135}$$

and

$$\frac{A_n}{Nk_BT} = \frac{1}{2n!}\rho\int u_1^*(r)g_0(r)\left[\frac{g_1(r)}{g_0(r)}\right]^{n-1} d\vec{r}. \tag{7.136}$$

Equation (7.134) has been tested only for the square-well potential with $\lambda = 1.5$. We have already seen in Fig. 43 that at high densities, (7.134) is very slightly inferior, for this potential, to the first-order expansion of $g(r)$.

5. Approximations based on integral equations for $g(r)$

In Sec. VI we discussed integral equations for $g(r)$. We can use the theories developed there to calculate the $g_n(r)$ for a given potential. If we used all of the $g_n(r)$ given by that theory, the perturbation series so obtained would be no different than $g(r)$ and thermodynamics generated by the theory using the methods of Sec. VI. On the other hand, we can follow the suggestion of Chen *et al.* (1969) and use these equations only to generate the higher-order $g_n(r)$ which can be used with the machine simulation values of $g_0(r)$ and $g_1(r)$. Thus,

$$g(r) = g_0(r) + \beta\epsilon g_1(r) + [g(r) - g_0(r) - \beta\epsilon g_1(r)]_{\text{approx}}, \tag{7.137}$$

where the quantities in the parenthesis have been calculated from some approximate integral equation. This approach is a generalization and justification of the procedure of replacing the integral equation approximation for $g_0(r)$ by the correct result which was introduced in an *ad hoc* manner in Sec. VI. Depending upon one's taste, this technique can be regarded as using perturbation theory to improve the integral equation methods or using the integral equations to given the higher-order perturbation terms.

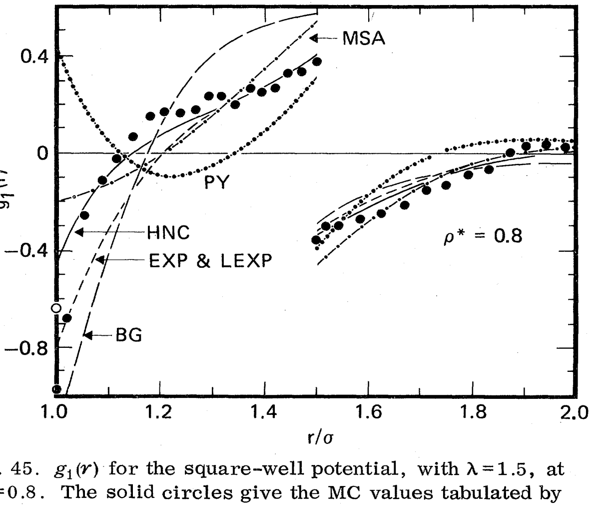

FIG. 45. $g_1(r)$ for the square-well potential, with $\lambda = 1.5$, at $\rho\sigma^3 = 0.8$. The solid circles give the MC values tabulated by Smith *et al*. (1971) and the open circle gives the value of $g_1(\sigma)$ calculated from (7.88). The curves give the results of several approximations.

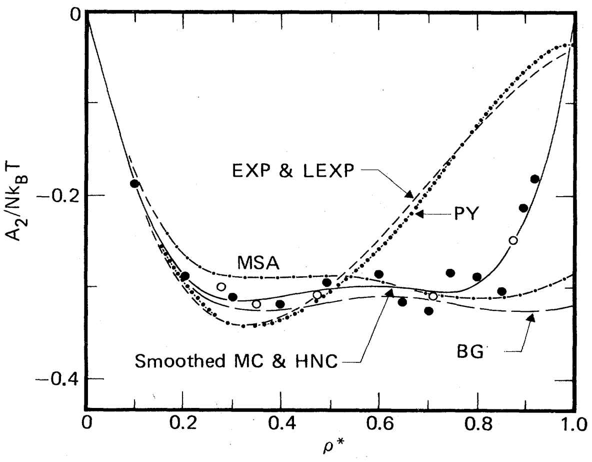

FIG. 46. A_2 for the square-well potential with $\lambda = 1.5$. The solid and open circles and the solid curve have the same meaning as in Fig. 35. The other curves give the results of several approximations. The HNC result is virtually identical with the result obtained from (7.84).

The earliest calculation of this type is that of Chen *et al.* (1969) [corrections and additional detail are given in Henderson and Chen (1975)] who calculated the PY approximation to $g_1(r)$ and A_2 for the square-well potential with $\lambda = 1.5$. The PY $g_0(r)$ can be obtained from the earlier work of Wertheim (1963, 1964), Thiele (1963), and Smith and Henderson (1970). We have already seen that the PY hard-sphere $g_0(r)$ is quite good. As may be seen in Fig. 35, the A_1 calculated from the PY hard-sphere $g_0(r)$ differs from the MC results only at the highest densities. The PY values for $g_1(r)$ and A_2 for the square-well potential, shown in Figs. 45 and 46, are much less satisfactory. At high densities, the PY A_3 is negative and, thus, not in agreement with the simulation studies which indicate that A_3 is positive at high densities. If these calculations of the PY $g_0(r)$ and $g_1(r)$ for the square-well potential are combined with calculations of Smith *et al.* (1974), the PY estimates of the higher-order terms can be obtained. The resulting RDF is plotted in Fig. 47 for a high density. The results are somewhat worse than for the truncated perturbation series but better than those of the PY theory itself. This is consistent with our earlier conclusion that, at high densities, the PY theory gives a poor estimate of $g_1(r)$ and the higher-order perturbation terms. On the other hand, the PY $g_n(r)$ are exact in the limit of low densities.

Smith *et al.* (1976) have calculated the MSA $g(r)$ and $g_1(r)$ for the square-well potential with $\lambda = 1.5$. The MSA $g_0(r)$ and A_1 are identical with the PY $g_0(r)$ and A_1. The MSA $g_1(r)$ and A_2 are shown in Figs. 45 and 46. They are a considerable improvement over the PY results. However, the MSA $g_1(r)$ is not sufficiently negative for $r \sim \sigma$. This, in turn, results in an A_2 which is too negative at high densities. The preliminary evidence is that the MSA A_3 is small and positive at high densities. The $g(r)$ resulting from (7.137) using the MSA

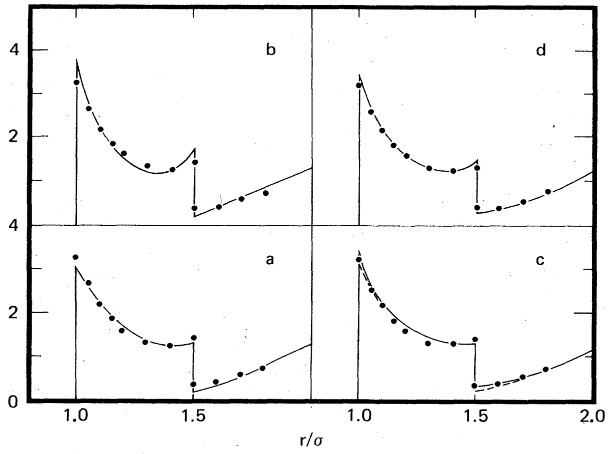

FIG. 47. RDF of the square-well fluid, with $\lambda=1.5$, at $\rho\sigma^3=0.8$. The points have the same meaning as in Fig. 43. The curve a gives the results of first-order perturbation theory while the curves b and d give the results of Eq. (7.137) using the PY and HNC theories, respectively. The broken and solid curves c give the results of Eq. (7.137) using the MSA and LEXP approximations, respectively.

values for the quantities in parenthesis is plotted in Fig. 47 for a high density and is seen to be quite good.

At low densities this procedure of using (7.137) with the MSA will not lead to exact results because in the limit of low densities

$$g_{\text{MSA}}(r)=e_0[1-\beta u_1(r)]. \tag{7.138}$$

Henderson, Madden, and Fitts (1976) have calculated the HNC $g(r)$, $g_0(r)$, and $g_1(r)$ for the square-well potential with $\lambda=1.5$. The HNC $g(r)$ and $g_0(r)$ are plotted for a high density in Fig. 32. The HNC $g_0(r)$ is much less satisfactory than the PY $g_0(r)$. On the other hand, the HNC $g_1(r)$, plotted in Fig. 45 for a high density, is very good. It is better than that given by any of the other integral equations. The HNC A_1 and A_2 are plotted in Figs. 35 and 46 for the square-well potential. The HNC A_1 is poorer than the PY A_1. This is to be expected in view of the errors in the HNC $g_0(r)$. On the other hand, the HNC A_2 is in excellent agreement with the MC results.

The $g(r)$, resulting from (7.138) using the HNC $g(r)$, $g_0(r)$, and $g_1(r)$ is plotted in Fig. 47 and is very good. Evidently, the HNC theory, although in error for the hard-sphere reference system, correctly accounts for the effects of the perturbation and gives good values for $g_1(r)$ and A_2 and the higher-order perturbation terms. It is of interest to note that the HNC A_3 is small and positive at high densities. The HNC $g_n(r)$ have the further virtue of being exact in the limit of low densities.

Finally, we mention that Lincoln *et al.* (1975a) have used the BG theory to obtain $g_0(r)$ through $g_3(r)$ and A_1 through A_4 for the square-well potential with $\lambda=1.5$. The BG $g_0(r)$ is rather poor. Thus, it is no surprise that the BG A_1, which is plotted in Fig. 35, is also poor. The BG $g_1(r)$ and A_2 are surprisingly good although not as good as either the MSA or HNC results. It is conceivable that the BG theory, like the HNC theory, gives good results for the higher-order $g_n(r)$. It is not possible to examine this conjecture since BG values for the complete $g(r)$ for the square-well potential with $\lambda=1.5$ are not available at present. However, it is worth noting that, at high densities, the values of A_3 calculated by Lincoln *et al.* are considerably more negative than one expects.

6. Optimized cluster theory

Andersen and Chandler (1970, 1972) and Andersen *et al.* (1972) have proposed a series of related approximations for the higher-order perturbation terms which they call the *optimized cluster theory* (OCT). These approximations have been discussed in part in Sec. VI.D.

They write the direct correlation function as

$$c(r)=c_0(r)-\beta\phi(r). \tag{7.139}$$

Outside the core, $\phi(r)=u_1(r)$. Inside the core $\phi(r)$ cannot be taken as zero. If $\phi(r)$ were zero inside the core, the $g(r)$ calculated from (7.139) by means of the Ornstein–Zernike equation would not be zero inside the core. Anderson *et al.* chose $\phi(r)$ inside the core so that $g(r)=0$ inside the core. They refer to their procedure of calculating $\phi(r)$ as *optimization.* If $c_0(r)$ is the PY hard-sphere direct correlation function, their procedure is entirely equivalent to the MSA. On the other hand, one can use a more accurate expression for $c_0(r)$, as do Andersen *et al.*, and then Eq. (7.139) specifies the ORPA. The ORPA expression for $g(r)$ is

$$g(r)=g_0(r)+\mathcal{C}(r), \tag{7.140}$$

where $g_0(r)$ is the exact hard-sphere RDF and $\mathcal{C}(r)$ is a chain sum, similar to Eq. (7.105).

This chain sum, $\mathcal{C}(r)$, is to a good approximation just the difference between the MSA $g(r)$ and $g_0(r)$. Viewed in this way the ORPA is similar in spirit to Eq. (7.137), but with only $g_0(r)$ required to be exact. the ORPA $g_1(r)$ will be nearly identical to that given by the MSA and so will not be negative enough at high densities for $r\sim\sigma$. The ORPA renormalized potential is a weak function of the temperature and is rather similar to the renormalized potential plotted in Fig. 42. Some ORPA results for $g(r)$ for the square-well potential have been plotted in Fig. 31. At low temperatures the ORPA $g(r)$ is too large for $r\sim\sigma$. This is because the ORPA $g_1(r)$ is not sufficiently negative for $r\sim\sigma$. The $g(r)$ resulting from Eq. (7.138) using the ORPA values for $g(r)$, $g_0(r)$, and $g_1(r)$ for the SW potential will be very nearly identical to the corresponding MSA results plotted in Fig. 47. The results are good.

Somewhat better results can be obtained from the LEXP approximation

$$g(r)=g_0(r)[1+\mathcal{C}(r)]. \tag{7.141}$$

The LEXP $g_1(r)$ and A_2 are plotted in Figs. 45 and 46. The LEXP $g_1(r)$ is an improvement on the MSA and ORPA result but is too negative for $r\sim\sigma$. This results in an A_2 which is surprisingly poor. It is no better than the lc or PY results. Some LEXP values of $g(r)$ for the SW potential have been plotted in Fig. 31 and the $g(r)$ resulting from (7.138) using the LEXP values of $g(r)$, $g_0(r)$, and $g_1(r)$ for the SW potential is plotted in Fig. 47. In both cases the results are good.

The MSA, ORPA, and LEXP approximations all lead to Eq. (7.138) at low densities and hence, will not be exact at low densities. This problem can be overcome by using the EXP approximation

$$g(r)=g_0(r)\exp\{\mathcal{C}(r)\}. \tag{7.142}$$

This approximation leads to the same $g_1(r)$ and A_2 as does the LEXP approximation. For potentials such as the square-well potential, the LEXP approximation gives results for $g(r)$ which are about the same as for the LEXP approximation. However, for strong perturbations, such as the dipolar hard spheres, the EXP approximation is less satisfactory than the LEXP approximation.

Andersen *et al.* have proposed overcoming the defects in the ORPA or LEXP $g(r)$ at low densities through the use of the renormalized potential $\psi(r)=-k_BT\mathcal{C}(r)$. They propose adding

$$\Delta\left(\frac{A}{Nk_BT}\right)=\frac{1}{4}\rho\int[\beta\psi(r)]^2d\vec{r}\\ -\frac{1}{2}\rho\int[\exp\{-\beta\psi(r)\}-1+\beta\psi(r)]g_0(r)d\vec{r} \tag{7.143}$$

to the ORPA expression for the free energy. The reason for the separate treatment of the β^2 term, is because in the ORPA

$$\frac{A_2}{Nk_BT}=-\frac{1}{4}\rho\int\{u^*(r)\}^2d\vec{r}+\cdots, \tag{7.144}$$

at low densities, rather than the correct low density expression which has $g_0(r)$ in the integrand. Andersen *et al.* refer to Eq. (7.143) as the B_2 *approximation.*

In the case of the LEXP approximations, the correct expression is given for A_2 at low densities. Thus, for the LEXP approximation we should add

$$\Delta\left(\frac{A}{Nk_BT}\right)=-\frac{1}{2}\rho\int[\exp\{-\beta\psi(r)\}-1+\beta\psi(r)\\ -\tfrac{1}{2}\{\beta\psi(r)\}^2]g_0(r)d\vec{r} \tag{7.145}$$

to the expression for the free energy.

The B_2 approximation is most useful when the renormalized potential is strongly damped at high densities. For the SW potential at least, the ORPA renormalized potential does not appear to meet this requirement. Thus when used with the ORPA $\psi(r)$, Eqs. (7.144) and (7.145) may make excessively large contributions at high densities and low temperatures and should be used with care.

On the other hand, Stell's renormalized potential, Eq. (7.104), is damped out at high densities (in fact excessively so). Thus, (7.144) and (7.145) can be used with Stell's renormalized potential without any danger of difficulties at high densities.

7. Summary

We have discussed several methods which can be used to obtain higher-order terms in perturbation theory. For a potential such as the square-well potential with cut off at 1.5σ, there is little need for such corrections at high densities since the truncated perturbation expansion yields such good results. However, the convergence of the perturbation expansions for $g(r)$ and A is less rapid at low densities. Thus, these corrections are useful at low densities. In addition, they may be useful in applications of perturbation theory to other potentials where the convergence is less rapid.

The simplest approximations are the compressibility approximations. Using their predictions for A_2 as a criterion, the local compressibility approximation is the best of these types of approximations for potentials such as the square-well potential. This approximation gives an A_2 which is as good as that given by the PY theory or the OCT. The thermodynamic properties calculated using this approximation are in good agreement with experiment for systems like the square-well fluid. The approximation is very useful for simple practical calculations. The main drawback of the approximation is that it does not give a useful approximation to $g(r)$.

The Padé approximant seems to overestimate the higher-order A_n and does not yield the correct results in the low density limit. Furthermore, it does not give a useful approximation to $g(r)$. The main advantage of this method is its simplicity. As we shall see, it has proven useful in the theory of dipolar hard spheres. However, even here the evidence seems to indicate that the higher-order perturbation terms are overestimated (Patey and Valleau, 1976). It is possible that, even for this system, some of the other methods we have discussed will be more useful.

The approximations based on the distribution function $p_0(N_1,\ldots)$ which we have discussed are potentially very useful. Even the simplest approximation yields a result similar to, but more reliable than, the Padé approximant. When the method is generalized so that all the information in $\langle N_iN_j\rangle_0$ is utilized, this should be a very powerful method.

The approximations based upon integral equations are the most accurate at present. Of these the HNC equation is the most reliable. However, the MSA/OCT is quite good also.

D. Potentials with a "soft core"

We have seen that perturbation theory gives excellent results for the equation of state of the square-well fluid even at very low temperatures if the attractive potential is treated as a perturbation on a hard-sphere system. This suggests that the failure of earlier perturbation theories at low temperatures is due either to the lack of a satisfactory treatment of the "softness" of the repulsive potential, with a consequent extreme sensitivity to the choice of the hard-sphere diameter (Zwanzig, 1954; Smith and Alder, 1959; Frisch *et al.*, 1966), or to the use of the large r^{-6} term as a perturbation (McQuarrie and Katz, 1966). In this section we outline some recent theories which attempt to overcome these defects.

1. Barker–Henderson theory

The earliest successful perturbation for potentials with a "soft" core is that of Barker and Henderson (1967b) who assumed the potential to be of the form

$$u(r)=u_0(r)+u_1(r), \tag{7.146}$$

where $u_0(r)$ is the reference potential, given by

$$u_0(r) = u(r), \quad r < \sigma$$
$$= 0, \quad r > \sigma, \tag{7.147}$$

and $u_1(r)$ is the perturbation, given by

$$u_1(r) = 0, \quad r < \sigma$$
$$= u(r), \quad r > \sigma, \tag{7.148}$$

where σ is the value of r for which $u(r)$ is equal to zero. Thus,

$$A = \sum_{n=0}^{\infty} (\beta\epsilon)^n A_n, \tag{7.149}$$

where ϵ is the depth of the potential, and A_0 is the free energy of the reference system. The reference system, defined by (7.147) is not convenient for computation because its properties are not well known. However, Barker and Henderson have shown that A_0 and $g_0(r)$ may be systematically approximated by

$$A_0 = A_{\mathrm{HS}} \tag{7.150}$$

and

$$g_0(r) = g_{\mathrm{HS}}(r), \tag{7.151}$$

where A_{HS} and $g_{\mathrm{HS}}(r)$ are the free energy and RDF of a system of hard spheres of diameter d, defined by

$$d = \int_0^{\sigma} [\exp\{-\beta u(r)\} - 1] dr, \tag{7.152}$$

which accounts for the "softness" of $u_0(r)$. Note that d is a function of temperature but not density. Equation (7.150) has been tested by direct computer simulation by Levesque and Verlet (1969) and found to be very accurate.

The expansion (7.149) is an inverse temperature expansion. Thus, (7.149) will be most accurate at high temperatures. On the other hand, Eqs. (7.150) and (7.151) are most reliable when $u_0(r)/k_BT$ is steeply repulsive, i.e., at low temperatures. This is not a practical problem because, for realistic potentials, $u_0(r)/k_BT$ is steep for all temperatures of physical interest. However, if the BH theory is to be applied at exceedingly high temperatures, the corrections terms to (7.150) and (7.151) must be obtained. These can be obtained in a systematic manner using the procedure of Barker and Henderson (1967b). Smith (1973) has given the first correction term to (7.150).

Thus, the procedure of Barker and Henderson is to write

$$A = A_{\mathrm{HS}} + \beta\epsilon A_1 + (\beta\epsilon)^2 A_2, \tag{7.153}$$

where A_{HS} is calculated from the CS expression, and A_1 and A_2 are calculated from (7.53) and (7.54) or (7.70) with $g_0(r)$ given by (7.151) and d given by (7.152).

Even though (7.153) is similar to those obtained in the the earlier theories, the Barker–Henderson (BH) theory does not share the difficulties of these theories. Note that there is no contribution to A_n for $r < \sigma$ and that the diameter d has been chosen to account for the "softness" of $u_0(r)$. For potentials with a hard core, $u_0(r) = u_{\mathrm{HS}}(r)$ in Eq. (7.152) gives $d = \sigma$, as desired. Equations (7.150) to (7.152) can be regarded as the key to the BH theory.

The BH theory has been applied to the 6–12 potential (Barker and Henderson, 1967b; Henderson and Barker, 1971; Barker and Henderson, 1971b, 1972). Some of these results for the thermodynamic properties are tabulated in Tables VI to IX. We have listed values calculated from first-order perturbation theory using the PY $g_{\mathrm{HS}}(r)$, which we call BH1(PY), from first-order perturbation theory using the MC $g_{\mathrm{HS}}(r)$, which we call BH1, and from second-order perturbation theory using MC values for A_1 and A_2, which we call BH2. The agreement of the BH2 results with the simulation results is excellent. The second-order term is required to get this good agreement. The effect of the neglected higher-order terms appears to be very small.

The BH theory can be used to calculate the RDF of the 6–12 fluid (Barker and Henderson, 1971b; 1972). In Fig. 48 we show the results of a calculation of $g(r)$ for the 6–12 fluid near its triple point. The agreement with the simulation values (Verlet, 1968) is very good. It is much better than the corresponding PY result in Fig. 25. The broken curve in Fig. 48 is $g_{\mathrm{HS}}(r)$, determined by the hard-sphere packing, and the solid curve is the first-order result. It is the attractive potential which produces the rounding of the peak. The effect of the "softness" of the repulsive potential is apparent only for $r < 1.03\sigma$, where $g(r)$ has fallen to about 1.5.

At high densities there appears to be no need to go beyond second order in the thermodynamic properties of first order in $g(r)$. However, higher-order terms are required at low densities. These can be computed using the techniques developed in the preceding section.

Leonard *et al.* (1970), Henderson and Leonard (1971) and Grundke, Henderson, Barker, and Leonard (1973) have applied the BH theory to liquid mixtures and obtained excellent results for the excess thermodynamic properties. Lee *et al.* (1975) have used the BH theory for liquid mixtures to determine Ar + Kr and Kr + Xe intermolecular potentials.

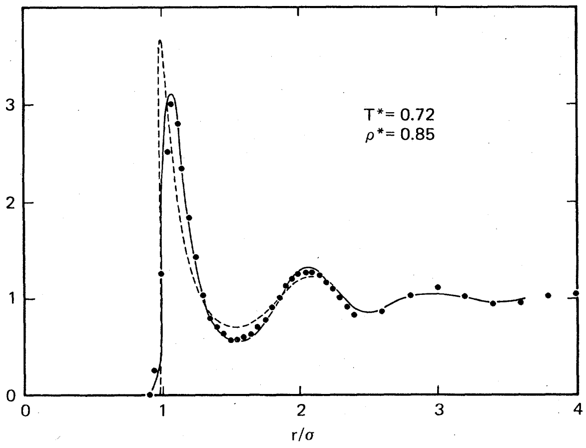

FIG. 48. RDF of the 6–12 liquid near its triple point. The points give the results of simulation studies (Verlet, 1968) and the broken and solid curves give the results for the zeroth- and first-order BH perturbation theory, respectively.

2. Variational method

Mansoori and Canfield (1969, 1970) and Rasaiah and Stell (1970a,b) have drawn attention to the fact that if

$$u(r)=u_{\mathrm{HS}}(r)+u_1(r), \tag{7.154}$$

where $u_{\mathrm{HS}}(r)$ is the hard-sphere potential, then

$$A \leq A_{\mathrm{HS}}+2\pi N\rho\int_d^{\infty} u_1(r)g_{\mathrm{HS}}(r)r^2dr. \tag{7.155}$$

This inequality is based upon the inequality $e^x \geq 1+x$. Mansoori and Canfield, and Rasaiah and Stell propose applying (7.155) to potentials such as the 6–12 potential as well as to potentials of the form of (7.154). The most appropriate choice of d is that for which the RHS of (7.155) is a minimum. This provides a criterion for d which is missing in the original Zwanzig formulation. The hard-sphere diameter so obtained is a function of both density and temperature and must be found by iteration and so is more difficult to compute than the BH choice for d.

The difficulty with this approach is that the tendency of the theory is to describe a system whose intermolecular potential is given by (7.154) rather than a system with a soft core. The "softness" of the potential for $r<d$ is much less of a problem at low temperatures than at high temperatures. This may be seen in Tables VIII and IX where the results of the variational theory, computed using the PY and Verlet-Weis (VW) $g_{\mathrm{HS}}(r)$ are listed for the 6–12 fluid. At low temperatures the variational theory results are roughly comparable with the BH1 theory but are somewhat less satisfactory at high temperatures. Replacing the PY $g_{\mathrm{HS}}(r)$ by the VW $g_{\mathrm{HS}}(r)$ tends to make the results of the variational theory slightly worse.

Mansoori and Leland (1970) and Mansoori (1972) have applied the variational method to binary mixtures and obtained very good results for the excess thermodynamic properties.

3. Weeks–Chandler–Andersen theory

Weeks, Chandler, and Andersen (WCA) (Weeks and Chandler, 1970; Weeks *et al.*, 1971a,b) and, independently, Gubbins *et al.* (1971) have proposed the choice

$$\begin{aligned} u_0(r)&=u(r)+\epsilon,\ r<r_m\\ &=0,\ r>r_m \end{aligned} \tag{7.156}$$

$$\begin{aligned} u_1(r)&=-\epsilon,\ r<r_m\\ &=u(r),\ r>r_m, \end{aligned} \tag{7.157}$$

where r_m is the value of r for which $u(r)$ is a minimum, and $u(r_m)=-\epsilon$. For the 6–12 potential, $r_m=2^{1/6}\sigma$. To first order

$$A=A_0+\frac{1}{2}N\rho\int u_1(r)g_0(r)d\vec{r}, \tag{7.158}$$

where A_0 and $g_0(r)$ are the free energy and RDF of the reference fluid. This is an excellent division of $u(r)$ into the reference and perturbation potentials because $u_1(r)$ varies slowly and the importance of fluctuations, and thus the second-order term, are reduced. Since the properties of the reference fluid are not well known, further approximations are necessary. Here WCA show that A_0 and $g_0(r)$ may be systematically approximated by

$$A_0=A_{\mathrm{HS}} \tag{7.159}$$

and

$$g_0(r)=\exp\{-\beta u_0(r)\}y_{\mathrm{HS}}(r), \tag{7.160}$$

where A_{HS} and y_{HS} are the free energy and distribution function for hard spheres of diameter d, defined by

$$\int_0^{r_m} r^2y_{\mathrm{HS}}(r)dr=\int_0^{r_m} r^2\exp\{-\beta u_0(r)\}y_{\mathrm{HS}}(r)dr. \tag{7.161}$$

WCA refer to Eqs. (7.158) to (7.161) as the *high temperature approximation* (HTA).

The hard-sphere diameter obtained from (7.161) is a function of both density and temperature and must be found by iteration and so is more difficult to compute than the BH choice for d. Barker and Henderson (1971c) and Verlet and Weis (1972a) have shown these approximations to be very good, in fact better than using the PY theory for the reference fluid (Henderson, 1971). In addition, they show that the WCA theory converges very rapidly.

Some results of the HTA of the WCA theory for a 6–12 fluid are shown in Tables VIII and IX. These results have been calculated using the PY $y_{\mathrm{HS}}(r)$ and the VW/GH $y_{\mathrm{HS}}(r)$. The numbers in parentheses were calculated using a hard-sphere system which was so dense that these results are of uncertain accuracy.

The HTA of the WCA leads to very good agreement with the machine simulation results. It is much better than the BH1 results. This is indicative of the fast convergence of the WCA theory. However, the slower convergence of the BH theory is not a serious problem because the BH2 results can be easily calculated from Eq. (7.70). In the BH theory $d\sim\sigma$ whereas in the WCA theory $d\sim r_m$. As a result, for a liquid at high densities, the WCA hard sphere, in contrast to the BH hard-sphere, reference system is at a value of ρd^3 which may be so large that the properties of the hard spheres are uncertain or possibly so large that the hard spheres have solidified. For the states considered in Tables VIII and IX, this does not appear to be a practical problem. However, it may explain the failure, noted by Lee and Levesque (1973), of the HTA of the WCA theory to give satisfactory excess thermodynamic properties of liquid mixtures.

Andersen, Chandler, and Weeks (1972), Andersen and Chandler (1972), and Sung and Chandler (1974) have used the OCT to obtain corrections to the HTA for the 6–12 fluid. Some of their calculations are listed in Tables VII, VIII, and IX. They are able to account for most of the small errors in the HTA.

The RDF has also been computed by WCA. The HTA to $g(r)$, Eq. (7.160), is plotted in Fig. 49. It is a good first approximation. As is seen in Fig. 49, if the EXP version of OCT is used to compute the corrections to the HTA, excellent results are obtained.

Chandler (1974), Andersen (1975), and Andersen *et al.* (1976) have recently reviewed the WCA theory.

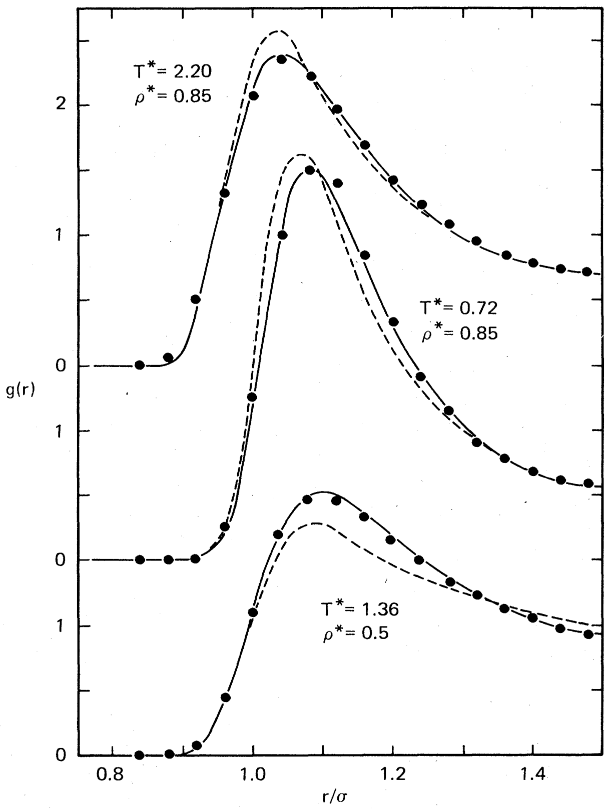

FIG. 49. RDF's of the 6–12 fluid. The points give the results of simulation studies (Verlet, 1968) and the broken and solid curves give the results of HTA of the WCA theory and the EXP approximation, respectively.

E. Perturbation theory for more complex systems

1. Quantum effects

Kim, Henderson, and Barker (1969) have successfully calculated the equation of state of neon and hydrogen and helium at high temperatures by using Eq. (4.59). They computed A_{c1} from the BH theory and used Eq. (7.151) for $g_{c1}(r)$.

There have been no perturbation theory calculations of the effect of quantum corrections on $g(r)$ for liquids.

2. Three-body interactions

Barker *et al.* (1968, 1969) have applied perturbation theory to real fluids in which three-body interactions are present. They used Eq. (4.61) and computed A_{2b} from the BH perturbation theory, using the Barker–Pompe potential for argon and the lc approximation for the second-order term. They made calculations of the last term on the RHS of (4.61), using the triple–dipole (Axilrod–Teller) three-body interaction and the perturbation approximation

$$g_{2b}(123) \simeq g_{\mathrm{HS}}(123), \tag{7.162}$$

with the hard-sphere diameter given by (7.152). They made both computer simulations of this term and direct numerical integrations using the superposition approximation. In either case they found that this term could be fit by the expression

$$\frac{d^9 A_{3b}}{N\nu} = \rho d^3 \frac{2.707\,97 + 1.689\,18\rho d^3 - 0.315\,70\rho^2 d^6}{1 - 0.590\,56\rho d^3 + 0.200\,59\rho^2 d^6}. \tag{7.163}$$

Using these techniques, Barker *et al.* obtained good agreement with the experimental results for argon. It would be desirable to repeat these calculations using the more accurate BFW potential, Eq. (7.70) for the second-order term in the BH theory, and including the dipole–dipole–quadrupole and fourth-order triple–dipole three-body potentials. Presumably, even better results would be obtained.

There have been no perturbation theory calculations of the effect of three-body forces on $g(r)$ for liquids.

3. Nonspherical potentials

We give only a brief review here. More detailed treatments can be found in the recent reviews of Gray (1975) and Egelstaff *et al.* (1975) which are devoted specifically to liquids with nonspherical potentials.

a. Spherical cores

Nonspherical molecules with spherical cores can be treated straightforwardly by perturbation theory. Thus, if

$$u(r_{12}, \Omega_1, \Omega_2) = u_0(r_{12}) + \gamma u_1(r_{12}, \Omega_1, \Omega_2), \tag{7.164}$$

our earlier expressions, Eqs. (7.23) and (7.24), apply. The only change from our earlier applications is that e_γ, $e_{\gamma\gamma}$, and u_1 are functions of the orientations of the molecules as well as their separation. Hence,

$$\frac{A_1}{Nk_BT} = \frac{1}{2}\rho \int g_0(r_{12})d\vec{r}_2 \int u_1^*(12)d\Omega_1 d\Omega_2, \tag{7.165}$$

where, for simplicity, $u_1(ij)$ has been used to denote $u(r_{ij}, \Omega_i, \Omega_j)$.

For many systems of interest

$$\int u_1(12)d\Omega_1 d\Omega_2 = 0 \tag{7.166}$$

so that $A_1 = 0$. The second-order term is given by a simple generalization of (7.24). For systems such that (7.166) is satisfied, the last term vanishes. Thus,

$$\frac{A_2}{Nk_BT} = -\frac{1}{4}\rho \int g_0(r_{12})d\vec{r}_2 \int \{u_1^*(12)\}^2 d\Omega_1 d\Omega_2 - \frac{1}{2}\rho^2 \int g_0(123)d\vec{r}_2 d\vec{r}_3 \int u_1^*(12)u_1^*(13)d\Omega_1 d\Omega_2 d\Omega_3. \tag{7.167}$$

It is sometimes helpful to expand $u_1(ij)$ in spherical harmonics. Thus,

$$u_1^*(r_{ij}, \Omega_i, \Omega_j) = \sum_{l_i l_j m} \gamma_{l_i l_j m}(r_{ij}) Y_{l_i m}(\theta_i, \varphi_i) Y_{l_j m}(\theta_j, \varphi_j), \tag{7.168}$$

where θ_i, ϕ_i, θ_j, and ϕ_j are angles specifying the orientations of molecules i and j. For systems for which (7.166) is satisfied, $\gamma_{000}(r_{ij}) = 0$. Using (7.168) becomes

$$\frac{A_2}{Nk_BT}=-\frac{1}{4}\rho\sum_{\substack{l_1l_2m\\ l_1\neq l_2}}\int\gamma^2_{l_1l_2m}(r_{12})g_0(r_{12})d\vec{r}_2$$
$$-\rho^2\sum_{l\neq 0}\int\gamma_{l00}(r_{12})\gamma_{l00}(r_{13})P_l(\cos\theta_{23})g_0(123)d\vec{r}_2d\vec{r}_3. \qquad (7.169)$$

For a large class of potentials, $\gamma_{l00}(r_{ij})=0$. These are called *multipolelike potentials*. Examples of such potentials are the dipole and quadrupole interactions. For such interactions, the second term in (7.169) vanishes and we obtain the result of Pople (1954a)

$$\frac{A_2}{Nk_BT}=-\frac{1}{4}\rho\int g_0(r_{12})d\vec{r}_2\int\{u_1^*(12)\}^2d\Omega_1d\Omega_2$$
$$=-\frac{1}{4}\rho\sum_{\substack{l_1l_2m\\ l_1\neq l_2}}\int\gamma^2_{l_1l_2m}(r_{12})g_0(r_{12})d\vec{r}_2. \qquad (7.170)$$

For the special case where $\gamma_{l00}(r_{ij})=0$,

$$\frac{A_3}{Nk_BT}=\frac{1}{12}\rho\int g_0(r_{12})d\vec{r}_2\int\{u_1^*(12)\}^3d\Omega_1d\Omega_2$$
$$+\frac{1}{6}\rho^2\int g_0(123)d\vec{r}_2d\vec{r}_3$$
$$\times\int u_1^*(12)u_1^*(13)u_1^*(23)d\Omega_1d\Omega_2d\Omega_3. \qquad (7.171)$$

Gubbins and Gray (1972) have obtained analogous expressions for the pair distribution function. Here

$$g(r_{12},\Omega_1,\Omega_2)=g_0(r_{12})+\beta\epsilon g_1(r_{12},\Omega_1,\Omega_2)+\cdots, \qquad (7.172)$$

where $g_0(r_{12})$ is the RDF of the reference fluid with pair potential $u_0(r_{12})$ and

$$\epsilon g_1(r_{12},\Omega_1,\Omega_2)=-u_1^*(r_{12},\Omega_1,\Omega_2)g_0(r_{12})$$
$$-\rho\int g_0(123)d\vec{r}_3\int\{u_1^*(13)+u_1^*(23)\}d\Omega_3. \qquad (7.173)$$

The term involving $g_0(1234)$ vanishes because of (7.166). For the special case where $\gamma_{l00}(r_{ij})=0$, the second term in (7.173) vanishes so that to first order

$$g(r_{12},\Omega_1,\Omega_2)=g_0(r_{12})[1-\beta u_1(r_{12},\Omega_1,\Omega_2)]. \qquad (7.174)$$

Equation (7.174) implies that $g_s(r_{12})=g_0(r_{12})$. Although this may be a reasonably good approximation for some systems, it is clearly a deficiency of (7.174). This problem can be removed by going to next highest order. Gubbins and Gray give an expression for $g_2(r_{12},\Omega_1,\Omega_2)$. Perram and White (1972, 1974) have shown that with an exponential expansion $g_s(r_{12})\neq g_0(r_{12})$ in first order. We discuss their approach in more detail in Sec. VII.E.3b.

Rushbrooke *et al.* (1973) have applied perturbation theory to the system of dipolar hard spheres, defined by Eqs. (4.64) and (4.65). For this system $u_0(r_{12})$ is the hard-sphere potential and

$$u_1(r_{12},\Omega_1,\Omega_2)=-(\mu^2/r_{12}^3)D(1,2). \qquad (7.175)$$

Hence,

$$A=A_0+\sum_{n=1}^{\infty}(\beta\mu^2)^nA_n, \qquad (7.176)$$

where A_0 is the hard-sphere free energy. Because of (6.69), $A_1=0$. Using (7.170)

$$\frac{A_2}{Nk_BT}=-\frac{1}{6}\rho\int r^{-6}g_0(r)d\vec{r}. \qquad (7.177)$$

In third order, only the second integral in (7.171) is nonvanishing. Using a theorem of Barker (1954) it can be shown that

$$\frac{A_3}{Nk_BT}=\frac{1}{54}\rho^2\int u_{123}g_0(123)d\vec{r}_2d\vec{r}_3, \qquad (7.178)$$

where

$$u_{123}=\frac{1+3\cos\theta_1\cos\theta_2\cos\theta_3}{(r_{12}r_{13}r_{23})^3}. \qquad (7.179)$$

Thus, the integral in (7.178) is formally identical to the integral giving the effect of the triple-dipole (Axilrod-Teller) three-body potential in the BH theory. Therefore, Rushbrooke *et al.* do not integrate Eq. (7.168) but instead use the result of Barker *et al.* (1968, 1969) given in Eq. (7.163).

Rushbrooke *et al.* find that (7.176) converges slowly for dipole moments of physical interest. As a result, they find a perturbation expansion, truncated after A_3, unsatisfactory. However, they find that the Padé approximant,

$$A=A_0+\beta^2\mu^4\frac{A_2}{1-\beta\mu^2A_3/A_2}, \qquad (7.180)$$

more promising since the contribution of the dipoles is, in the limit of $\mu\to\infty$, finite and proportional to μ^2 with a coefficient which is close to the known exact result for dipoles on a lattice.

Patey and Valleau (1973, 1974, 1976) and Verlet and Weis (1974) have made MC calculations of the thermodynamic properties of this system and have found (7.180) to be a good approximation for the total thermodynamic properties. Patey and Valleau (1976), however, find evidence that (7.180) overestimates the individual A_n. This is in agreement with our observation following the comparison of (7.113) and (7.114). Possibly an appropriate generalization of (7.125) would overcome this difficulty.

The pair distribution function for the dipolar hard spheres can be obtained in a manner similar to (7.176). The result is

$$g(r_{12},\Omega_1,\Omega_2)=g_0(r_{12})+\sum_{n=1}^{\infty}(\beta\mu^2)^ng_n(r_{12},\Omega_1,\Omega_2), \qquad (7.181)$$

where $g_0(r_{12})$ is the hard-sphere distribution function,

$$g_1(r_{12},\Omega_1,\Omega_2)=\frac{g_0(r_{12})}{r_{12}^3}D(1,2), \qquad (7.182)$$

$$g_2(r_{12},\Omega_1,\Omega_2)$$
$$=\frac{1}{2}\frac{g_0(r_{12})}{r_{12}^6}D^2(1,2)$$
$$-\frac{1}{6}\rho\left[\int\frac{1+3\cos\theta_1\cos\theta_2\cos\theta_3}{(r_{13}r_{23})^2}g_0(123)d\vec{r}_3\right]D(1,2)$$
$$+\frac{1}{3}\rho\left[\int\frac{3\cos^2\theta_3-1}{(r_{13}r_{23})^2}g_0(123)d\vec{r}_3\right]\Delta(1,2), \qquad (7.183)$$

and $\Delta(1,2)$ is defined in Eq. (6.68).

Høye and Stell (1975b) have proposed an approximation for $g(r_{12}, \Omega_1, \Omega_2)$ for dipolar hard spheres. They suggest that Eq. (6.74) be used with $h_s(r_{12}) \neq h_0(r_{12})$. Although $g_s(r_{12}) \simeq g_0(r_{12})$, the machine simulations show that $g_s(r_{12})$ is not equal to $g_0(r_{12})$. They propose a scheme whereby $h_D(r_{12})$ can be chosen so as to reproduce the Padé approximant, (7.180), when the energy equation, (6.77), is used, $h_\Delta(1,2)$ can be chosen so as to give the dielectric constant correctly both through (6.80) and another relation which they give; and $h_s(r_{12})$ can be chosen so as to give (7.180) both through the pressure and compressibility equations, (6.75) and (6.77), respectively. Clearly this is an approximate procedure both because (7.180) is approximate and because (6.74) is approximate. Using (6.74) means that the noncentral portion of terms such as the first term in (7.169), which is proportional to $D^2(1,2)$, are neglected. However, such terms are "inactive" in the sense that they do not contribute either to the thermodynamic functions or the dielectric constant and are hopefully small. Neither the terms in (7.168) and (7.169) or the Høye–Stell $g(r_{12}, \Omega_1, \Omega_2)$ have yet been calculated.

Stell *et al.* (1972, 1974) and McDonald (1974) have made similar calculations for the Stockmayer potential, (4.68). Madden and Fitts (1974a) have made approximate calculations of the first-order perturbation term of the RDF for the Stockmayer potential (but not the full pair distribution function) using formulae similar to (7.168) and (7.169) but with angle averages performed.

Melynk and Smith (1974) have applied the procedure of Rushbrooke *et al.* (1973) to a mixture of dipolar hard spheres whose components have differing dipole moments but equal diameters. They find that if (7.180) is used, the results are (apart from an entropy of mixing term) identical to those of a pure fluid with an averaged dipole moment.

Patey and Valleau (1976) have made machine simulation and perturbation theory studies of pure quadrupolar hard spheres and mixtures of dipolar and quadrupolar hard spheres. They find that although a perturbation expansion, truncated after A_3, is inadequate, Eq. (7.180) is a remarkably good representation of the machine simulation results. They also make the interesting observation that the quadrupolar potential induces larger structural changes in the hard-sphere fluid than the dipolar potential.

From (7.178) we see that the free energy is identical, to order β^2, with the first-order perturbation expansion for a fluid with a spherical potential, given by

$$u(r) = u_0(r) - \frac{1}{2}\beta \int \{u_1(12)\}^2 d\Omega_1 d\Omega_2 . \qquad (7.184)$$

The above observation is of limited usefulness because the correspondence between the real fluid and the fluid with the pseudo-potential defined by (7.181) breaks down in the next order of perturbation theory and because Eq. (7.181) sheds no light on the pair or radial distribution function beyond $g_s(r) = g_0(r)$.

This has not been an exhaustive review of what has been done or what can be done for systems with spherical cores. Perturbation theories based upon exponential expansions, $\ln g(r_{12}, \Omega_1, \Omega_2)$ series, etc., are possible both for the dipolar and quadrupolar hard spheres, the Stockmayer potential, and for other systems.

b. Nonspherical cores

Molecules with nonspherical cores are more difficult to treat. The most straightforward procedure is that of Pople (1954a) who observed that Eq. (7.164) can be written for any potential if $u_0(r_{12})$ is defined by

$$u_0(r_{12}) = \int u(r_{12}, \Omega_1, \Omega_2) d\Omega_1 d\Omega_2 . \qquad (7.185)$$

Thus,

$$u_1(r_{12}, \Omega_1, \Omega_2) = u(r_{12}, \Omega_1, \Omega_2) - u_0(r_{12}) \qquad (7.186)$$

and hence,

$$\int u_1(r_{12}, \Omega_1, \Omega_2) d\Omega_1 d\Omega_2 = 0 . \qquad (7.187)$$

Therefore, all the formalism developed for the spherical core case can be applied.

This procedure of Pople (1954a) and Gubbins and Gray (1972) can be expected to be successful only when

$$u_1(12) = u(12) - \int u(12) d\Omega_1 d\Omega_2 \qquad (7.188)$$

is small in some sense. If the repulsive core of the potential is nonspherical, there will be regions in which $u_1(12)$ will be large and an expansion in the strength of $u_1(12)$ may converge poorly or not at all.

One way of avoiding this problem is to use an exponential expansion. There have been two applications of exponential expansions to angular dependent potentials. The first is that of Bellemans (1968) who considered fluids composed of hard nonspherical molecules. For such systems the pair potential is

$$u(r_{12}, \Omega_1, \Omega_2) = \begin{cases} \infty, & r_{12} < d(\Omega_1, \Omega_2) \\ 0, & r_{12} > d(\Omega_1, \Omega_2) \end{cases} , \qquad (7.189)$$

where $d(\Omega_1, \Omega_2)$ is the distance of closest approach of the two molecules with orientations specified by Ω_1 and Ω_2. Bellemans introduced the parametrization

$$d(\Omega_1, \Omega_2) = d_0[1 + \lambda\gamma(\Omega_1, \Omega_2)] , \qquad (7.190)$$

where λ is the expansion parameter which is eventually set equal to unity and d_0 is defined by

$$d_0 = \int d(\Omega_1, \Omega_2) d\Omega_1 d\Omega_2 . \qquad (7.191)$$

Thus

$$\gamma(\Omega_1, \Omega_2) = [d(\Omega_1, \Omega_2)/d_0] - 1 , \qquad (7.192)$$

and

$$\int \gamma(\Omega_1, \Omega_2) d\Omega_1 d\Omega_2 = 0 . \qquad (7.193)$$

Now

$$\partial e/\partial\lambda = -d_0 \gamma(\Omega_1, \Omega_2) \delta(r - d_0) . \qquad (7.194)$$

Therefore,

$$A = A_0 + \sum_{n=1}^{\infty} A_n , \qquad (7.195)$$

where A_0 is the free energy of a system of hard spheres of diameter d_0,

$$\frac{A_1}{Nk_BT} = 12\eta y_0(d_0) \int \gamma(\Omega_1, \Omega_2) d\Omega_1 d\Omega_2$$

$$= 0 \,, \tag{7.196}$$

$$\eta = (\pi/6)\rho d_0^3 \,, \tag{7.197}$$

and $y_0(d_0)$ is value of $y(r)$ at contact for the reference hard-sphere system. Because of (7.193), the four-molecule term in A_2 vanishes. Thus,

$$\begin{aligned}\frac{A_2}{Nk_BT} &= 6\eta[2y_0(d_0) + d_0 y_0'(d_0)]\gamma^2(\Omega_1, \Omega_2) \\ &\quad - \frac{1}{2}\rho^2 d_0^2 \int e_0(13) y_0(123) \delta(r_{12} - d_0) \delta(r_{23} - d_0) d\vec{r}_2\, d\vec{r}_3 \\ &\quad \times \int \gamma(\Omega_1, \Omega_2)\gamma(\Omega_2, \Omega_3) d\Omega_1 d\Omega_2 d\Omega_3 \,.\end{aligned} \tag{7.198}$$

From the PY theory

$$d_0 y_0'(d_0) = -\frac{9}{2}\eta \frac{1+\eta}{(1-\eta)^3} \,. \tag{7.199}$$

Equation (7.199) could be used with (7.198). On the other hand, a more accurate expression for $y_0'(d_0)$ could be obtained from the VW/GH $y_0(r)$. However, (7.199) is probably sufficiently accurate, especially since $y_0(123)$ must be approximated.

The expansion of $y(r_{12}, \Omega_1, \Omega_2)$ is

$$\begin{aligned} y(r_{12}, \Omega_1, \Omega_2) &= y_0(r_{12}) - \rho d_0 \int e_0(13) y_0(123) \delta(r_{23} - d_0) d\vec{r}_3 \int \gamma(\Omega_2, \Omega_3) d\Omega_3 \\ &\quad - \rho d_0 \int e_0(23) y_0(123) \delta(r_{13} - d_0) d\vec{r}_3 \int \gamma(\Omega_2, \Omega_3) d\Omega_3 \,.\end{aligned} \tag{7.200}$$

The only calculations using this approach are those of Bellemans (1968) who made a few calculations for prolate ellipsoids. It is hard to judge the utility of this theory until more calculations have been made. However, this approach is very similar to that of Henderson and Barker (1968a) who developed a perturbation theory of hard-sphere mixtures using a single-component hard-sphere reference system whose diameter is chosen to annul the first-order term in the expansion of A. The Henderson–Barker approach has been thoroughly examined and the expressions for the thermodynamic properties are useful even when the large spheres in the mixture have a diameter twice as large as that of the small spheres. Based on this, the Bellemans theory would probably be useful for the thermodynamic properties even for molecules whose length divided by width is as great as two. On the other hand, the Henderson–Barker theory of hard-sphere mixtures is much less useful for the distribution functions (Smith and Henderson, 1972). Conceivably, Eq. (7.200) will be less useful than (7.195) to (7.198).

Perram and White (1972, 1974) have used an exponential expansion based upon

$$e(r_{12}, \Omega_1, \Omega_2) = e_0(r_{12})[1 + f_1(r_{12}, \Omega_1, \Omega_2)] \,, \tag{7.201}$$

where

$$e_0(r_{12}) = \int \exp\{-\beta u(r_{12}, \Omega_1, \Omega_2)\} d\Omega_1 d\Omega_2 \,, \tag{7.202}$$

$$f_1(r_{12}, \Omega_1, \Omega_2) = \exp\{-\beta u_1(r_{12}, \Omega_1, \Omega_2)\} - 1 \,, \tag{7.203}$$

$$u_1(r_{12}, \Omega_1, \Omega_2) = u(r_{12}, \Omega_1, \Omega_2) - u_0(r_{12}) \,, \tag{7.204}$$

and

$$u_0(r_{12}) = -kT \ln e_0(r_{12}) \,. \tag{7.205}$$

In this approach,

$$\begin{aligned}\frac{A_1}{Nk_BT} &= -\frac{1}{2}\rho \int g_0(r_{12}) d\vec{r}_2 \int f_1(12) d\Omega_1 d\Omega_2 \\ &= -\frac{1}{2}\rho \int y_0(r_{12}) d\vec{r}_2 \int \{e(12) - e_0(r_{12})\} d\Omega_1 d\Omega_2 \\ &= 0 \,.\end{aligned} \tag{7.206}$$

In contrast to the Pople expansion, Eq. (7.188), this expansion is well behaved if $u_1(12)$ is large and positive. On the other hand, for regions where $u_1(12)$ is large and negative, it is not at all obvious that this approach will always be satisfactory except, of course, at low densities.

Mo and Gubbins (1974) and Sandler (1974) have considered $u_1(12)$ expansions based upon nonspherical reference potentials which can be chosen as either the positive or the repulsive part of the potential. This approach is more close in spirit to the BH and WCA theories, which have been successful for liquids with spherically symmetric interactions, than either the Pople or the Perram and White procedures.

The properties of the reference fluid can be related to those of some appropriate hard molecules by a generalization of the procedures of Barker and Henderson (Mo and Gubbins, 1974) or Weeks, Chandler, and Andersen (Sung and Chandler, 1972; Steele and Sandler, 1974). The properties of the hard-molecule system can then be determined by machine simulations, the SPT, some generalization of the integral equation techniques discussed in Sec. VI, such as RISM, or the Bellemans theory discussed above.

c. Extensions of the van der Waals and LHW equation of state

The van der Waals and Longuet-Higgins and Widom (LHW) equation of state is

$$p = p_0 - \rho^2 a \,. \tag{7.207}$$

Rigby (1972) has suggested using (7.207) with p_0 chosen to be the equation of state of some hard nonspherical system. In the specific application which he considers, he uses the SPT result for hard prolate spherocylinders and finds that as molecules deviate increasing from spherical shape, the value of pV/Nk_BT at the critical point decreases. This is in accord with experiment.

Another possibility, based on Eq. (7.184), would be to use a hard sphere equation of state for p_0 but to replace (7.207) by

$$p = p_0 - \beta\rho^2 a \,. \tag{7.208}$$

Equation (7.208) is probably less useful than Rigby's procedure.

VIII. CELL AND CELL CLUSTER THEORIES

Among the earliest theories of liquids were "cell" or "free-volume" theories which were based on the intuitive idea that a molecule in a liquid is essentially confined to a cell or cage formed by its neighbors. If the molecules were regarded as moving independently in their cells this led, for hard spheres, to an expression for the canonical configuration integral of the form

$$Q_N = v_f^N , \tag{8.1}$$

where v_f is the "free volume" available to a single molecule moving in its cell. Much of the early development of these ideas, including the inclusion of the effect of attractive forces and of empty cells or vacancies, was done by Eyring and his collaborators (Eyring, 1936; Eyring and Hirschfelder, 1937; Cernuschi and Eyring, 1939). Since that time, Eyring and a number of collaborators have developed these ideas into the "Significant Structures Theory of Liquids," in which the liquid is regarded as a mixture of solidlike and gaslike degrees of freedom. The aim of this theory is to predict the properties of liquids on the basis of the known properties of the corresponding solids and gases, without explicit reference to intermolecular forces. The theory correlates a very wide range of properties of a wide range of liquids. It has been extensively reviewed in recent books (Eyring and Jhon, 1969; Jhon and Eyring, 1971).

There have also been a number of attempts, until recently relatively unsuccessful, to use the cell concept as the basis for a theory relating dense fluid properties directly to intermolecular forces. Most of this work was based on the formulation of the cell model by Lennard-Jones and Devonshire (1939a, b); and a detailed review of the period up to 1963 is given by Barker (1963). The most important formal development was the idea of a cell-cluster expansion, introduced independently and in somewhat different forms by de Boer (1954), Barker (1955), and Taylor (1956). Since this idea has recently been developed in a fruitful way we shall give a brief account of it using a more recent and more flexible formulation due to Barker (1966) based on the grand canonical partition function.

Suppose that the whole of space is divided into a set of identical space-filling cells, numbered by $\lambda = 1, 2, \ldots$; the size of the cells need not yet be specified. We can specify the configuration of the whole system *either* by giving the absolute coordinates of all the molecules *or* by giving the number of molecules N_λ in each cell and their coordinates relative to the cell center $\vec{r}'_{\lambda j}, j = 1 \ldots N_\lambda$. For brevity let us use i_λ to denote the set of variables $\{N_\lambda; \vec{r}'_{\lambda j}, j = 1 \ldots N_\lambda\}$. Let us use the symbol $\sum_{i_\lambda}$ to denote integration over the *cell* volume with respect to $\vec{r}'_{\lambda j}$ for $\lambda = 1 \ldots N_\lambda$ followed by summation over N_λ. The advantage of the description in terms of i_λ over that in terms of absolute coordinates is that we can be certain that molecules in cells remote one from another will not interact. Let us define

$$U(i_\lambda) = -N_\lambda \mu + k_B T \ln(N_\lambda !) + \sum_{m < n = 1}^{N_\lambda} u(|\vec{r}'_{\lambda m} - \vec{r}'_{\lambda n}|) \tag{8.2}$$

and

$$U(i_\lambda, i_\nu) = \sum_{m=1}^{N_\lambda} \sum_{n=1}^{N_\nu} u(|\vec{r}'_{\lambda m} - \vec{r}'_{\nu n}|) , \tag{8.3}$$

in which μ is the chemical potential. Then a little reflection will show that the grand partition function for the whole system is given *exactly* by

$$\Xi = \sum_{i, i_2 \cdots} \exp\left[-\beta \sum_\lambda U(i_\lambda) - \beta \sum_{\lambda < \nu} U(i_\lambda, i_\nu) \right] . \tag{8.4}$$

Further, if the interactions are of short enough range $U(i_\lambda, i_\nu)$ will be nonzero only when the cells λ and ν are reasonably close in the lattice.

Thus, at the cost of a somewhat abstract notation we have cast the problem into the relatively familiar form of a problem in lattice statistics such as one meets in connection with the Ising model for magnetism. The advantage is that we can proceed to use approximations and expansions familiar in the latter context. We can deal *exactly* with the terms $U(i_\lambda)$ and introduce approximations only involving $U(i_\lambda, i_\nu)$. In particular, if the cells are small enough so that two molecules cannot fit in a single cell, we deal exactly with $U(i_\lambda)$ by restricting the configurations so that $N_\lambda = 0$ or 1 for every λ.

Suppose that we introduce an approximation to $U(i_\lambda, i_\nu)$ of the form

$$U(i_\lambda, i_\nu) = W_\nu(i_\lambda) + W_\lambda(i_\nu) \tag{8.5}$$

and define

$$\Delta_{\lambda\nu} = U(i_\lambda, i_\nu) - W_\nu(i_\lambda) - W_\lambda(i_\nu) \tag{8.6}$$

$$f_{\lambda\nu} = \exp[-\beta \Delta_{\lambda\nu}] - 1, \tag{8.7}$$

and

$$U'(i_\lambda) = U(i_\lambda) + \sum_\nu W_\nu(i_\lambda) . \tag{8.8}$$

Then Eq. (8.4) becomes

$$\Xi = \sum_{i, i_2 \cdots} \exp\left[-\beta \sum_\lambda U(i_\lambda) \right] \prod_{\lambda < \nu} (1 + f_{\lambda\nu}) . \tag{8.9}$$

By expanding the product in (8.9), performing the summations and formally taking the logarithm, one generates a *cell-cluster expansion* similar to (but more complex than) the Mayer cluster expansion. The properties of the expansion depend on the choice of the approximating functions $W_\nu(i_\lambda)$. The earlier cell cluster theory was based on the choice (for 1 molecule in each cell),

$$W_\nu(i_\lambda) = \tfrac{1}{2} u(|\vec{a}|) + [u(|\vec{a} + \vec{r}_\lambda|) - u(|\vec{a}|)] , \tag{8.10}$$

where $\vec{a}$ is the vector joining cell centers, which is motivated by the theory of Lennard-Jones and Devonshire (1939a, b), and in lowest order reproduces that theory exactly (for a detailed discussion see Barker, 1963). As a *consequence* of this choice, the theory gave a good description of solids (Rudd *et al.*, 1969; Westera and Cowley, 1975) but could not describe fluids.

On the other hand, one could choose W_ν to be *zero*. In this case one is generating the same terms that appear in the Mayer expansion, though combined in unusual ways. There is reason to suppose that this would lead to a description of fluids (though rapid convergence is not guaranteed!).

There is an even more interesting possibility; one can choose W_ν by a self-consistency criterion,

$$\langle f_{\lambda\nu}\rangle' = 0\,, \tag{8.11}$$

where $\langle\ \rangle'$ means "average for a system with probability density $\exp[-\beta\sum_\nu U'(i_\nu)]$ over the configuration of all cells except λ." This can be seen to be equivalent to the Bethe or quasichemical approximation in lattice statistics (Barker, 1966; Lloyd, 1964). Approximate solutions for these self-consistency equations were found by Barker (1975), and Barker and Gladney (1975) for hard spheres with one molecule per cell (single-occupancy models) in three, two, and one dimensions at high densities. In one dimension the results were exact, as was to be expected. In two and three dimensions, one approximate solution gave an excellent description of the corresponding solids, especially when higher cluster corrections were included. However, in both cases there was a *second* approximate solution, yielding one-particle distribution functions much less strongly peaked at the cell center, which was tentatively associated with the fluid phase.

Honda (1974a) derived the self-consistency Eq. (8.10) for single-occupancy systems independently using the cluster-variation method of Morita and Tanaka (1966) based ultimately on the work of Kikuchi (1951). A similar but slightly less explicit derivation was given by Allnatt (1968). Honda (1974b) solved the equations numerically for the two-dimensional single-occupancy hard-sphere system, and found that there were indeed two kinds of solution, one solidlike and one fluidlike. Further, the free energy curves as functions of density indicated a first-order phase transition. The density of the fluid phase at the transition was somewhat lower than that found by computer experiments on the unconstrained hard-disk system. This was to be expected because the single-occupation model does not include the "communal entropy" (Hoover and Ree, 1968).

Thus, it appears that the self-consistent cell-cluster theory may contain a unified description of solid, fluid and melting, although some details remain to be filled in. This would fill, in a rather pleasing way, a gap in our theoretical understanding. Apart from the Monte Carlo calculations discussed in Sec. III, most other theories of melting (which are reviewed by Hoover and Ross, 1971) either used different models for solid and fluid phases (e.g., Henderson and Barker, 1968b) or used the known melting properties of hard spheres to predict those of more realistic systems (Rowlinson, 1964b; Crawford, 1974).

Another approach to the cell theory was used by Caron (1972), who assumed the neighbors of a central molecule to have a distribution of distances corresponding to "random close packing," following the ideas of Bernal (Bernal and King, 1968). The "entropy of disorder" associated with "degeneracy of ideal structures" was calculated from experimental data and found to be remarkably constant.

IX. THE LIQUID-GAS INTERFACE

The subject of liquid surfaces is such an enormous one that we shall seek here to do no more than indicate the various theoretical approaches that have been used and provide entry points to the literature.

In the neighborhood of the critical point the interface between liquid and gas phases becomes very wide compared with the range of the intermolecular forces. In these conditions the quasithermodynamic theory of surface structure developed by van der Waals (1894), Cahn and Hilliard (1958) and Fisk and Widom (1969) among others provides useful insights. An excellent critical review of this theory with detailed references is given by Widom (1972). The basic idea is that there exists a local free energy density, $\Psi(z)$ (where z is a coordinate normal to the interface) given by

$$\Psi(z) = \Psi_0[\rho(z)] + \tfrac{1}{2}A(\partial\rho(z)/\partial z)^2\,, \tag{9.1}$$

where $\Psi_0[\rho(z)]$ is the free energy density of a *uniform* fluid at the density $\rho(z)$, extrapolated in some way into the metastable region, and A is some function of temperature. The density profile through the interface is determined by minimizing the total free energy. With appropriate assumptions on the form of the function $\Psi[\rho]$ and the temperature dependence of A, the theory gives a good description of surface tension and the interface thickness in the critical region. The relationship between this theory and detailed microscopic theories is discussed by Lovett *et al.* (1973), Felderhof (1970), Triezenberg and Zwanzig (1972), and Abraham (1975).

Kirkwood and Buff (1949) and Buff (1952) derived from a general expression for the stress in a fluid an expression for the surface tension γ of the form

$$\gamma = \frac{1}{2}\int_{-\infty}^{\infty} dz_1 \int d\vec{r}_2 u'(r_{12})\left(\frac{x_{12}^2 - z_{12}^2}{r_{12}}\right) n^{(2)}(\vec{r}_1, \vec{r}_2)\,. \tag{9.2}$$

Here $n^{(2)}(\vec{r}_1, \vec{r}_2)$ is the two body distribution function for the inhomogeneous system. This result is valid for pair-additive spherical potentials; the generalization to nonspherical potentials is given by Gray and Gubbins (1975). Buff (1952) showed that Eq. (9.2) could also be derived by a scaling procedure similar to that used to derive the virial pressure equation for a homogeneous fluid (see Sec. II). Some alternative forms of this equation are given by Lovett *et al.* (1973).

A different equation for the surface tension can be derived which involves the direct correlation function $c(r_1, r_2)$ for the inhomogeneous fluid. This function, which was introduced in an important paper on nonuniform fluids by Lebowitz and Percus (1963) satisfies the generalized Ornstein–Zernike equation

$$h(\vec{r}_1, \vec{r}_2) = c(\vec{r}_1, \vec{r}_2) + \int n^{(1)}(\vec{r}_3) h(\vec{r}_1, \vec{r}_3) c(\vec{r}_2, \vec{r}_3) d\vec{r}_3\,, \tag{9.3}$$

where

$$h(\vec{r}_1, \vec{r}_2) = [n^{(1)}(\vec{r}_1) n^{(1)}(\vec{r}_2)]^{-1} [n^{(2)}(\vec{r}_1, \vec{r}_2) - n^{(1)}(\vec{r}_1) n^{(1)}(\vec{r}_2)]\,. \tag{9.4}$$

Thus, if the distribution functions $n^{(2)}, n^{(1)}$ for the inhomogeneous fluid are known, $c(r_1, r_2)$ can be calculated.

In terms of this function the surface tension is given by

$$\gamma=\frac{1}{4}k_BT\int_{-\infty}^{\infty}dz_1\int d\vec{r}_2\frac{dn^{(1)}(z_1)}{dz_1}\frac{dn^{(1)}(z_2)}{dz_2}c(\vec{r}_1,\vec{r}_2)(x_{12}^2+y_{12}^2)\,. \tag{9.5}$$

Two different derivations of this equation are given by Lovett *et al.* (1973) and Triezenberg and Zwanzig (1972).

If the width of the interface is large compared to the range of the direct correlation function, this reduces to the expression used in the quasithermodynamic theory (Lovett *et al.*, 1973). Note that (9.5) is much more general than (9.2) in that it makes no assumption about pair additivity. In this sense the relation between (9.5) and (9.2) is similar to that between the compressibility equation and virial pressure equations for homogeneous fluids. Of course these equations are useful only if we know or can approximate the one- and two-body distribution functions in the interface. The simplest approximation proposed by Kirkwood and Buff (1949) was to set $n^{(2)}(\vec{r}_1,\vec{r}_2)$ in Eq. (9.2) equal to 0 for z_1 or z_2 greater than 0, and to the bulk liquid value otherwise; this corresponds to a plane discontinuous surface with negligible vapor density. This model, also used by Fowler (1937), has been tested recently by Freeman and McDonald (1973); earlier references are listed in that paper. They used the 6–12 potential and found good agreement with experiment, for example for argon, for surface tension but bad agreement for surface energy. Furthermore, the surface tension and surface energy values were not thermodynamically consistent. It is almost certain that the good agreement for surface tension is fortuitous, since several independent MC calculations, as well as perturbation theories (are below) indicate that the true surface tension for the 6–12 fluid is substantially higher than that of argon (see Table XVII). One would certainly have expected that this simple model would be better for surface *energy* than for surface tension.

Monte Carlo simulations of liquid surfaces have been made in two dimensions (Croxton and Ferrier, 1971) and in three dimensions (Lee *et al.*, 1974; Lui, 1974; Abraham *et al.*, 1975; Chapela *et al.*, 1975; Miyazaki *et al.*, 1976). Also Opitz (1974) made a molecular dynamics simulation. Lee *et al.* (1974) and Chapela *et al.* (1975) calculated the surface tension using equations equivalent to (9.2); the calculations used the 6–12 potential. The results for a temperature near the triple point are given in Table XVII. Because the integrand in (9.2) fluctuates widely, surface tensions derived in this way have rather high uncertainties. Miyazaki *et al.* (1976) used a modified periodic boundary condition to separate a bulk liquid into slabs and thus calculated directly the reversible work required to create a surface; this surface free energy is equal to the surface tension. The surface tension calculated this way has smaller uncertainty (see Table XVII). Miyazaki *et al.* also used the 6–12 potential, but estimated by a perturbation technique the *difference* between the surface tension for "6–12 argon" and "argon with accurate pair potential and three-body interactions." The results for argon estimated in this way are in fair agreement with experiment, whereas all calculations other than the simple Kirkwood–Buff–Fowler model indicate that the surface tension for "6–12 argon" is appreciably higher than that for "real argon."

The work of Croxton and Ferrier (1971) and Lee *et al.* (1974) suggested the existence of oscillatory behavior in the density profile through the interface. However, it is now certain as a result of the work of Abraham *et al.* (1975) and Chapela *et al.* (1975) that this oscillatory behavior, though it persists over surprisingly long MC chains, is not present in a true canonical average. The

TABLE XVII. Calculated and experimental surface properties for liquid argon at triple point.

Method	Potential	Surface tension (erg cm^{-2})	Surface energy (erg cm^{-2})
Monte Carlo [a] (surface stress)	6–12	16.5 ± 2.6	
Monte Carlo [b] (surface stress)	6–12	~19	
Monte Carlo [c] (surface free energy)	6–12	18.3 ± 0.3	38.9
Perturbation theory [d]	6–12	19.7	
Estimated from Monte Carlo [c, e]	BFW alone	17.7	38.3
Estimated from Monte Carlo [c, e]	BFW with Axilrod-Teller	14.1	34.7
Experiment [f]		13.35	34.8

[a] Lee *et al.* (1974).
[b] Chapela *et al.* (1975).
[c] Miyazaki *et al.* (1976).
[d] Abraham (1975).
[e] Estimate from c by perturbation theory by Miyazaki *et al.* (1976).
[f] Sprow and Prausnitz (1966).

equilibrium density profile is monotonic.

Toxvaerd (1971) generalized the Barker–Henderson perturbation theory (Sec. VII) to apply to an inhomogeneous fluid and calculated surface tension after minimizing the free energy with respect to the density profile; for the detailed assumptions of this theory we refer to the original paper. Abraham (1975) made calculations of surface tension using both this theory and a version incorporating the Weeks–Chandler–Anderson perturbation theory (Sec. VII); the two methods gave results in good agreement. Note that these perturbation theories do not use either Eq. (9.2) or (9.5); the free energy is calculated directly. However, near the critical point the theory can be recast into a form similar to the quasithermodynamic theory (Abraham 1975).

The normal component $p_N(z)$ of the stress tensor at a point in the interface is given by (Irving and Kirkwood, 1950)

$$p_N = k_BTn(\vec{r}_1) - \frac{1}{2}\int d\vec{r}_{12}\frac{z_{12}^2}{r_{12}}u'(r_{12}) \times \int_0^1 n^{(2)}[\vec{r}_1 - \alpha\vec{r}_{12}, \vec{r}_1 + (1-\alpha)\vec{r}_{12}]\,d\alpha\,. \tag{9.6}$$

Since for equilibrium p_N must be constant, this provides and integral equation relating $n^{(1)}(\vec{r}_1)$ and $n^{(2)}(\vec{r}_1, \vec{r}_2)$. This equation is equivalent (Harasima, 1958) to an integrated form of the first member of the BG hierarchy of equations (see Sec. VI). There is a relatively large body of work (Toxvaerd, 1975, 1976, and references therein) based on the idea of approximating $n^{(2)}(\vec{r}_1, \vec{r}_2)$ by a closure approximation in terms of $n^{(1)}(\vec{r}_1)$ and solving the resulting integral equation for $n^{(1)}(\vec{r}_1)$. The closure approximations use homogeneous fluid radial distribution functions $g(r, \rho)$. The results obtained depend on the detailed form of the closure approximations; for details we refer to the review of Toxvaerd (1975) and the original papers.

Recently, Mandell and Reiss (1975a, b) have developed a thermodynamic formalism for a bulk phase bounded by a hard wall, and used scaled particle theory (Sec. V) to study the structure of a hard-sphere fluid bounded by a hard wall.

We note that the apparent divergence to infinity of the mean square displacement of a surface in zero gravity discussed by Buff *et al.* (1965) and Widom (1972) is prevented by the finite size of the system in the same way as the related apparent divergence of mean-square displacement in a two-dimensional solid discussed in Sec. III.D.1. If we carry through the calculation described by Buff *et al.* for a square surface of edge D we find that the root-mean-square displacement is $(k_BT/4\pi\gamma_0)^{1/2}[\ln(\cdot 69D/L)]^{1/2}$ where γ_0 is the surface tension unmodified by long wavelength distortions, and L the interface width. If we consider the case they discuss of liquid argon with $T = 90\text{K}$, $\gamma = 11.9$ dyne cm^{-1}, $L \simeq 4$Å, this formula gives 4.1Å for the root mean square displacement with $D = 1$cm. This is a perfectly finite and consistent result. The corresponding result for $D = 1$m is 4.2Å. Surface tensions are usually measured in somewhat smaller capillaries! The finite size of the system plays the same role as gravity in providing a long wave cutoff.

ACKNOWLEDGMENTS

The authors are grateful to their co-workers in the theory of liquids for discussions and for providing preprints of their work in advance of publication. Particular thanks are due to Drs. F. F. Abraham and G. Stell for extensive discussions, and to Drs. D. D. Fitts, W. G. Madden, and W. R. Smith for expediting their numerical calculations so that they could be incorporated in this paper. It is a pleasure to acknowledge the stimulus to our personal interest in this subject which was provided by J. H. Hildebrand and H. Eyring. The typing was done by Colleen DeLong and Linda Ferguson.

BIBLIOGRAPHY

Barton, A. F. M., 1974, *The Dynamic Liquid State* (Longman, London).
Egelstaff, P. A., 1967, *An Introduction to the Liquid State* (Academic Press, London).
Fitts, D. D., 1972, in *Theoretical Chemistry,* in *Physical Chemistry Section, MTP International Review of Science,* Series 1, edited by W. Byers-Brown (Butterworths, London), Vol. 1, Chap. 6.
Henderson, D., 1971, editor, *Liquid State*, in *Physical Chemistry - An Advanced Treatise*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8.
Hill, T. L., 1956, *Statistical Mechanics* (McGraw-Hill, New York).
Klein, M. L., and J. A. Venables, 1976, editors, *Rare Gas Solids* (Academic Press, New York), Vol. 1.
Kohler, F., 1972, *The Liquid State* (Verlag Chemie, Weinheim).
Münster, A., 1969, *Statistical Thermodynamics* (Academic Press, New York), Vols. 1 and 2 (especially Vol. 2).
Prigogine, I., and S. A. Rice, 1975, editors, *Non-Simple Liquids* in *Advances in Chemical Physics* (Wiley-Interscience, New York), Vol. 31.
Pryde, J. A., 1966, *The Liquid State* (Hutchinson, London).
Rice, S. A., and P. Gray, 1965, *The Statistical Mechanics of Simple Liquids* (Wiley-Interscience, New York).
Rowlinson, J. S., 1969, *Liquids and Liquid Mixtures* (Butterworths, London), 2nd ed.
Singer, K., 1973, editor, *Specialist Periodical Report*, *Statistical Mechanics* (Chemical Society, London), Vol. 1 and Vol. 2.
Temperley, H. N. V., J. S. Rowlinson, and G. S. Rushbrooke, 1968, editors, *Physics of Simple Liquids* (North-Holland, Amsterdam).
Wood, W. W., 1976, Annu. Rev. Phys. Chem. **27**, in press.

REFERENCES

Abraham, F. F., 1975, J. Chem. Phys. **63**, 157.
Abraham, F. F., D. E. Schreiber, and J. A. Barker, 1975, J. Chem. Phys. **62**, 1957.
Adams, D. J., 1974, Mol. Phys. **28**, 1241.
Adams, D. J., 1975, Mol. Phys. **29**, 307.
Adams, D. J., and I. R. McDonald, 1976, "Thermodynamic and Dielectric Properties of Polar Lattices," preprint.
Adelman, S. A., and J. M. Deutch, 1973, J. Chem. Phys. **59**, 3971.
Ahn, S., and J. L. Lebowitz, 1973, Phys. Lett. **A44**, 424.
Ahn, S., and J. L. Lebowitz, 1974, J. Chem. Phys. **60**, 523.
Alder, B. J., 1964, Phys. Rev. Lett. **12**, 317.
Alder, B. J., and C. E. Hecht, 1969, J. Chem. Phys. **50**, 2032.
Alder, B. J., and J. H. Hildebrand, 1973, I. and E. C. Fund.

12, 387.
Alder, B. J., and T. E. Wainwright, 1957, J. Chem. Phys. **27**, 1208.
Alder, B. J., and T. E. Wainwright, 1959, J. Chem. Phys. **31**, 459.
Alder, B. J., and T. E. Wainwright, 1960, J. Chem. Phys. **33**, 1439.
Alder, B. J., and T. E. Wainwright, 1962, Phys. Rev. **127**, 359.
Alder, B. J., and T. E. Wainwright, 1967, Phys. Rev. Lett. **18**, 988.
Alder, B. J., and T. E. Wainwright, 1970, Phys. Rev. **A1**, 18.
Alder, B. J., D. M. Gass, and T. E. Wainwright, 1970, J. Chem. Phys. **53**, 3813.
Alder, B. J., W. G. Hoover, and D. A. Young, 1968, J. Chem. Phys. **49**, 3688.
Alder, B. J., D. A. Young, and M. A. Mark, 1972, J. Chem. Phys. **56**, 3013.
Allnatt, A. R., 1966, Physica **32**, 133.
Allnatt, A. R., 1968, Mol. Phys. **14**, 289.
Andersen, H. C., 1972, private communication.
Andersen, H. C., 1975, Annu. Rev. Phys. Chem. **26**, 145.
Andersen, H. C., and D. Chandler, 1970, J. Chem. Phys. **53**, 547.
Andersen, H. C., and D. Chandler, 1972, J. Chem. Phys. **57**, 1918.
Andersen, H. C., D. Chandler, and J. D. Weeks, 1972, J. Chem. Phys. **56**, 3812.
Andersen, H. C., D. Chandler, and J. D. Weeks, 1976, Adv. Chem. Phys. (in press).
Anderson, J. B., 1975, J. Chem. Phys. **63**, 1499.
Ashurst, W. T., and W. G. Hoover, 1975, Phys. Rev. **A11**, 658.
Axilrod, B. M., and E. Teller, 1943, J. Chem. Phys. **11**, 299.
Barker, A. A., 1965, Aust. J. Phys. **18**, 119.
Barker, J. A., 1953, Proc. R. Soc. Lond. **A219**, 367.
Barker, J. A., 1954, Aust. J. Chem. **7**, 127.
Barker, J. A., 1955, Proc. R. Soc. Lond. **A230**, 390.
Barker, J. A., 1957, Proc. R. Soc. Lond. **A241**, 547
Barker, J. A., 1963, *Lattice Theories of the Liquid State* (Pergamon, Oxford).
Barker, J. A., 1966, J. Chem. Phys. **44**, 4212.
Barker, J. A., 1973, unpublished work.
Barker, J. A., 1975, J. Chem. Phys. **63**, 632.
Barker, J. A., 1976, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic Press, New York), Vol. 1, Chap. 4.
Barker, J. A., and H. M. Gladney, 1975, J. Chem. Phys. **63**, 3870.
Barker, J. A., and D. Henderson, 1967a, J. Chem. Phys. **47**, 2856.
Barker, J. A., and D. Henderson, 1967b, J. Chem. Phys. **47**, 4714.
Barker, J. A., and D. Henderson, 1967c, Can. J. Phys. **45**, 3959.
Barker, J. A., and D. Henderson, 1968, in *Proceedings of the Fourth Symposium on Thermophysical Properties*, edited by J. R. Moszynski (ASME, New York), p. 30.
Barker, J. A., and D. Henderson, 1971a, Mol. Phys. **21**, 187.
Barker, J. A., and D. Henderson, 1971b, Acc. Chem. Res. **4**, 303.
Barker, J. A., and D. Henderson, 1971c, Phys. Rev. **A4**, 806.
Barker, J. A., and D. Henderson, 1972, Annu. Rev. Phys. Chem. **23**, 439.
Barker, J. A., and M. L. Klein, 1973, Phys. Rev. **B7**, 4707.
Barker, J. A., and J. J. Monaghan, 1962a, J. Chem. Phys. **36**, 2558.
Barker, J. A., and J. J. Monaghan, 1962b, J. Chem. Phys. **36**, 2564.
Barker, J. A., and J. J. Monaghan, 1966, J. Chem. Phys. **45**, 3482.
Barker, J. A., and F. Smith, 1960, Aust. J. Chem. **13**, 171.
Barker, J. A., and R. O. Watts, 1969, Chem. Phys. Lett. **3**, 144.
Barker, J. A., and R. O. Watts, 1973, Mol. Phys. **26**, 792.
Barker, J. A., R. A. Fisher, and R. O. Watts, 1971, Mol. Phys. **21**, 657.
Barker, J. A., D. Henderson, and W. R. Smith, 1968, Phys. Rev. Lett. **21**, 134.
Barker, J. A., D. Henderson, and W. R. Smith, 1969, Mol. Phys. **17**, 579.
Barker, J. A., D. Henderson, and R. O. Watts, 1970, Phys. Lett. **31A**, 48.
Barker, J. A., P. J. Leonard, and A. Pompe, 1966, J. Chem. Phys. **44**, 4206.
Barker, J. A., R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, 1974, J. Chem. Phys. **61**, 3081.
Barojas, J., D. Levesque, and B. Quentrec, 1973, Phys. Rev. **A7**, 1092.
Baxter, R. J., 1964a, Phys. Fluids **7**, 38.
Baxter, R. J., 1964b, J. Chem. Phys. **41**, 553.
Baxter, R. J., 1967a, Phys. Rev. **154**, 170.
Baxter, R. J., 1967b, J. Chem. Phys. **47**, 4855.
Baxter, R. J., 1968a, Aust. J. Phys. **21**, 563.
Baxter, R. J., 1968b, Ann. Phys. (N.Y.) **46**, 509.
Baxter, R. J., 1971, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8A, Chap. 4.
Bearman, R. J., F. Theeuwes, M. Y. Bearman, F. Mandel, and G. J. Throop, 1970, J. Chem. Phys. **52**, 5486.
Beck, D. E., 1968, Mol. Phys. **14**, 311.
Bellemans, A., 1968, Phys. Rev. Lett. **21**, 527.
Ben-Naim, A., 1970, J. Chem. Phys. **52**, 5531.
Ben-Naim, A., and F. H. Stillinger, 1972, in *Structure and Transport Processes in Water and Aqueous Solutions*, edited by R. A. Horne (Wiley-Interscience, New York), Chap. 8.
Bennett, C. H., 1974, "Optimum Estimation of Free Energy Differences From Monte Carlo Data," preprint.
Bennett, C. H., and B. J. Alder, 1971, J. Chem. Phys. **54**, 4796.
Bernal, J. D., and S. V. King, 1968, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (North-Holland, Amsterdam), Chap. 6.
Berne, B. J., 1971, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8B, Chap. 9; and references therein.
Blum, L., 1972, J. Chem. Phys. **57**, 1862.
Blum, L., 1973, J. Chem. Phys. **58**, 3295.
Blum, L., 1974, Chem. Phys. Lett. **26**, 200.
Blum, L., and A. H. Narten, 1972, J. Chem. Phys. **56**, 5197.
Blum, L., and A. J. Torruella, 1972, J. Chem. Phys. **56**, 303.
Bobetic, M., and J. A. Barker, 1970, Phys. Rev. **B2**, 4169.
de Boer, J., 1954, Physica **20**, 655.
de Boer, J., J. M. J. van Leeuwen, and J. Groeneveld, 1964, Physica **30**, 2265.
Boltzmann, L., 1899, Proc. R. Acad. Sci. Amst. **1**, 398.
Bogoliubov, N. N., 1946, J. Phys. (Moscow) **10**, 256.
Born, M., and H. S. Green, 1946, Proc. R. Soc. Lond. **A188**, 10.
Born, M., and H. S. Green, 1947, Proc. R. Soc. Lond. **A191**, 168.
Born, M., and J. R. Oppenheimer, 1927, Ann. Phys. (Leipz), **84**, 457.
Boublik, T., 1974, Mol. Phys. **27**, 1415.
Broyles, A. A., 1960, J. Chem. Phys. **33**, 456.
Broyles, A. A., 1961a, J. Chem. Phys. **34**, 359.
Broyles, A. A., 1961b, J. Chem. Phys. **34**, 1068.
Broyles, A. A., S. U. Chung, and H. L. Sahlin, 1962, J. Chem. Phys. **37**, 2462.
Bruch, L. W., 1971, J. Chem. Phys. **54**, 4281.
Bruch, L. W., 1973, Prog. Theor. Phys. **50**, 1835.

Bruch, L. W., I. J. McGee, and R. O. Watts, 1974, Phys. Lett. **50A**, 1835.

Brush, S. G., H. L. Sahlin, and E. Teller, 1966, J. Chem. Phys. **45**, 2102.

Buckingham, A. D., and J. A. Pople, 1955, Trans. Faraday Soc. **51**, 1173.

Buckingham, A. D., and B. D. Utting, 1970, Annu. Rev. Phys. Chem. **21**, 287.

Buff, F. P., 1952, Z. Elektrochem. **56**, 311.

Buff, F. P., and R. Brout, 1955, J. Chem. Phys. **23**, 458.

Buff, F. P., and F. M. Schindler, 1958, J. Chem. Phys. **29**, 1075.

Buff, F. P., R. A. Lovett, and F. H. Stillinger, 1965, Phys. Rev. Lett. **15**, 621.

Burgmans, A. L. J., J. M. Farrar, and Y. T. Lee, 1976, J. Chem. Phys. **64**, 1345.

Cahn, J. W., and J. E. Hilliard, 1958, J. Chem. Phys. **28**, 258.

Caligaris, R. E., and D. Henderson, 1975, Mol. Phys. **30**, 1853.

Carley, D. D., and F. Lado, 1965, Phys. Rev. **137**, A42.

Carnahan, N. F., and K. E. Starling, 1969, J. Chem. Phys. **51**, 635.

Caron, L. G., 1972, J. Chem. Phys. **55**, 5227.

Casanova, G., R. J. Dulla, D. A. Jonah, J. S. Rowlinson, and G. Saville, 1970, Mol. Phys. **18**, 589.

Cernuschi, F., and H. Eyring, 1939, J. Chem. Phys. **7**, 547.

Certain, P. R., and L. W. Bruch, 1972, in *Theoretical Chemistry*, in *Physical Chemistry Section*, *MTP International Review of Science*, Series 1, edited by W. Byers-Brown (Butterworths, London), Vol. 1, Chap. 4.

Chandler, D., 1973, J. Chem. Phys. **59**, 2742.

Chandler, D., 1974, Acc. Chem. Res. **7**, 246.

Chandler, D., and H. C. Andersen, 1972, J. Chem. Phys. **57**, 1930.

Chae, D. G., F. H. Ree, and T. Ree, 1969, J. Chem. Phys. **50**, 1581.

Chapela, G. A., G. Saville, and J. S. Rowlinson, 1975, Discuss. Faraday Soc. **59**, 22.

Chen, M., D. Henderson, and J. A. Barker, 1969, Can. J. Phys. **47**, 2009.

Chen, R., D. Henderson, and S. G. Davison, 1965, Proc. Natl. Acad. Sci. USA **54**, 1514.

Chen, S.-H., 1971, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8A, Chap. 2.

Chen, Y.-D., and W. A. Steele, 1969, J. Chem. Phys. **50**, 1428.

Chen, Y.-D., and W. A. Steele, 1970, J. Chem. Phys. **52**, 5284.

Chen, Y.-D., and W. A. Steele, 1971, J. Chem. Phys. **54**, 103.

Cheng, I.-Y. S., and J. J. Kozak, 1973, J. Math. Phys. **14**, 632.

Chihara, J., 1973, Prog. Theor. Phys. **50**, 1156.

Chung, H. S., 1969, Mol. Phys. **16**, 553.

Chung, H. S., and W. F. Espenscheid, 1968, Mol. Phys. **14**, 317.

Cotter, M. A., and D. E. Martire, 1970a, J. Chem. Phys. **52**, 1909.

Cotter, M. A., and D. E. Martire, 1970b, J. Chem. Phys. **53**, 4500.

Cotter, M. A., and F. H. Stillinger, 1972, J. Chem. Phys. **57**, 3356.

Crawford, R. K., 1974, J. Chem. Phys. **60**, 2169.

Croxton, C. A., 1972, Phys. Lett. **42A**, 229.

Croxton, C. A., 1973, Phys. Lett. **46A**, 139.

Croxton, C. A., 1974a, J. Phys. **C7**, 3723.

Croxton, C. A., 1974b, Phys. Lett. **49A**, 469.

Croxton, C. A., 1974c, *Liquid State Physics—A Statistical Mechanical Introduction* (University Press, Cambridge).

Croxton, C. A., and R. P. Ferrier, 1971, J. Phys. **C4**, 2447.

Curro, J. G., 1974, J. Chem. Phys. **61**, 1203.

Dulla, R. J., J. S. Rowlinson, and W. R. Smith, 1971, Mol. Phys. **21**, 299.

Doran, M. B., and I. J. Zucker, 1971, J. Phys. **C4**, 307.

Dymond, J. H., and B. J. Alder, 1971, Ber. Bunsenges. Phys. Chem. **75**, 394.

Dymond, J. H., and E. B. Smith, 1969, *The Virial Coefficients of Gases* (University Press, Oxford).

Egelstaff, P. A., C. G. Gray, and K. E. Gubbins, 1975, in *MTP International Review of Science, Physical Chemistry, Series 2*, edited by A. D. Buckingham (Butterworths, London), Vol. 2, p. 299.

Elgin, R. L., and D. L. Goodstein, 1974, Phys. Rev. **A9**, 2657.

Evans, D. J., and R. O. Watts, 1974, Mol. Phys. **28**, 1233.

Evans, D. J., and R. O. Watts, 1975, Mol. Phys. **29**, 777.

Evans, D. J., and R. O. Watts, 1976a, Mol. Phys. **31**, 83.

Evans, D. J., and R. O. Watts, 1976b, Mol. Phys. in press.

Ewing, G., 1975, Acc. Chem. Res. **8**, 185.

Eyring, H., 1936, J. Chem. Phys. **4**, 283.

Eyring, H., and J. O. Hirschfelder, 1937, J. Phys. Chem. **41**, 429.

Eyring, H., and M. S. Jhon, 1969, *Significant Liquid Structures* (Wiley, New York).

Farrar, J. M., and Y. T. Lee, 1972, J. Chem. Phys. **56**, 5801.

Farrar, J. M., Y. T. Lee, V. V. Goldman, and M. L. Klein, 1973, Chem. Phys. Lett. **19**, 359.

Fehder, P. L., 1969, J. Chem. Phys. **50**, 2617.

Fehder, P. L., 1970, J. Chem. Phys. **52**, 791.

Felderhof, U., 1970, Physica **48**, 541.

Feller, W., 1950, *An Introduction to Probability Theory and Its Applications* (Wiley, New York), Vol. 1, Sec. 15.

Le Fevre, E. J., 1972, Nature **235**, 20.

Few, G. A., and M. Rigby, 1973, Chem. Phys. Lett. **20**, 433.

Feynman, R. P., and A. R. Hibbs, 1965, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York), p. 289.

Fisher, I. Z., 1964, Statistical Theory of Liquids (University Press, Chicago).

Fisher, R. A., and R. O. Watts, 1972a, Mol. Phys. **23**, 1051.

Fisher, R. A., and R. O. Watts, 1972b, Aust. J. Phys. **25**, 529.

Fisk, S., and B. Widom, 1969, J. Chem. Phys. **50**, 3219.

Flory, P. J., 1969, *Statistical Mechanics of Chain Molecules* (Wiley-Interscience, New York).

Fosdick, L. D., and H. F. Jordan, 1966, Phys. Rev. **143**, 58.

Fowler, R. H., 1937, Proc. R. Soc. Lond. **A159**, 229.

Fowler, R. H., 1973, J. Chem. Phys. **59**, 3435.

Francis, W. P., G. V. Chester, and L. Reatto, 1970, Phys. Rev. **A1**, 86.

Freeman, D. E., K. Yoshino, and Y. Tanaka, 1974, J. Chem. Phys. **61**, 4880.

Freeman, K. S. C., and I. R. McDonald, 1973, Mol. Phys. **26**, 529.

Frenkel, J., 1946, *Kinetic Theory of Liquids* (University Press, Oxford), pp. 124–125.

Frisch, H. L., 1964, Adv. Chem. Phys. **6**, 229.

Frisch, H. L., J. L. Katz, E. Praestgaard, and J. L. Lebowitz, 1966, J. Phys. Chem. **70**, 2016.

Geilikman, B. T., 1950, Proc. Acad. Sci. USSR **70**, 25.

Gibbons, R. M., 1969, Mol. Phys. **17**, 81.

Gibbons, R. M., 1970, Mol. Phys. **18**, 809.

Gibson, J. B., A. N. Goland, M. Milgram, and G. H. Vineyard, 1960, Phys. Rev. **120**, 1229.

Gibson, W. G., 1970, Phys. Rev. **A2**, 996.

Gibson, W. G., 1972, Phys. Rev. **A5**, 862.

Gibson, W. G., 1974, Mol. Phys. **28**, 793.

Gibson, W. G., 1975a, Mol. Phys. **30**, 1.

Gibson, W. G., 1975b, Mol. Phys. **30**, 13.

Gibson, W. G., and S. G. Byrnes, 1975, Phys. Rev. **A11**, 270.

Gilbert, T. L., and A. C. Wahl, 1967, J. Chem. Phys. **47**, 3425.

Golden, S. 1965, Phys. Rev. **B137**, 1127.

Gordon, R. G., and Y. S. Kim, 1972, J. Chem. Phys. **56**, 3122.

Gordon, R. G., and G. Starkschall, 1972, J. Chem. Phys. **56**, 2801.

Gosling, E. M., I. R. McDonald, and K. Singer, 1973, Mol. Phys. 26, 1475.

Gray, C. G., 1975, in *Specialist Periodical Reports, Statistical Mechanics*, edited by K. Singer (Chemical Society, London), Vol. 2, p. 300.

Gray, C. G., and K. E. Gubbins, 1975, Mol. Phys. **30**, 179.

Green, H. S., 1951, J. Chem. Phys. **19**, 955.

Green, H. S., 1965, Phys. Fluids 8, 1.

Grundke, E. W., and D. Henderson, 1972, Mol. Phys. **24**, 269.

Grundke, E. W., D. Henderson, and R. D. Murphy, 1971, Can. J. Phys. **49**, 1593.

Grundke, E. W., D. Henderson, and R. D. Murphy, 1973, Can. J. Phys. **51**, 1216.

Grundke, E. W., D. Henderson, J. A. Barker, and P. J. Leonard, 1973, Mol. Phys. **25**, 883.

Gubbins, K. E., and C. G. Gray, 1972, Mol. Phys. **23**, 187.

Gubbins, K. E., W. R. Smith, M. K. Tham, and E. W. Tiepel, 1971, Mol. Phys. **22**, 1089.

Guerrero, M. I., J. S. Rowlinson, and B. L. Sawford, 1974, Mol. Phys. **28**, 1603.

Guggenheim, E. A., 1965a, Mol. Phys. **9**, 43.

Guggenheim, E. A., 1965b, Mol. Phys. **9**, 199.

ter Haar, D., 1971, in *Physical Chemistry-An Advanced Treatise: Liquid State*, edited by D. Henderson, H. Eyring, and W. Jost (Academic Press, New York), Vol. 8B, Chap. 8.

Haberlandt, R., 1964, Phys. Lett. **8**, 172.

Handelsman, R. A., and J. B. Keller, 1966, Phys. Rev. **148**, 94.

Hansen J.-P., 1970, Phys. Rev. **A2**, 221.

Hansen, J.-P., and E. L. Pollock, 1975, J. Chem. Phys. **62**, 4581.

Hansen, J.-P., and L. Verlet, 1969, Phys. Rev. **184**, 151.

Hansen, J.-P., and J.-J. Weis, 1969, Phys. Rev. **188**, 314.

Hansen, J.-P., D. Levesque, and D. Schiff, 1971, Phys. Rev. **A3**, 776.

Harasima, A., 1958, Adv. Chem. Phys. **1**, 203.

Harp, G. D., and B. J. Berne, 1970, Phys. Rev. **A2**, 1975.

Harris, S. J., and D. M. Tully-Smith, 1971, J. Chem. Phys. **55**, 1104.

Hart, R. W., R. Wallis, and L. Pode, 1951, J. Chem. Phys. **19**, 139.

Hauge, E. H., 1965, Thesis, Trondheim.

Helfand, E., H. L. Frisch, and J. L. Lebowitz, 1961, J. Chem. Phys. **34**, 1037.

Helfand, E., and F. H. Stillinger, 1962, J. Chem. Phys. **37**, 2646.

Heller, E. J., 1975, Chem Phys. Lett. **34**, 321.

Hemmer, P. C., 1964, J. Math. Phys. **5**, 75.

Hemmer, P. C., 1968, Phys. Lett. **27A**, 377.

Hemmer, P. C., and K. J. Mork, 1967, Phys. Rev. **158**, 114.

Hemmer, P. C., M. Kac, and G. E. Uhlenbeck, 1964, J. Math. Phys. **5**, 60.

Henderson, D., 1965, Mol. Phys. **10**, 73.

Henderson, D., 1971, Mol. Phys. **21**, 841.

Henderson, D., 1974, Annu. Rev. Phys. Chem. **25**, 461.

Henderson, D., 1975a, J. Chem. Phys. **63**,

Henderson, D., 1975b, Mol. Phys. **30**, 971.

Henderson, D., and J. A. Barker, 1968a, J. Chem. Phys. **49**, 3377.

Henderson, D., and J. A. Barker, 1968b, Mol. Phys. **14**, 587.

Henderson, D., and J. A. Barker, 1971, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8A, Chap. 6.

Henderson, D., and M. Chen, 1975, J. Math. Phys. **16**, 2042.

Henderson, D., and S. G. Davison, 1967, in *Physical Chemistry—An Advanced Treatise: Statistical Mechanics*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 2, Chap. 7.

Henderson, D., and E. W. Grundke, 1975, J. Chem. Phys. **63**, 601.

Henderson, D., and P. J. Leonard, 1971, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8B, Chap. 7.

Henderson, D., and R. D. Murphy, 1972, Phys. Rev. **A6**, 1224.

Henderson, D., and L. Oden, 1966, Mol Phys. **10**, 405.

Henderson, D., F. Abraham, and J. A. Barker, 1976, Mol. Phys. **31**, 1291.

Henderson, D., J. A. Barker, and W. R. Smith, 1972, Utilitas Mathematica **1**, 211.

Henderson, D., J. A. Barker, and W. R. Smith, 1976, J. Chem. Phys. **64**, 4244.

Henderson, D., J. A. Barker, and R. O. Watts, 1970, IBM J. Res. Dev. **14**, 668.

Henderson, D., S. Kim, and L. Oden, 1967, Discuss. Faraday Soc. **43**, 26.

Henderson, D., W. G. Madden, and D. D. Fitts, 1976, J. Chem. Phys. **64**, 5026.

Henderson, D., G. Stell, and E. Waisman, 1975, J. Chem. Phys. **62**, 4247.

Hildebrand, J. H., J. M. Prausnitz, and R. L. Scott, 1970, *Regular and Related Solutions* (Van Nostrand, Reinhold, New York).

Hill, R. N., 1968, J. Math. Phys. **9**, 1534; see references therein.

Hill, R. N., 1974, J. Stat. Phys. **11**, 207.

Hiroike, K., 1972, J. Phys. Soc. (Japan) **32**, 904.

Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, 1954, *Molecular Theory of Gases and Liquids* (Wiley, New York).

Honda, K., 1974a, Prog. Theor. Phys. (Japan) **52**, 385.

Honda, K., 1974b, Prog. Theor. Phys. (Japan) **53**, 889.

Hoover, W. G., and W. T. Ashurst, 1975, Theor. Chem. **1**, 1.

Hoover, W. G., and A. G. DeRocco, 1961, J. Chem. Phys. **34**, 1059.

Hoover, W. G., and A. G. DeRocco, 1962, J. Chem. Phys. **36**, 3141.

Hoover, W. G., and J. C. Poirier, 1962, J. Chem. Phys. **37**, 1041.

Hoover, W. G., and F. H. Ree, 1967, J. Chem. Phys. **47**, 4873.

Hoover, W. G., and F. H. Ree, 1968, J. Chem. Phys. **49**, 3609.

Hoover, W. G., and M. Ross, 1971, Contemp. Phys. **12**, 339.

Hoover, W. G., W. T. Ashurst, and R. J. Olness, 1973, J. Chem. Phys. **60**, 4043.

Hoover, W. G., K. W. Johnson, D. Henderson, J. A. Barker, and B. C. Brown, 1971, J. Chem. Phys. **52**, 4931.

Høye, J. S., and G. Stell, 1975a, unpublished work.

Høye, J. S., and G. Stell, 1975b, J. Chem. Phys. **63**, 5342.

Høye, J. S., J. L. Lebowitz, and G. Stell, 1974, J. Chem. Phys. **61**, 3253.

Hutchinson, P., and G. S. Rushbrooke, 1963, Physica **29**, 675.

Irving, J. H., and J. G. Kirkwood, 1950, J. Chem. Phys. **18**, 817.

Isbister, D., and R. J. Bearman, 1974, Mol. Phys. **28**, 1297.

Isihara, A., 1950, J. Chem. Phys. **18**, 1446.

Isihara, A., and T. Hayashida, 1951a, J. Phys. Soc. Jpn. **6**, 40.

Isihara, A., and T. Hayashida, 1951b, J. Phys. Soc. Jpn. **6**, 46.

Jansoone, V. M., 1974, Chem. Phys. **3**, 79.

Jancovici, B., 1969a, Phys. Rev. **178**, 295.

Jancovici, B., 1969b, Phys. Rev. **184**, 119.

Jepsen, D. W., 1966, J. Chem. Phys. **44**, 774.

Jhon, M. S., and H. Eyring, 1971, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8A, Chap. 5.

Johnson, C. H. J., and T. H. Spurling, 1971a, Aust. J. Chem. **24**, 1567.

Johnson, C. H. J., and T. H. Spurling, 1971b, Aust. J. Chem. **24**, 2205.

Johnson, C. H. J., and T. H. Spurling, 1974, Aust. J. Chem. **27**, 241.

Johnson, C. H. J., A. Pompe, and T. H. Spurling, 1972, Aust.

J. Chem. **25**, 2021.
Jordan, H. F., and L. D. Fosdick, 1968, Phys. Rev. **171**, 128.
Jorish, V. S., and V. Yu. Zitserman, 1975, Chem. Phys. Lett. **34**, 378.
Kac, M., G. E. Uhlenbeck, and P. C. Hemmer, 1963, J. Math. Phys. **4**, 216.
van Kampen, N. G., 1961, Physica **27**, 783.
Katsura, S., 1959, Phys. Rev. **115**, 1417.
Katsura, S., 1966, J. Chem. Phys. **45**, 3480.
Katsura, S., and Y. Abe, 1963, J. Chem. Phys. **39**, 2068.
Kalos, M. H., 1970 Phys. Rev. **A2**, 250.
Kalos, M. H., D. Levesque, and L. Verlet, 1974, Phys. Rev. **A9**, 2178.
Keesom, W. H., 1912, Commun. Phys. Lab. Univ. Leiden, Suppl. 24b, Section 6.
Keesom, W. H. 1915, Commun. Phys. Lab. Univ. Leiden, Suppl. 39a.
Kihara, T., 1951, J. Phys. Soc. Jpn. **6**, 289.
Kihara, T., 1953a, Rev. Mod. Phys. **25**, 831.
Kihara, T., 1953b, J. Phys. Soc. Jpn. 8, 686.
Kihara, T., 1955, Rev. Mod. Phys. **27**, 412.
Kihara, T., 1963, Adv. Chem. Phys. **5**, 147.
Kikuchi, R., 1951, Phys. Rev. **81**, 988.
Kilpatrick, J. E., and S. Katsura, 1966, J. Chem. Phys. **45**, 1866.
Kim, S., and D. Henderson, 1966, Proc. Natl. Acad. Sci. USA **55**, 705.
Kim, S., and D. Henderson, 1968a, Phys. Lett. **27A**, 379.
Kim, S., and D. Henderson, 1968b, Chem. Phys. Lett. **2**, 619.
Kim, S., D. Henderson, and J. A. Barker, 1969, Can. J. Phys. **47**, 99.
Kim, S., D. Henderson, and L. Oden, 1969, Trans. Faraday Soc. **65**, 2308.
Kim, Y. S., 1975a, Phys. Rev. **A11**, 796.
Kim, Y. S., 1975b, Phys. Rev. **A11**, 804.
Kim, Y. S., and R. G. Gordon, 1974, J. Chem. Phys. **61**, 1.
Kirkwood, J. G., 1933a, Phys. Rev. **44**, 31.
Kirkwood, J. G., 1933b, J. Chem. Phys. **1**, 597.
Kirkwood, J. G., 1935, J. Chem. Phys. **3**, 300.
Kirkwood, J. G., 1938, J. Chem. Phys. **6**, 70.
Kirkwood, J. G., and F. P. Buff, 1949, J. Chem. Phys. **17**, 338.
Kirkwood, J. G., and Z. W. Salsburg, 1953, Discuss. Faraday Soc. **15**, 28.
Kirkwood, J. G., V. A. Lewison, and B. J. Alder, 1952, J. Chem Phys. **20**, 929.
Kirkwood, J. G., E. K. Maun, and B. J. Alder, 1950, J. Chem. Phys. **18**, 1040.
Kistenmacher, H., G. C. Lie, H. Popkie, and E. Clementi, 1974, J. Chem. Phys. **61**, 546.
Kitaigorodsky, A. I., 1973, *Molecular Crystals and Molecules* (Academic Press, New York).
Kittel, C., 1958, *Elementary Statistical Physics* (Wiley, New York).
Klein, M., 1963, J. Chem. Phys. **39**, 1388.
Klein, M., and M. S. Green, J. Chem. Phys **39**, 1367.
Klein, W., 1973, J. Math. Phys. **14**, 1049.
Klein, M. L., and T. R. Koehler, 1976, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic Press, New York), Chap. 6.
Klemm, A. D., and R. G. Storer, 1973, Aust. J. Phys. **26**, 43.
Konowalow, D., and D. S. Zakheim, 1972, J. Chem. Phys. **57**, 4375.
Kozak, J. J., I. B. Schrodt, and K. D. Luks, 1972, J. Chem. Phys. **57**, 206.
van Laar, J. J., 1899, Proc. R. Acad. Sci. Amst. **1**, 273.
Landanyi, B. M., and D. Chandler, 1975, J. Chem. Phys. **62**, 4308.
Lado, F., and W. W. Wood, 1968, J. Chem. Phys. **49**, 4244.
Lal, M., and D. Spencer, 1973, Chem. Soc. Faraday Trans. II **69**, 1502; and references therein.
Landau, L. D., 1937, Phys. Z. Sowjetunion **11**, 545.
Landau, L. D., and E. M. Lifshitz, 1969, *Statistical Physics*, (Addison-Wesley, Reading, Mass.) 2nd edition.
Lebowitz, J. L., 1964, Phys. Rev. **133**, A895.
Lebowitz, J. L., and J. K. Percus, 1961, Phys. Rev. **122**, 1675.
Lebowitz, J. L., and J. K. Percus, 1963a, J. Math. Phys. **4**, 116.
Lebowitz, J. L., and J. K. Percus, 1963b, J. Math. Phys. **4**, 1495.
Lebowitz, J. L., and J. K. Percus, 1966, Phys. Rev. **144**, 251.
Lebowitz, J. L., and E. Praestgaard, 1964, J. Chem. Phys. **40**, 2951.
Lebowitz, J. L., and D. Zomick, 1971, J. Chem. Phys. **54**, 3335.
Lebowitz, J. L., E. Helfand, and E. Praestgaard, 1965, J. Chem. Phys. **43**, 774.
Lee, J. K., J. A. Barker, and F. F. Abraham, 1973, J. Chem. Phys. **58**, 3166.
Lee, J. K., J. A. Barker, and G. M. Pound, 1974, J. Chem. Phys. **60**, 1976.
Lee, J. K., D. Henderson, and J. A. Barker, 1975, Mol. Phys. **29**, 429.
Lee, L. L., and D. Levesque, 1973, Mol. Phys. **26**, 1351.
Lee, Y.-T., F. H. Ree, and T. Ree, 1968, J. Chem. Phys. **48**, 3506.
Lee, Y.-T., F. H. Ree, and T. Ree, 1969, Chem. Phys. Lett. **4**, 379.
Lee, Y.-T., F. H. Ree, and T. Ree, 1971, J. Chem. Phys. **55**, 234.
Leeuwen, J. M. J., J. Groeneveld, and J. de Boer, 1959, Physica **25**, 792.
LeFevre, E. J., 1972, Nature **235**, 20.
Lennard-Jones, J. E., and A. F. Devonshire, 1939a, Proc. R. Soc. Lond. **A169**, 317.
Lennard-Jones, J. E., and A. F. Devonshire, 1939b, Proc. R. Soc. Lond. **A170**, 464.
Leonard, P. J., 1968, M. Sc. Thesis, University of Melbourne.
Leonard, P. J., and J. A. Barker, 1975, Theor. Chem. **1**, 117.
Leonard, P. J., D. Henderson, and J. A. Barker, 1970, Trans. Faraday Soc. **66**, 2439.
Leonard, P. J., D. Henderson, and J. A. Barker, 1971, Mol. Phys. **21**, 107.
Levesque, D., 1966. Physica **32**, 1985.
Levesque, D., and L. Verlet, 1969, Phys. Rev. **182**, 307.
Levesque, D., and L. Verlet, 1970, Phys. Rev. **A2**, 2514.
Levesque, D., D. Schiff, and J. Vieillard-Baron, 1969, J. Chem. Phys. **51**, 3625.
Levesque, D., L. Verlet, and J. Kurkijarvi, 1973, Phys. Rev. **A7**, 1690.
Lewis, G. N., and M. Randall, 1961, *Thermodynamics*, (McGraw-Hill, New York) 2nd edition, revised by K. S. Pitzer and L. Brewer.
Lie, G., and E. Clementi, 1975, J. Chem. Phys. **62**, 2195.
Lincoln, W., J. J. Kozak, and K. D. Luks, 1975a, J. Chem. Phys. **62**, 1116.
Lincoln, W., J. J. Kozak, and K. D. Luks, 1975b, J. Chem. Phys. **62**, 2171.
Lincoln, W., Y. Tago, K. D. Luks, 1974, J. Chem. Phys. **61**, 4129.
Liu, B., and A. D. McLean, 1974, J. Chem. Phys. **59**, 4557.
Liu, B., and A. D. McLean, 1975, unpublished results.
Liu, K. S., 1974, J. Chem. Phys. **60**, 4226.
Lloyd, P., 1964, Aust. J. Phys. **17**, 269.
Longuet-Higgins, H. C., 1951, Proc. R. Soc. Lond. **A205**, 247.
Longuet-Higgins, H. C., and B. Widom, 1964, Mol. Phys. **8**, 549.
Lovett, R., P. W. De Haven, J. J. Vieceli, and F. P. Buff, 1973, J. Chem. Phys. **58**, 1880.
Lowden, L. J., and D. Chandler, 1973, J. Chem. Phys. **59**, 6587.
Lowden, L. J., and D. Chandler, 1974, J. Chem. Phys. **61**,

5228.

Lowry, G. G., 1970, Editor, *Markov Chains and Monte Carlo Calculations in Polymer Science* (Marcel Dekker, New York).

Lux, E., and A. Münster, 1967, Z. Phys. **199**, 465.

Lux, E., and A. Münster, 1968, Z. Phys. **213**, 46.

McCarty, M., Jr., and S. V. K. Babu, 1970, J. Phys. Chem. **74**, 1113.

McDonald, I. R., 1969, Chem. Phys. Lett. **3**, 241.

McDonald, I. R., 1973, in *Specialist Periodical Report, Statistical Mechanics*, edited by K. Singer (Chemical Society, London), Vol. 1, p. 134.

McDonald, I. R., 1974, J. Phys. **C7**, 1225.

McDonald, I. R., and J. C. Rasaiah, 1975, Chem. Phys. Lett. **34**, 382.

McDonald, I. R., and K. Singer, 1967, J. Chem. Phys. **47**, 4766.

McDonald, I. R., and K. Singer, 1969, J. Chem. Phys. **50**, 2308.

McLellan, A. G., 1952, Proc. R. Soc. Lond. **A210**, 509.

McMillan, W. L., 1965, Phys. Rev. **A138**, 442.

McQuarrie, D. A., 1964, J. Chem. Phys. **40**, 3455.

McQuarrie, D. A., and J. L. Katz, 1966, J. Chem. Phys. **44**, 2393.

Madden, W. G. and D. D. Fitts, 1974a, Chem. Phys. Lett. **28**, 427.

Madden, W. G. and D. D. Fitts, 1974b, J. Chem. Phys. **61**, 5475.

Madden, W. G. and D. D. Fitts, 1975, Mol. Phys. **30**, 809.

Mandel, F., 1973, J. Chem. Phys. **59**, 3907.

Mandel, F., and R. J. Bearman, 1969, J. Chem. Phys. **50**, 4121.

Mandel, F., R. J. Bearman, and M. Y. Bearman, 1970, J. Chem. Phys. **52**, 3315.

Mandell, M. J., and H. Reiss, 1975a, J. Stat. Phys. **13**, 107.

Mandell, M. J., and H. Reiss, 1975b, J. Stat. Phys. **13**, 113.

Mansoori, G. A., 1972, J. Chem. Phys. **56**, 5335.

Mansoori, G. A., and F. B. Canfield, 1969, J. Chem. Phys. **51**, 4958.

Mansoori, G. A., and F. B. Canfield, 1970, J. Chem. Phys. **53**, 1618.

Mansoori, G. A., and T. W. Leland, Jr., 1970, J. Chem. Phys. **53**, 1931.

March, N. H., 1968, *Liquid Metals* (Pergamon, Oxford).

Mason, E. A., and T. H. Spurling, 1969, *The Virial Equation* of State (Pergamon, Oxford).

Mayer, J. E., and M. G. Mayer, 1940, *Statistical Mechanics* (Wiley, New York).

Mayer, J. E., 1958, in *Handbuch der Physik*, edited by S. Flugge (Springer, Berlin), Vol. 12, Chap. 2.

Mazo, R., and J. G. Kirkwood, 1958, J. Chem. Phys. **28**, 644.

Meeron, E., 1960a, J. Math. Phys. **1**, 192.

Meeron, E., 1960b, Physica **26**, 445.

Meeron, E., 1960c, Prog. Theor. Phys. **24**, 588.

Meeron, E., and A. J. F., Siegert, 1968, J. Chem. Phys. **48**, 3139.

Melnyk, T. W., and W. R. Smith, 1974, Chem. Phys. Lett. **28**, 213.

Melnyk, T. W., J. S. Rowlinson, and B. L. Sawford, 1972, Mol. Phys. **24**, 809.

Metropolis, N., A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, 1953, J. Chem. Phys. **21**, 1087.

Michels, A., J. M. H. Levelt, and W. de Graaff, 1958, Physica **24**, 659.

Michels, A., Hub. Wijker, and Hk. Wijker, 1949, Physica **15**, 627.

Mikeska, H.-J., and H. Schmidt, 1970, J. Low Temp. Phys. **2**, 371.

Miyazaki, J., and J. A. Barker, 1975, unpublished results.

Miyazaki, J., J. A. Barker, and G. M. Pound, 1976, J. Chem. Phys. **64**, 3364.

Mo, K. C., and K. E. Gubbins, 1974, Chem. Phys. Lett. **27**, 144.

Morita, T., 1958, Prog. Theor. Phys. **20**, 920.

Morita, T., 1960, Prog. Theor. Phys. **23**, 829.

Morita, T., and K. Hiroike, 1960, Prog. Theor. Phys. **23**, 1003.

Morita, T., and K. Hiroike, 1961, Prog. Theor. Phys. **25**, 537.

Morita, T., and T. Tanaka, 1966, Phys. Rev. **145**, 288.

Murphy, R. D., 1971, Phys. Rev. **A5**, 331.

Murphy, R. D., and M. L. Klein, 1973, Phys. Rev. **A8**, 2640.

Murphy, R. D., and R. O. Watts, 1970, J. Low Temp. Phys. **2**, 507.

Narten, A. H., L. Blum, and R. H. Fowler, 1974, J. Chem. Phys. **60**, 3378.

Nesbet, R. K., 1968, J. Chem. Phys. **48**, 1419.

Nijboer, B. R. A., and R. Fieschi, 1953, Physica **19**, 545.

Nijboer, B. R. A., and L. van Hove, 1952, Phys. Rev. **85**, 771.

Nilsen, T. S., 1969, J. Chem. Phys. **51**, 4675.

Nordsieck, A., 1962, Math. Comput. **16**, 22.

Norman, G. E., and V. S. Filinov, 1969, High Temp. USSR **7**, 216.

Oden, L., D. Henderson, and R. Chen, 1966, Phys. Lett. **21**, 420.

Onsager, L., 1936, J. Am. Chem. Soc. **58**, 1486.

Onsager, L., 1942, Phys. Rev. **62**, 558.

Onsager, L., 1949, Ann. N. Y. Acad. Sci. **51**, 627.

Opitz, A. C. L., 1974, Phys. Lett. **47**, 439.

Ornstein, L. S., and F. Zernike, 1914, Proc. Acad. Sci. Amsterdam **17**, 793.

O'Shea, S. F., and W. J. Meath, 1974, Mol. Phys. **28**, 1431.

Oxtoby, D. W., and W. M. Gelbart, 1976, Phys. Rev. **A122**, 227.

Patey, G. N., and J. P. Valleau, 1973, Chem. Phys. Lett. **21**, 297.

Patey, G. N., and J. P. Valleau, 1974, J. Chem. Phys. **61**, 534.

Patey, G. N., and J. P. Valleau, 1975, J. Chem. Phys. **63**, 2324.

Patey, G. N., and J. P. Valleau, 1976, J. Chem. Phys. **64**, 170.

Peierls, R., 1936, Helv. Phys. Acta Suppl. ii, 81.

Penrose, O., and J. L. Lebowitz, 1972, J. Math. Phys. **13**, 604.

Percus, J. K., 1962, Phys. Rev. Lett. 8, 462.

Percus, J. K., and G. J. Yevick, 1958, Phys. Rev. **110**, 1.

Perram, J. W., 1975, Mol. Phys. 30, 1505.

Perram, J. W., and L. R. White, 1972, Mol. Phys. **24**, 1133.

Perram, J. W., and L. R. White, 1974, Mol. Phys. **28**, 527.

Pitzer, K. S., 1939, J. Chem. Phys. **7**, 583.

Pompe, A., and T. H. Spurling, 1973, Aust. J. Chem. **26**, 855.

Popkie, H., H. Kistenmacher, and E. Clementi, 1973, J. Chem. Phys. **59**, 1325.

Pople, J. A., 1954a, Proc. R. Soc. Lond. **A221**, 498.

Pople, J. A., 1954b, Proc. R. Soc. Lond. **A221**, 508.

Powell, M. J. D., 1964, Mol. Phys. **7**, 591.

Praestgaard, E., and S. Toxvaerd, 1970, J. Chem. Phys. **53**, 2389.

Quentrec, B., and C. Brot, 1973, J. Comput. Phys. **13**, 430.

Rahman, A., 1964, Phys. Rev. **A136**, 405.

Rahman, A., 1968, in *Neutron Inelastic Scattering* (International Atomic Energy Agency, Vienna), p. 561.

Rahman, A., 1970, in *Interatomic Potentials and Simulation of Lattice Defects*, edited by P. C. Gehlen, J. R. Beeler, and R. I. Jaffee (Plenum, New York), p. 233.

Rahman, A., and F. H. Stillinger, 1971, J. Chem. Phys. **55**, 3336.

Rasaiah, J. C., and G. Stell, 1970a, Mol. Phys. **18**, 249.

Rasaiah, J. C., and G. Stell, 1970b, Chem. Phys. Lett. **4**, 651.

Raveché, H. J., and C. A. Stuart, 1975, J. Chem. Phys. **63**, 1099.

Raveché, H. J., R. D. Mountain, and W. B. Streett, 1974, J. Chem. Phys. **61**, 1970.

Raveché, H. J., R. D. Mountain, and W. B. Streett, 1975, J.

Chem. Phys. **62**, 4582.
Ree, F. H., 1970, J. Chem. Phys. **53**, 920.
Ree, F. H., 1971, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8A, Chap. 3.
Ree, F. H., and W. G. Hoover, 1964a, J. Chem. Phys. **40**, 939.
Ree, F. H., and W. G. Hoover, 1964b, J. Chem. Phys. **40**, 2048.
Ree, F. H., and W. G. Hoover, 1967, J. Chem. Phys. **46**, 4181.
Ree, F. H., R. N. Keeler, and S. L. McCarthy, 1966, J. Chem. Phys. **44**, 3407.
Reiss, H., 1965, Adv. Chem. Phys. **9**, 1.
Reiss, H., and R. V. Casberg, 1974, J. Chem. Phys. **61**, 1107.
Reiss, H., H. L. Frisch, and J. L. Lebowitz, 1959, J. Chem. Phys. **31**, 369.
Reiss, H., and D. M. Tully-Smith, 1971, J. Chem. Phys. **55**, 1674.
Rice, S. A., and J. Lekner, 1965, J. Chem. Phys. **42**, 3559.
Rice, S. A., and D. A. Young, 1967, Discuss. Faraday Soc. **43**, 16.
Rigby, M., 1970, J. Chem. Phys. **53**, 1021.
Rigby, M., 1972, J. Chem. Phys. **76**, 2014.
Rotenberg, A., 1965, J. Chem. Phys. **43**, 1198.
Rowley, L. A., D. Nicholson, and N. G. Parsonage, 1975, J. Comput. Phys. **17**, 401.
Rowlinson, J. S., 1949, Trans. Faraday Soc. **45**, 974.
Rowlinson, J. S., 1951a, J. Chem. Phys. **19**, 927.
Rowlinson, J. S., 1951b, Trans. Faraday Soc. **47**, 120.
Rowlinson, J. S., 1963, Mol. Phys. **6**, 517.
Rowlinson, J. S., 1964a, Proc. R. Soc. **A279**, 147.
Rowlinson, J. S., 1964b, Mol. Phys. **7**, 349.
Rowlinson, J. S., 1964c, Mol. Phys. **8**, 107.
Rowlinson, J. S., 1965, Mol. Phys. **9**, 217.
Rowlinson, J. S., 1966, Mol. Phys. **10**, 533.
Rowlinson, J. S., 1967, Mol. Phys. **12**, 513.
Rudd, W. G., Z. W. Salsburg, A. P. Yu, and F. H. Stillinger, 1969, J. Chem. Phys. **49**, 4857.
Rushbrooke, G. S., 1960, Physica **26**, 259.
Rushbrooke, G. S., and P. Hutchinson, 1961, Physica **27**, 647.
Rushbrooke, G. S., and I. Scoins, 1951, Phil. Mag. **42**, 582.
Rushbrooke, G. S., and M. Silbert, 1967, Mol. Phys. **12**, 505.
Rushbrooke, G. S., G. Stell, and J. S. Høye, 1973, Mol. Phys. **26**, 1199.
Sabry, A. A., 1954, Physica **54**, 60.
Sandler, S. I., 1974, Mol. Phys. **28**, 1207.
Schiff, D., 1969, Phys. Rev. **186**, 151.
Schiff, D., and L. Verlet, 1967, Phys. Rev. **160**, 208.
Schofield, P., 1966, Proc. Phys. Soc. Lond. **88**, 149.
Schrodt, I. B., and K. D. Luks, 1972, J. Chem. Phys. **57**, 200.
Schrodt, I. B., J. J. Kozak, and K. D. Luks, 1974, J. Chem. Phys. **60**, 170.
Schrodt, I. B., J. S. Ku, and K. D. Luks, 1972, J. Chem. Phys. **57**, 4589.
Scott, R. A., and H. A. Scheraga, 1966, J. Chem. Phys. **45**, 2091.
Scott, R. L., 1971, in *Physical Chemistry—An Advanced Treatise: Liquid State*, edited by H. Eyring, D. Henderson, and W. Jost (Academic Press, New York), Vol. 8A, Chap. 1.
Shipman, L. L., and H. A. Scheraga, 1974, J. Chem. Phys. **78**, 909.
Singh, Y., 1974, Mol. Phys. **27**, 1687.
Singh, Y., and K. K. Datta, 1970, J. Chem. Phys. **53**, 1184.
Singh, Y., and J. Ram, 1973, Mol. Phys. **25**, 145.
Singh, Y., and J. Ram, 1974, Mol. Phys. **28**, 197.
Smith, E. B., and B. J. Alder, 1959, J. Chem. Phys. **30**, 1190.
Smith, E. R., and J. W. Perram, 1975, Mol. Phys. **30**, 31.
Smith, W. R., 1973, in *Specialist Periodical Report, Statistical Mechanics*, edited by K. Singer (Chemical Society, London), Vol. 1, p. 71.
Smith, W. R., and D. Henderson, 1970, Mol. Phys. **19**, 411.
Smith, W. R., and D. Henderson, 1972, Mol. Phys. **24**, 773.
Smith, W. R., D. Henderson, and J. A. Barker, 1970, J. Chem. Phys. **53**, 508.
Smith, W. R., D. Henderson, and J. A. Barker, 1971, J. Chem. Phys. **55**, 4027.
Smith, W. R., D. Henderson, and J. A. Barker, 1975, Can. J. Phys. **53**, 5.
Smith, W. R., D. Henderson, and R. D. Murphy, 1974, J. Chem. Phys. **61**, 2911.
Smith, W. R., D. Henderson, and Y. Tago, 1976, unpublished work.
Sprow, F. B., and J. M. Prausnitz, 1966, Trans. Faraday Soc. **62**, 1097.
Squire, D. R., and W. G. Hoover, 1969, J. Chem. Phys. **50**, 701.
Squire, D. R., and Z. W. Salsburg, 1964, J. Chem. Phys. **40**, 2364.
Starkschall, G., and R. G. Gordon, 1971, J. Chem. Phys. **54**, 663.
Steele, W. A., and S. I. Sandler, 1974, J. Chem. Phys. **61**, 1315.
Stell, G., 1962, J. Chem. Phys. **36**, 1817.
Stell, G., 1963, Physica **29**, 517.
Stell, G., 1970, SUNY, Stony Brook, College of Engineering Report No. 182.
Stell, G., J. C. Rasaiah, and H. Narang, 1972, Mol. Phys. **23**, 393.
Stell, G., J. C. Rasaiah, and H. Narang, 1974, Mol. Phys. **27**, 1393.
Stephen, M. J., and J. P. Straley, 1974, Rev. Mod. Phys. **46**, 617.
Stillinger, F. H., and M. A. Cotter, 1971, J. Chem. Phys. **55**, 3449.
Stillinger, F. H., and A. Rahman, 1972, J. Chem. Phys. **57**, 1281.
Stillinger, F. H., and A. Rahman, 1974, J. Chem. Phys. **60**, 1545.
Stockmayer, W. H., 1941, J. Chem. Phys. **9**, 398.
Storer, R. G., 1968, Phys. Rev. **176**, 326.
Streett, W. B., H. J. Raveché, and R. D. Mountain, 1974, J. Chem. Phys. **61**, 1960.
Sung, S., and D. Chandler, 1972, J. Chem. Phys. **56**, 4989.
Sung, S., and D. Chandler, 1974, Phys. Rev. **A9**, 1688.
Sutherland, J. W. H., G. Nienhius, and J. M. Deutch, 1974, Mol. Phys. **27**, 721.
Sweet, J. R., and W. A. Steele, 1967, J. Chem. Phys. **47**, 3029.
Sweet, J. R., and W. A. Steele, 1969, J. Chem. Phys. **50**, 668.
Tago, Y., 1973a, J. Chem. Phys. **58**, 2096.
Tago, Y., 1973b, Phys. Lett. **44A**, 43.
Tago, Y., 1974, J. Chem. Phys. **60**, 1528.
Taylor, W. J., 1956, J. Chem. Phys. **24**, 454.
Theeuwes, F., and R. J. Bearman, 1970, J. Chem. Phys. **53**, 3114.
Thiele, E., 1963, J. Chem. Phys. **39**, 474.
Throop, G. J., and R. J. Bearman, 1965, J. Chem. Phys. **42**, 2408.
Throop, G. J., and R. J. Bearman, 1966a, Physica **32**, 1298.
Throop, G. J., and R. J. Bearman, 1966b, J. Chem. Phys. **44**, 1423.
Throop, G. J., and R. J. Bearman, 1967, J. Chem. Phys. **47**, 3036.
Timling, K. M., 1974, J. Chem. Phys. **61**, 465.
Tonks, L., 1936, Phys. Rev. **50**, 955.
Torrie, G. M., and J. P. Valleau, 1974, Chem. Phys. Lett. **28**, 578.
Torrie, G. M., J. P. Valleau, and A. Bain, 1973, J. Chem. Phys. **58**, 5479.
Torrie, G. M., and J. P. Valleau, 1976, J. Comput. Phys., to be published.
Toxvaerd, S., 1971, J. Chem. Phys. **55**, 3116.

Toxvaerd, S., 1975, in *Specialist Periodical Report, Statistical Mechanics*, edited by K. Singer (Chemical Society, London), Vol. 2, p. 256.

Toxvaerd, S., 1976, J. Chem. Phys., in press.

Trickey, S. B., F. R. Green, and F. W. Averill, 1973, Phys. Rev. **B8**, 4822.

Triezenberg, D. G., and R. W. Zwanzig, 1972, Phys. Rev. Lett. **28**, 1183.

Tsien, F. and J. P. Valleau, 1974, Mol. Phys. **27**, 177.

Tully-Smith, D. M., and H. Reiss, 1970, J. Chem. Phys. **53**, 4015.

Uhlenbeck, G. E., and E. Beth, 1936, Physica **3**, 729.

Uhlenbeck, G. E., and G. W. Ford, 1962, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland, Amsterdam), Vol. 1, p. 123.

Uhlenbeck, G. E., P. C. Hemmer, and M. Kac, 1963, J. Math. Phys. **4**, 229.

Valleau, J. P., and D. N. Card, 1972, J. Chem. Phys. **57**, 5457.

Valleau, J. P. and G. M. Torrie, 1976a, "A Guide to Monte Carlo for Statistical Mechanics: I. Highways", preprint.

Valleau, J. P. and G. M. Torrie, 1976b, "A Guide to Monte Carlo for Statistical Mechanics: 2. Byways", preprint.

Verlet, L., 1960, Nuovo Cimento **18**, 77.

Verlet, L., 1964, Physica **30**, 95.

Verlet, L., 1965, Physica **31**, 959.

Verlet, L., 1967, Phys. Rev. **159**, 98.

Verlet, L., 1968, Phys. Rev. **165**, 201.

Verlet, L., and D. Levesque, 1962, Physica **28**, 1124.

Verlet, L., and D. Levesque, 1967, Physica **36**, 254.

Verlet, L., and J.-J. Weis, 1972a, Phys. Rev. **A5**, 939.

Verlet, L., and J.-J. Weis, 1972b, Mol. Phys. **24**, 1013.

Verlet, L., and J.-J. Weis, 1974, Mol. Phys. **28**, 665.

Vieceli, J. J., and H. Reiss, 1972a, J. Chem. Phys. **57**, 3747.

Vieceli, J. J., and H. Reiss, 1972b, J. Stat. Phys. **7**, 143.

Vieceli, J. J., and H. Reiss, 1973, J. Stat. Phys. **8**, 299.

Vieillard-Baron, J., 1972, J. Chem. Phys. **56**, 4729.

Vieillard-Baron, J., 1974, Mol. Phys. **28**, 809.

Voronstov-Vel'yaminov, R. N., H. M. El'y-Ashevich, L. A. Morgenstern, and V. P. Chakovskikl, 1970, High Temp. USSR **8**, 261.

van der Waals, J. D., 1873, Thesis, Amsterdam.

van der Waals, J. D., 1894, Z. Phys. Chem. **13**, 657.

Waisman, E., 1973a, Mol. Phys. **25**, 45.

Waisman, E., 1973b, J. Chem. Phys. **59**, 495.

Waisman, E., 1974, unpublished work.

Waisman, E., and J. L. Lebowitz, 1970, J. Chem. Phys. **52**, 4307.

Waisman, E., and J. L. Lebowitz, 1972a, J. Chem. Phys. **56**, 3086.

Waisman, E., and J. L. Lebowitz, 1972b, J. Chem. Phys. **56**, 3093.

Wang Chang, C. S., 1944, Thesis, University of Michigan.

Watts, R. O., 1968, J. Chem. Phys. **48**, 50.

Watts, R. O., 1969a, J. Chem. Phys. **50**, 984.

Watts, R. O., 1969b, J. Chem. Phys. **50**, 1358.

Watts, R. O., 1969c, J. Chem. Phys. **50**, 4122.

Watts, R. O., 1969d, Can. J. Phys. **47**, 2709.

Watts, R. O., 1971, Aust. J. Phys. **24**, 53.

Watts, R. O., 1972, Mol. Phys. **23**, 445.

Watts, R. O., 1973, in *Specialist Periodical Report, Statistical Mechanics*, edited by K. Singer (Chemical Society, London), Vol. 1, p. 1.

Watts, R. O., 1974, Mol. Phys. **28**, 1069.

Watts, R. O., D. Henderson, and J. A. Barker, 1972, J. Chem. Phys. **57**, 5391.

Weeks, J. D., and D. Chandler, 1970, Phys Rev. Lett. **25**, 149.

Weeks, J. D., D. Chandler, and H. C. Andersen, 1971a, J. Chem. Phys. **54**, 5237.

Weeks, J. D., D. Chandler, and H. C. Andersen, 1971b, J. Chem. Phys. **55**, 5422.

Weir, R. D., I. Wynn-Jones, J. S. Rowlinson, and G. Saville, 1967, Trans. Faraday Soc. **63**, 1320.

Wertheim, M. S., 1963, Phys. Rev. Lett. **10**, 321.

Wertheim, M. S., 1964, J. Math. Phys. **5**, 643.

Wertheim, M. S., 1967, J. Math. Phys. **8**, 927.

Wertheim, M. S., 1971, J. Chem. Phys. **55**, 4291.

Westera, K., and E. R. Cowley, 1975, Phys. Rev. **B11**, 4008.

Widom, B., 1963, J. Chem. Phys. **39**, 2808.

Widom, B., 1972, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, New York), Vol. 2. Chap. 3.

Widom, B., and J. S. Rowlinson, 1970, J. Chem. Phys. **52**, 1670.

Wigner, E., 1932, Phys. Rev. **40**, 749.

Williams, D. E., 1967, J. Chem. Phys. **47**, 4680.

Wood, W. W., 1968a, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (North-Holland, Amsterdam), Chap. 5.

Wood, W. W., 1968b, J. Chem. Phys. **48**, 415.

Wood, W. W., 1970, J. Chem. Phys. **52**, 729.

Wood, W. W., and J. D. Jacobson, 1957, J. Chem. Phys. **27**, 1207.

Wood, W. W., and F. R. Parker, 1957, J. Chem. Phys. **27**, 720.

Workman, H., and M. Fixman, 1973, J. Chem. Phys. **58**, 5024.

Yarnell, J. L., M. J. Katz, R. G. Wenzel, and S. H. Koenig, 1973, Phys. Rev. **A7**, 2130.

Young, D. A., and B. J. Alder, 1974, J. Chem. Phys. **60**, 1254.

Young, D. A., and S. A. Rice, 1967a, J. Chem. Phys. **46**, 539.

Young, D. A., and S. A. Rice, 1967b, J. Chem. Phys. **47**, 4228.

Young, D. A., and S. A. Rice, 1967c, J. Chem. Phys. **47**, 5061.

Yvon, J., 1935, Actualités Scientifiques et Industrielles, Vol. **203**.

Zeiss, G. D., and W. J. Meath, 1975, Mol. Phys. **30**, 161.

Zucker, I. J., and M. B. Doran, 1976, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic Press, New York), Chap. 3.

Zwanzig, R. W., 1954, J. Chem. Phys. **22**, 1420.

Zwanzig, R. W., 1956, J. Chem. Phys. **24**, 855.

Zwanzig, R. W., 1963, J. Chem. Phys. **39**, 1714.

Zwanzig, R. W., J. G. Kirkwood, K. F. Stripp, and I. Oppenheim, 1953, J. Chem. Phys. **21**, 1268.

Zwanzig, R. W., J. G. Kirkwood, K. F. Stripp, and I. Oppenheim, 1954, J. Chem. Phys. **22**, 1625.