polarizabilities of the levels.

[11] E. Lindholm, Arkiv Mat. Astron. Fysik 32A, 17 (1945); H. M. Foley, Phys. Rev. 69, 616 (1946).

[12] S. G. Rautian and I. I. Sobelman, Usp. Fiz. Nauk 90, 209 (1966) [Sov. Phys. Usp. 9, 701 (1967)]. The velocity after a "strong" or "weak" collision is uncorrelated or highly correlated, respectively, to the velocity before the collision.

[13] M. I. D'Yakonov and V. I. Perel, Zh. Eksperim. i Teor. Fiz. 47, 1483 (1964) [Sov. Phys. JETP 20, 997 (1965)]. It should be noted that this radiation-trapping contribution was derived under the assumptions that (a) average separation of atoms $\gg$ resonant transition wavelength and (b) Doppler width $\gg$ collision or natural width. In Ref. 8, Sec. VIII, it was conjectured that condition (b) alone was sufficient for the validity of the radiation-trapping term. Even so, under typical conditions at a few Torr, the ratio of collision to Doppler width ≈ 0.1 so that errors of 10% may already be introduced at these pressures.

[14] M. I. D'Yakonov and V. I. Perel', Zh. Eksperim. i Teor. Fiz. 58, 1090 (1970) [Sov. Phys. JETP 31, 585 (1970)]. The same cautionary comments given in Ref. 13 still apply.

[15] For a discussion of quantum distribution functions and a related bibliography, see Leon Cohen, Ph. D. thesis (Yale University, 1966) (unpublished); J. Math. Phys. 7, 781 (1966). Wigner's paper on the subject is given in Phys. Rev. 40, 749 (1932).

[16] For example, in a Stern-Gerlach experiment where the external magnetic field does act in a state-dependent manner, there is no correct classical trajectory that one can associate with an off-diagonal density matrix element.

[17] K. Gottfried, *Quantum Mechanics* (Benjamin, New York, 1966), Vol. 1, Sec. 12.

[18] E. W. Smith, J. Cooper, W. R. Chappell, and T. Dillon, J. Quant. Spectry. Radiative Transfer 11, 1547 (1971); 11, 1567 (1971). The author would like to thank Dr. Smith for providing preprints of their articles, which contain results in agreement with those of Ref. 4.

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Equilibrium Theory of Simple Liquids

Loup Verlet and Jean-Jacques Weis
Laboratoire de Physique Théorique et Hautes Energies, 91-Orsay, France *

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The perturbation theory of liquids developed recently by Weeks, Chandler, and Andersen (WCA) is examined in detail: Each assumption introduced by these authors is tested by comparison with "exact" computer results. It is shown that the basic assumptions of WCA are justified. An improved expression for the radial distribution function of the hard-sphere gas enables us to correct for some further inconsistent assumptions of the WCA theory. We then succeed in giving simple analytical expressions for the thermodynamic functions of the Lennard-Jones fluid shown to be quite good at high density. We show that the remainder of the perturbation series, which converges slowly at lower density, can be evaluated with the help of the Percus-Yevick equation. We therefore possess a unified theory of liquids which is especially simple at high density. Finally we reexpress the original WCA theory in an analytical form.

I. INTRODUCTION

A perturbation theory of liquids has been introduced by Zwanzig,[1] and been revived and generalized recently by several authors[2-4]: The excess free energy is expanded as a series in a parameter λ multiplying some part of the interaction considered as a perturbation (e.g., the attractive part); the statistical averages of the terms of the series are calculated for a system interacting with the remaining part of the interaction, the so-called "reference system." The first-order term of the expansion involves the evaluation of the perturbing interaction averaged over the reference system. The next-order terms involve the averages of the fluctuations with respect to the average perturbed energy and they are very complicated to evaluate.

The method is feasible and useful because advantage can be taken of the similarity between the reference system interacting with repulsive interactions and that composed of hard spheres. Such a similarity is, as a matter of fact, already present for the full system at high density: It is well known that the structure factors of dense liquids can be interpreted with a hard-sphere model.[5]

A prerequirement of that kind of theory is therefore a correct knowledge of the hard-sphere system. The equation of state of a hard-sphere system is quite well known at present[6] owing to the extensive computer work of Alder and Wainwright.[7] The situation regarding the radial distribution function (rdf) is not so satisfactory. It is well known that the Wertheim[8]-Thiele[9] (WT) analytical solution of the Percus-Yevick (PY) equation is good when the density is not too high: It becomes quite unsatisfactory for very dense states. We use hard-sphere rdf obtained through computer experiments[10,11] in order to improve the WT solution.

Introducing essentially one empirical parameter, we can succeed in fitting very well the computer data up to the transition density (Sec. II).

In Sec. III we study the convergence of the λ expansion for various separations of the Lennard-Jones (LJ) potential into a reference and a perturbing part. In particular, a new way of handling the perturbation problem has been considered recently by Weeks, Chandler, and Andersen (WCA).[12] These authors take for the reference system potential $v_0(r)$ that part of the potential which gives rise to the repulsive force and vanishes when the force vanishes. The remainder of the LJ potential, $w(r)$, is treated as a perturbation. We show that in the dense states this separation leads to a very rapid convergence of the λ expansion: Near triple point the first-order term in the perturbation series for the free energy is 200 times as large as the remainder of the series. This constitutes an order-of-magnitude improvement over ways of handling the problem, and we shall concentrate on that division of the potential.

In the same section we examine another approximation made by WCA,[12] which, although in the same spirit as the λ expansion, is more restrictive. It consists in replacing, when calculating the pressure through the virial theorem, $g(r)$ the rdf of the total system by $g_0(r)$, the rdf of the reference system. We show that this assumption leads to incorrect results.

We then examine (Sec. IV) how the reference system can be replaced by hard spheres. Using an approximation already introduced by Kim,[13] WCA have proposed to replace the reference system rdf $g_0(r)$ by the approximation $\hat{g}_0(r)$ given by

$$\hat{g}_0(r) = e^{-\beta v_0(r)}\, y_{\mathrm{HS}}(r/d, \eta) \;, \qquad (1.1)$$

where $y_{\mathrm{HS}}(r/d, \eta)$ is the rdf of a hard-sphere gas of diameter d, and packing fraction $\eta = \frac{1}{6}\pi\rho d^3$, smoothly extrapolated when $r < d$. The diameter d is determined through a self-consistency criterion also due to WCA. We show that both this criterion and approximation (1.1) are excellent but that the use of the WT solution made by these authors is not correct for high densities where the results of Sec. II should be used.

It is possible to expand $y_{\mathrm{HS}}(r/d, \eta)$ around $r = d$ owing to the fact that $v_0(r)$ varies very fast in that region.[13] Then simple expressions can be given for the diameter: It is given by the well-known expression of Barker and Henderson[2] with a small correction. The pressure is, but for a small correction, that of a hard-sphere gas of packing fraction η.

In Sec. V, we consider the first-order free energy. We show that without appreciable loss of precision due to the approximations, it can be expressed analytically.

We are then ready (Sec. VI) to calculate the thermodynamic properties of the system: the excess free energy, the compressibility factor $p/\rho kT$, the excess internal energy, all of which are given expressions which can be calculated without computing facilities and which are shown to be very satisfactory at high density. The defects, seen at lower density, are not due to any numerical mistreatment but mainly to the lack of convergence of the λ expansion at low density, where the fluctuations of the perturbing potentials are large. We therefore resort to a mixed perturbation scheme.[14] We add to the free energy calculated to the first order in λ the remainder expanded in the density up to ρ^3.

Section VII is devoted to the results specifically obtained by WCA. There appears to be a miraculous cancellation of the errors entailed by the two unjustified approximations we have mentioned above: the replacement of $g(r)$ by $g_0(r)$ in the virial theorem and the use of the WT approximation at high density. It follows that using this coincidence and the analytical procedures developed in the present paper, we can give an equation of state which is simpler, although less justified, than that of Sec. VI. It reproduces exactly the results of WCA which are known to be quite good at high density.

Once it has been verified that the cancellation of errors mentioned above occurs for all high-density states, the WCA approach provides an easy and efficient way of calculating the rdf and gives a simple formula for the diameter of those equivalent hard spheres which determine the structure factor in the hard-sphere model.[5,15] Although there are some empirical elements in their foundations, these expressions for the rdf and the structure factors can be quite useful in practice.

II. RADIAL DISTRIBUTION FUNCTION FOR HARD SPHERES

We wish to give a simple approximation for the hard-sphere rdf for densities extending up to the transition density. We know that, at low density, the solution of the PY equation given analytically by Wertheim[8] and by Thiele[9] yields such a representation. The direct correlation function is equal to zero for $r \geq d$ and otherwise given by

$$c_W(r/d) = -\lambda_1 - 6\eta\lambda_2(r/d) - \tfrac{1}{2}\eta\lambda_1(r/d)^3 \;, \qquad (2.1)$$

with

$$\lambda_1 = (1+2\eta)^2/(1-\eta)^4 \;, \qquad (2.2)$$

$$\lambda_2 = -(1+\tfrac{1}{2}\eta)^2/(1-\eta)^4 \;. \qquad (2.3)$$

From there it is possible to obtain the rdf $g_W(r/d, \eta)$ using the Ornstein-Zernike relation which reads:

$$\tilde{h}_W(kd,\eta)=\int e^{i\vec{k}\cdot\vec{r}}[g_W(r/d,\eta)-1]\,d\vec{r}$$
$$=\frac{\tilde{c}_W(kd)}{1-\rho\tilde{c}_W(kd)}\ , \tag{2.4}$$

where $\tilde{c}_W(kd)$ is the Fourier transform of the direct correlation (2.1).

Computer experiments[10,11] show that the WT rdf is incorrect and should be improved. Such experiments have been performed on a system of 864 hard spheres by Schiff and Verlet[11] for the following values of the packing fraction: $\eta=0.35$, $\eta=0.4$, $\eta=0.45$, $\eta=0.47$, $\eta=0.49$. Of the order of 10^6 configurations were used in each case. A comparison of the rdf $g(r/d,\eta)$ thus obtained with the WT rdf $g_W(r/d,\eta)$ shows that the latter suffers from three defects, which become very apparent near the transition.

(1) $g_W(r/d,\eta)$ is too small near the core.

(2) Its oscillations for large r have the consequence that the main maximum of the structure factor, equal to $1+\rho\tilde{h}(kd,\eta)$, is too high.

(3) $g_W(r/d,\eta)$ oscillates slightly out of phase with respect to the exact rdf $g(r/d,\eta)$.

The last two defects can be corrected by approximating, for $r>d$, $g(r/d,\eta)$ by $g_W(r/d_W,\eta_W)$ where d_W is smaller than d and obeys the relation

$$d_W^3/\eta_W=d^3/\eta=6/\pi\rho\ . \tag{2.5}$$

As we shall see, d_W can be adjusted so that an almost perfect fit of the rdf is obtained except near the core where the first defect mentioned above is still worse. To correct for this, we add a short-range term $\delta g_1(r)$ designed so as to produce the correct behavior near the core. We thus write

$$g(r/d,\eta)=g_W(r/d_W,\eta_W)+\delta g_1(r)\ , \tag{2.6}$$

with

$$\delta g_1(r)=(A/r)\,e^{-\mu(r-d)}\cos\mu(r-d)\ . \tag{2.7}$$

In order to determine d_W, we use the rdf which are computed[11] for $r<3d$ and we minimize the integral

$$\int_{r_1}^{3d}|g(r/d,\eta)-g_W(r/d_W,\eta_W)|\,d\vec{r}\ , \tag{2.8}$$

where $r_1=1.6d$ is large enough so that the second term in (2.6) is negligible. The results can be represented using (2.5) and the empirical formula

$$\eta_W=\eta-\tfrac{1}{16}\eta^2\ . \tag{2.9}$$

A is fixed so that the correct value for the rdf at core is obtained:

$$A/d=g(1,\eta)-g_W(d/d_W,\eta_W)\ . \tag{2.10}$$

$g(1,\eta)$ is obtained using the virial theorem and the excellent equation of state for hard spheres recently suggested by Carnahan and Stirling[6]:

$$Z_{\mathrm{HS}}(\eta)=1+4\eta\,g(1,\eta)$$
$$=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\ . \tag{2.11}$$

Since d/d_W is nearly equal to 1, we may expand $g_W(x,\eta)$ around 1 and use the fact that the values of the WT rdf and of its derivatives at core can be calculated using the continuity at core of $g_W(x,\eta)-c_W(x,\eta)$ and that of its three first derivatives.

We then find easily, using (2.9) and neglecting small terms,

$$\frac{A}{d}=\frac{3}{4}\,\frac{\eta_W^2(1-0.7117\eta_W-0.114\eta_W^2)}{(1-\eta_W)^4}\ . \tag{2.12}$$

The last parameter μ is obtained from the following remark. The Fourier transform of the correlation function is, using (2.6),

$$\tilde{h}(kd,\eta)=\tilde{h}_W(kd_W,\eta_W)+\delta\tilde{h}_1(k)+\delta\tilde{h}_2(k)\ , \tag{2.13}$$

where $\tilde{h}_W(kd_W,\eta_W)$ is given by (2.4) and $\tilde{h}(kd,\eta)$ is similarly the Fourier transform of $g(r/d,\eta)-1$, and where

$$\delta\tilde{h}_1(k)=\int e^{+i\vec{k}\cdot\vec{r}}\,\delta g_1(r)\,d\vec{r} \tag{2.14}$$

and

$$\delta\tilde{h}_2(k)=-\frac{4\pi}{k}\int_{d_W}^{d}g_W\left(\frac{r}{d_W},\eta_W\right)\sin kr\,r\,dr\ . \tag{2.15}$$

$\delta\tilde{h}_1(k)$ is trivially obtained from (2.7). $\delta\tilde{h}_2(k)$ can be calculated by expanding $g_W(x,\eta_W)$ around $x=1$ as above. In the $k=0$ limit, (2.13) reduces to

$$kT\left(\frac{\partial\rho}{\partial p}\right)_{\mathrm{HS}}-kT\left(\frac{\partial\rho}{\partial p}\right)_W=\delta\tilde{h}_1(0)+\delta\tilde{h}_2(0)\ . \tag{2.15$'$}$$

The left-hand side is the difference between the hard-sphere compressibilities calculated using the "exact" expression (2.11) and the Wertheim approximation, respectively. It is of the order of 1/200 at the transition. In the same density region, $\delta\tilde{h}_2(0)$ is of the order of unity. It is therefore a good approximation to determine μ by the condition

$$\delta\tilde{h}_1(0)+\delta\tilde{h}_2(0)=0\ . \tag{2.16}$$

We then get

$$\mu d\simeq\frac{24A/d}{\eta_W g_W(1,\eta_W)}\ . \tag{2.17}$$

The rdf obtained in this way differs from the "exact" one by at most 0.03; the statistical error in the rdf is estimated to be of the order of 0.01.

The same kind of agreement is obtained when the rdf obtained by Alder and Hecht[7] are considered, if one takes into account the fact that those computations are admittedly less precise than those used in the present study.

Another important fact to be noted is that $\delta\tilde{h}_1(k)+\delta\tilde{h}_2(k)$ is quite small. It yields for $\eta=0.49$ a correction of 0.5% on the structure factor at its first maximum and a contribution of about 4% at its next secondary maxima. The smallness of this correction explains why the WT solution can be used to fit the experimental structure factors of liquids.[5,15] The packing fraction η_W determined through this fit should be replaced by η obtained from (2.9) if the "exact" value of the packing fraction is wanted.

III. CONVERGENCE OF λ EXPANSION

Let us consider that the potential $v(r)$ which acts between the particles is replaced by

$$v_\lambda(r) = v_0(r) + \lambda w(r), \quad 0 \leq \lambda \leq 1 . \tag{3.1}$$

$v_0(r)$ contains mostly the repulsive part of the potential. $w(r)$, which contains the attractive part of the potential, will be considered as a perturbation: The free energy of the system will be expanded in powers of λ [ultimately λ will be taken equal to 1 so as to recover the original potential $v(r)$.]

The total free energy per particle f is given through

$$f - f_0 = \frac{\langle W \rangle_0}{N} + \int_0^1 d\lambda \, \frac{\langle W \rangle_\lambda - \langle W \rangle_0}{N} , \tag{3.2}$$

where f_0 is the free energy per particle of the "reference system," i.e., of the system of particles interacting through $v_0(r)$, and W is the total perturbation. The average is to be taken for particles interacting through $v_\lambda(r)$.

The λ expansion consists in expanding $\langle W \rangle_\lambda$ in powers of λ and in integrating this expansion term by term. One gets

$$f - f_0 = \frac{\langle W \rangle_0}{N} - \frac{\beta}{2}\left(\frac{\langle W^2 \rangle_0 - \langle W \rangle_0^2}{N} \right) + \cdots . \tag{3.3}$$

"Exact" computations using the Monte Carlo method enable us to calculate $\langle W \rangle_\lambda$ for various values of λ. If we plot $(\langle W \rangle_\lambda - \langle W_0 \rangle)/N$ as a function of λ, we obtain the second-order term of (3.3) as the slope of this curve for $\lambda = 0$, and the sum of the second- and higher-order terms as the area under the curve. We have done such a calculation for a state near the triple point ($\rho = 0.84$, $T = 0.75$) using a system of 864 particles with 10^6 configurations. The division of the potential was that due to WCA:

$$\begin{aligned} v_0(r) &= v_{\mathrm{LJ}}(r) + 1 , && r \leq r_m = 2^{1/6} \\ &= 0 , && \text{otherwise} \end{aligned} \tag{3.4}$$

$$\begin{aligned} w(r) &= -1 , && r \leq r_m \\ &= v_{\mathrm{LJ}}(r) , && r \geq r_m \end{aligned} \tag{3.5}$$

where

$$v_{\mathrm{LJ}}(r) = 4[(1/r)^{12} - (1/r)^6] \tag{3.6}$$

(reduced units $\epsilon = \sigma = 1$ are used throughout).

The results of this computation are shown in Table I. It is seen that the ratio of the remainder of the λ expansion [second term in (3.2)] to the first-order term $\langle W \rangle_0/N$ is less than 1/200 in magnitude. Good results are expected for dense states if only the first-order term is kept. There are two reasons for the good convergence. The first one is well known: Owing to the repulsion of the reference potential there is little space available for the motion in the liquids and the potential fluctuations are therefore prevented. Another reason is peculiar to the WCA division, where $w(r)$ is perfectly smooth in the core region where important fluctuations are most likely to occur for the dense state.

TABLE I. Convergence of the λ expansion of the free energy for the potential separation schemes of McQuarrie and Katz (MK) [cf. (3.9) and (3.10)], Barker and Henderson (BH) [cf. (3.7) and (3.8), and Weeks, Chandler, and Andersen (WCA) [cf. (3.4) and (3.5)]. Column 4: first-order term of the λ expansion. Column 5: remainder of the λ expansion [cf. (3.2)].

Potential separation scheme	ρ	T	$\frac{\beta \langle W \rangle_0}{N}$	$\beta \int_0^1 d\lambda \, \frac{\langle W \rangle_\lambda - \langle W \rangle_0}{N}$
MK	0.84	0.75	−14.99	−0.30
BH	0.85	0.72	− 7.79	−0.45
WCA	0.84	0.75	− 8.81	−0.038

This last argument is not true for the potential separation proposed by Barker and Henderson[2]:

$$\begin{aligned} v_0(r) &= v_{\mathrm{LJ}}(r) , && r \leq 1 \\ &= 0 , && \text{otherwise} \end{aligned} \tag{3.7}$$

$$\begin{aligned} w(r) &= v_{\mathrm{LJ}}(r) , && r \geq 1 \\ &= 0 , && \text{otherwise.} \end{aligned} \tag{3.8}$$

For this case a computation similar to the one just described has already been performed near the triple point.[15,16] We give the results for the sake of comparison.[17] There the convergence ratio is only of the order of 1/17. If quantitative answers are wanted, it will be necessary to evaluate the complicated second-order terms.[18]

Still another division of the potential has been proposed by McQuarrie and Katz (MK).[19] It consists in writing

$$v_0(r) = 4/r^{12}, \tag{3.9}$$

$$w(r) = -4/r^6. \tag{3.10}$$

This problem has been studied theoretically by Lebowitz[20] and numerically by Hansen.[21] The advantage is that some scaling laws hold which make it possible to study only one isotherm. The drawback is that the reference system is rather different from a hard-sphere one. This division of the potential seems to be more attractive at very high temperature,[2,21] where it leads to a very rapid convergence. The convergence of the λ expansion can be examined near triple point for that case also. We therefore have made a direct computation of

TABLE II. Comparison of the compressibility factors obtained through the virial equation using the exact rdf $g(r)$ of the total system (column 3) and the exact rdf $g_0(r)$ of the reference system (column 4).

ρ	T	Z	Z_{WCA}
1.10	3.05	9.87	10.12
0.85	2.81	4.35	4.59
0.84	0.75	0.37	1.57
0.65	1.35	0.85	0.92
0.40	1.35	0.27	0.02

(3.2) for the state $\rho = 0.84$, $T = 0.75$. It can be seen that the convergence ratio is substantially smaller than in the BH case, of the order of 1/50. The improvement over the BH treatment is however less spectacular than it seems, because the first-order term is anomalously large for the MK division of the potential. Finally, the correction to the free energy due to the remainder of the λ expansion is not much smaller than in the BH case, as may be seen in Table I.

Returning to the division of the potential due to WCA, we examine the proposal of these authors to approximate the rdf $g(r)$ of the full system by that of the reference system $g_0(r)$.

If this approximation were true, then the virial equation of state yielded by

$$Z = 1 - \frac{\rho}{6kT} \int g(r)\, r \frac{\partial v}{\partial r}\, d\vec{r} \tag{3.11}$$

and by the WCA approximation

$$Z_{\mathrm{WCA}} = 1 - \frac{\rho}{6kT} \int g_0(r)\, r \frac{\partial v}{\partial r}\, d\vec{r} \tag{3.12}$$

would give the same result.

Monte Carlo computations have been made for the reference system (864 particles, 10^6 configurations) for a variety of states in the ρ, T plane, which have enabled us to calculate Z_{WCA} "exactly." We have chosen states for which we knew the exact compressibility factor. The comparison is made in Table II. It is seen that the difference between Z and Z_{WCA} is quite large. We can see directly that the difference between $g(r)$ and $g_0(r)$ is not negligible. For instance, for $\rho = 0.84$, $T = 0.75$, the difference between the heights of the first maxima of $g(r)$ and $g_0(r)$ reaches 0.05; the difference between the heights of the first peaks of the structure factors amounts to 0.32.

IV. REDUCTION OF REFERENCE SYSTEM

We can always write the rdf of the reference system as

$$g_0(r) = e^{-\beta v_0(r)}\, y(r) \; . \tag{4.1}$$

$y(r)$ contains the effect on the singled out pair of the other particles of the liquid. $y(r)$ is formally obtained as

$$y(r) = \frac{2}{\rho} \frac{\delta \beta f_0}{\delta\, e^{-\beta v_0(r)}} \; . \tag{4.1$'$}$$

If $v_0(r)$ is very repulsive, it is reasonable to follow WCA[12] and to replace $y(r)$ by $y_{\mathrm{HS}}(r/d, \eta)$ where the hard-sphere diameter d has to be determined in the best possible way. We thus obtain an approximate rdf $\hat{g}_0(r)$ for the reference system:

$$\hat{g}_0(r) = e^{-\beta v_0(r)}\, y_{\mathrm{HS}}(r/d, \eta) \; . \tag{4.2}$$

[In what follows we put carets on the quantities obtained using (4.2).]

We shall need $y_{\mathrm{HS}}(r/d, \eta)$ inside the hard core. It is given by (4.1$'$) in the limit of $v_0(r)$ going to a hard-sphere potential with diameter d. $y_{\mathrm{HS}}(r/d, \eta)$ is seen to be smoother at the core. In the PY approximation, $y_{\mathrm{HS}}(r/d, \eta)$ is simply given by

$$y_W(r/d, \eta) = g_W(r/d, \eta) - c_W(r/d, \eta) \; . \tag{4.3}$$

In general we shall write, using (2.6),

$$y_{\mathrm{HS}}(r/d, \eta) = y_W(r/d_W, \eta_W) + \delta g_1(r) \; . \tag{4.4}$$

There is obviously some arbitrariness in this extension, but we shall see, later on, that in fact only the value at core $\delta g_1(r)$ and of its first derivatives are used and that the extrapolation inside the core is really not needed.

In order to determine d, we shall require that for the reference system, where $v_0(r)$ is steep, the hard-sphere model for the structure factor[5] applies, i.e., that in some sense the structure factor

$$\hat{S}_0(k) = 1 + \rho \int [\hat{g}_0(r) - 1]\, e^{i\vec{k}\cdot\vec{r}}\, d\vec{r} \tag{4.5}$$

can be identified with a hard-sphere structure factor. Because we have for $r > r_m$

$$\hat{g}_0(r) = y_{\mathrm{HS}}(r/d, \eta) \; , \tag{4.6}$$

it is obvious that the hard-sphere diameter for the model must be d. Then we can determine that diameter by requiring, for instance, that

$$\int | \hat{S}_0(k) - S_{\mathrm{HS}}(kd, \eta) |\, dk \tag{4.7}$$

be a minimum.

Another way of determining d is provided by the remark that $\hat{S}_0(0)$ is an extremely sensitive function of d. To describe reasonably the very repulsive reference system, we should have $\hat{S}_0(0)$ very small, and a way of enforcing this is to impose with WCA

$$\hat{S}_0(0) = S_{\mathrm{HS}}(0, \eta) \; . \tag{4.8}$$

It is remarkable that the similarity of a repulsive system to a hard-sphere gas imposes definite relations on its structure factor which are sufficient to determine the hard-sphere diameter. It is the great merit of WCA to have proposed the approximation (4.2) and the self-consistency criterion (4.8) to determine d.

We shall now give a typical numerical example which illustrates the preceding statement. For $\rho = 0.84$ and $T = 0.75$, we have $Z_0 = 10.23$ and $U_{0i} = 0.73$. When criterion (4.7) is used we obtain $d = 1.0220$. Using the virial theorem and the excess internal energy formula, we obtain $\hat{Z}_0 = 10.34$ and $\hat{U}_{0i} = 0.74$. The value of $\hat{S}_0(0)$ obtained with this value of the diameter is -0.002.

If now we use the WCA criterion (4.8) we obtain $d = 1.0225$ and then we get $\hat{Z}_0 = 10.40$, $\hat{U}_{0i} = 0.74$. We see that both criteria give very similar results (as they should if the ideas behind the model are any good) and that approximation (4.2) is quite reliable. Other examples are given in Table III.

If now we follow WCA and use the PY approximation instead of the exact hard-sphere solution, we see that the good agreement just mentioned no longer holds. We obtain for the same state, using (4.8) again,

$$d = 1.0239, \quad \hat{Z}_0^W = 9.31, \quad U_{0i}^W = 0.65 \;.$$

Using criterion (4.8) and Eqs. (4.2) and (4.5), we easily see that d is determined by

$$\int_0^d dr\, r^2 y_{\mathrm{HS}}(r/d, \eta) = \int_0^\infty dr\, r^2 y_{\mathrm{HS}}(r/d, \eta)\left(1 - e^{-\beta v_0(r)}\right) \;. \tag{4.9}$$

Let us consider

$$\psi(r) = \sigma_0(r/d - 1) + \tfrac{1}{2}\sigma_1(r/d - 1)^2 + \cdots \;, \tag{4.10}$$

and let

$$d\,\frac{d\psi(r)}{dr} = \frac{r^2}{d^2}\, y_{\mathrm{HS}}\left(\frac{r}{d}, \eta\right) \;. \tag{4.11}$$

The condition (4.9) becomes:

$$\int_0^\infty \psi(r)\delta_{v_0}(r)\, dr = 0 \;, \tag{4.12}$$

where

$$\delta_{v_0}(r) = \frac{d}{dr}\, e^{-\beta v_0(r)} \tag{4.13}$$

behaves like a δ function.[13]

Using (4.10) we obtain

$$d = \int_0^\infty r\delta_{v_0}(r)\, dr + \frac{\sigma_1}{2\sigma_0}\, d\int_0^\infty \left(\frac{r}{d} - 1\right)^2 \delta_{v_0}(r)\, dr + \cdots \;. \tag{4.14}$$

The first term is

$$d_B = \int_0^\infty \left(1 - e^{-\beta v_0(r)}\right) dr \;. \tag{4.15}$$

It is Barker's expression for the hard-sphere diameter.

We shall put

$$\delta = \frac{d}{d_B}\int_0^\infty \left(\frac{r}{d} - 1\right)^2 \delta_{v_0}(r)\, dr \simeq \int_0^\infty \left(\frac{r}{d_B} - 1\right)^2 \delta_{v_0}(r)\, dr \;. \tag{4.16}$$

Typically δ is of the order of a few parts in a thousand.

We thus have

$$d = d_B\left[1 + (\sigma_1/2\sigma_0)\,\delta\right] \;. \tag{4.17}$$

We have neglected higher-order terms in the expansion (4.14). They are extremely small. d_B and δ are simple integrals depending on the temperature only. These integrals are tabulated in the

TABLE III. Compressibility factor and excess internal energy of the reference system using the approximate rdf (4.2) (columns 7 and 8, respectively). For each state the upper line contains the values obtained when the HS diameter d (column 6) entering the rdf (4.2) is determined via criterion (4.7). In the lower line, d is determined via criterion (4.8). Column 9 gives the compressibility for both choices of d. Columns 3 and 4: exact Monte Carlo computations.

ρ	T	Z_0	U_{i0}	Criterion for the choice of d	d	$\hat{Z}_0$	$\hat{U}_{i0}$	$\hat{S}_0(0)$
1.1	3.05	12.67	5.48	(4.7)	0.9610	12.79	5.36	−0.08
				(4.8)	0.9623	12.99	5.45	0.016
0.85	2.81	6.92	2.37	(4.7)	0.9692	6.99	2.39	0.016
				(4.8)	0.9701	7.04	2.41	0.042
0.84	0.75	10.23	0.73	(4.7)	1.0220	10.34	0.74	−0.002
				(4.8)	1.0225	10.40	0.74	0.024
0.65	1.35	4.89	0.62	(4.7)	1.0025	4.98	0.64	0.059
				(4.8)	1.0030	4.99	0.64	0.070
0.40	1.35	2.53	0.23	(4.7)	1.0045	2.55	0.24	0.192
				(4.8)	1.0047	2.55	0.24	0.194

Appendix (Table XII) and simple approximants are also given there [Eqs. (A1) and (A2)]. σ_0 is the value of the rdf $g(1,\eta)$ at core and σ_1, obtained simply in terms of $g(1,\eta)$ and of its first derivative at core, is given in the Appendix [Eq. (A.17)].

We now proceed to calculate the pressure of the reference system. Through the virial theorem we obtain

$$\hat{Z}_0 = 1 + 4\eta\int_0^\infty dr\,\frac{r^3}{d^3}\,y_{\mathrm{HS}}\left(\frac{r}{d},\eta\right)\delta_{v_0}(r)\ . \tag{4.18}$$

If we expand

$$\frac{r^3}{d^3}\,y_{\mathrm{HS}}\left(\frac{r}{d}\right) = \tau_0 + \tau_1\left(\frac{r}{d}-1\right) + \tfrac{1}{2}\tau_2\left(\frac{r}{d}-1\right)^2 + \cdots\ , \tag{4.19}$$

we obtain, using (4.14)–(4.16), the following approximation for $\hat{Z}_0$:

$$\hat{Z}_0^A = Z_{\mathrm{HS}}(\eta) + 4\eta\delta\left(\tfrac{1}{2}\tau_2 - \tau_1\sigma_1/2\sigma_0\right)\ . \tag{4.20}$$

$Z_{\mathrm{HS}}(\eta)$ is the hard-sphere compressibility factor given by (2.11). τ_1 and τ_2 are obtained in terms of the first and second derivatives of $g(x,\eta)$ at core. They are given in the Appendix [Eqs. (A15) and (A16)]. It is seen that both for d and $\hat{Z}_0^A$ these derivatives come in only multiplied by the very small factor δ. The precise form of the correction term $\delta g_1(r)$ as given by (2.7) plays only a minor role. The extrapolation of $g(r/d,\eta)$ inside the core does not enter at all in the approximate theory.

TABLE IV. Compressibility factor of the reference system obtained through exact Monte Carlo computations (column 3), through Eq. (4.18) (column 4) and the approximate equation (4.20).

ρ	T	Z_0	$\hat{Z}_0$	$\hat{Z}_0^A$
1.1	3.05	12.67	12.99	12.61
0.85	2.81	6.92	7.04	7.01
0.84	0.75	10.23	10.40	10.37
0.65	1.35	4.89	4.99	4.99
0.40	1.35	2.53	2.55	2.55

In Table IV, we compare the exact values of the compressibility factor Z_0 of the reference system with those yielded by the approximate theory of this section. $\hat{Z}_0$, as given by (4.18) contains only the basic approximation (4.2) with the WCA criterion (4.8). We see that the error is only slightly larger than the statistical error and therefore quite acceptable. There is an exception for the point $T=3.05$, $\rho=1.1$. This state is a fairly high-temperature state quite near the solidification line. Then, owing to the WCA division of the potential, it happens that the diameter of the reference system is larger than that of the total system (as could be determined from the HS model), so that it yields a packing fraction $\eta=0.51$ which dangerously extrapolates our formulas into the metastable region of the hard-sphere gas. This explains why the results are not so satisfactory for that case.

Further on it is seen that the approximations made when deriving $\hat{Z}_0^A$ entail negligible errors.

V. CALCULATION OF FIRST-ORDER CONTRIBUTION TO FREE ENERGY PER PARTICLE

$$\begin{aligned} f_1 &= \langle W\rangle_0/N \\ &= \tfrac{1}{2}\rho\int w(r)g_0(r)\,d\vec{r}\ . \end{aligned} \tag{5.1}$$

If we make the approximation (4.2), we obtain

$$\begin{aligned} \hat{f}_1 &= 2\pi\rho\left[\int_0^{r_m} w(r)\left(e^{-\beta v_0(r)}-1\right)y_{\mathrm{HS}}\left(\frac{r}{d},\eta\right)r^2dr + \int_0^\infty w(r)\,y_{\mathrm{HS}}\left(\frac{r}{d},\eta\right)r^2dr\right] \\ &= 2\pi\rho\int_d^\infty w(r)\,y_{\mathrm{HS}}\left(\frac{r}{d},\eta\right)r^2dr\ . \end{aligned} \tag{5.2}$$

The WCA criterion (4.9) has been used to go from the first to the second equation. Using (2.6), we obtain after obvious manipulations

$$\begin{aligned} \hat{f}_1 = 2\pi\rho\Big\{&\int_d^\infty \delta g_1(r)w(0)r^2dr + \int_d^{d_W} w(0)\,y_W(r/d_W,\eta_W)\,r^2dr + \int_{d_W}^\infty v_{\mathrm{LJ}}(r)\,y_W(r/d_W,\eta_W)\,r^2dr \\ &- \int_{d_W}^{r_m} v_0(r)\,y_W(r/d_W,\eta_W)\,r^2dr + \int_{r_m}^\infty [w(r)-w(0)]\,\delta g_1(r)\,r^2dr\Big\}\ . \end{aligned} \tag{5.3}$$

The first and second terms cancel because of condition (2.16). The third term may be written

$$\hat{f}_1^1 = 48\eta_W\left[\frac{I_1^{12}(\eta_W)}{d_W^{12}} - \frac{I_1^6(\eta_W)}{d_W^6}\right]\ , \tag{5.4}$$

where we have put

$$I_1^n(\eta_W) = \int_1^\infty x^2\,\frac{y_W(x,\eta_W)}{x^n}\,dx\ . \tag{5.5}$$

For these integrals, there exist approximants due to Kozak and Rice.[22] They are not quite precise enough for our purpose. Improved expressions are given in the Appendix.

The fourth term in (5.3) may be written

$$\hat{f}_1^2 = 48\eta_W\left[-\frac{I_2^{12}(\eta_W)}{d_W^{12}} + \frac{I_2^6(\eta_W)}{d_W^6} - \frac{I_2^0}{4}\right]\ , \tag{5.6}$$

with

$$I_2^n = \int_1^{r_m/d_W} x^2 \, \frac{y_W(x, \eta_W)}{x^n} \, dx \,. \tag{5.7}$$

These integrals are calculated in the Appendix by expanding $x y_W(x, \eta_W)$ around $x = 1$. The last term in (5.3) is the only one to depend explicitly on the exact hard-sphere solution. It turns out to be quite small. We can give an order-of-magnitude estimate of that term by expanding $w(r) - w(0)$ around its inflexion point given by $r_i = (\frac{26}{7})^{1/6}$,

$$\hat{f}_1^3 \simeq \frac{51\pi\rho}{169} \frac{A}{\mu} r_i \, e^{-\mu(r_m - d)} \times [\cos\mu(r_m - d) - \sin\mu(r_m - d)] \,. \tag{5.8}$$

This term turns out to be of the order of $\hat{f}_1^1/1000$ near triple point. It is negligible, so that the free energy due to the perturbation is taken as

$$\hat{f}_1^A = \hat{f}_1^1 + \hat{f}_1^2 \,. \tag{5.9}$$

In Table V we compare the Monte Carlo computed free energy f_1 with $\hat{f}_1$ yielded by the basic approximations (4.2) and (4.9). The relative error on f_1 entailed by those approximations is seen to be of the order of 1/200. It is therefore comparable to the error made by neglecting higher-order terms in the λ expansion near triple point. When the density is lower, the error due to the λ expansion is relatively much more important.

It is seen also here that the various approximations summarized in the Appendix which are made to reduce $\hat{f}_1$ to the easily computable form $\hat{f}_1^A$ lead to a negligible error.

VI. THERMODYNAMIC FUNCTIONS FOR LENNARD-JONES SYSTEM

Starting from the expressions given in the two preceding sections for Z_0 and f_1 we want to calculate the total free energy per particle, the total compressibility factor, and the excess internal energy.

In order to calculate the total free energy of the system, we must get the approximate free energy for the reference system which is given by

$$\hat{f}_0^A = \frac{1}{\beta} \int_0^\rho [\hat{Z}_0^A(\eta) - 1] \frac{d\rho}{\rho} = \hat{f}_{\mathrm{HS}}^{\mathrm{ex}} + 4\delta\Delta f \,, \tag{6.1}$$

where

$$\beta \hat{f}_{\mathrm{HS}}^{\mathrm{ex}} = \eta \frac{4 - 3\eta}{(1 - \eta)^2} \tag{6.2}$$

is the excess free energy of the hard-sphere system and where the expression for

$$\beta\Delta f = -3 \int_0^\eta [\hat{Z}_0^A(\eta) - 1] \frac{\partial \ln d}{\partial \eta} \, d\eta \tag{6.3}$$

is given explicitly in the Appendix.

TABLE V. First-order contribution to the free energy per particle in the λ expansion. Column 3: exact values obtained by Monte Carlo computations. Column 4: values obtained from Eq. (5.2). Column 5: values obtained using the approximate equations (5.4), (5.6), and (5.9).

ρ	T	βf_1	$\beta\hat{f}_1$	$\beta\hat{f}_1^A$
1.1	3.05	−2.83	−2.82	−2.81
0.85	2.81	−2.33	−2.34	−2.34
0.84	0.75	−8.82	−8.85	−8.84
0.65	1.35	−3.62	−3.63	−3.62
0.40	1.35	−2.05	−2.06	−2.06

Andersen, Weeks, and Chandler[23] have pointed out to us that one can perform a functional Taylor expansion of the free energy f_0 of the reference system in terms of $(e^{-\beta v_0(r)} - e^{-\beta v_{\mathrm{HS}}(r/d)})$, where $v_{\mathrm{HS}}(r/d)$ is the hard-core potential of diameter d. The zero-order term of the expansion is $\hat{f}_{\mathrm{HS}}^{\mathrm{ex}}$.

Using (4.1′) and (4.2), the first-order term is proportional to

$$\int d\vec{r} \, [e^{-\beta v_0(r)} - e^{-\beta v_{\mathrm{HS}}(r)}] \, y_{\mathrm{HS}}(r/d, \eta)$$

and is seen to vanish if (4.9) is used. The next-order term is in δ^2 and thus altogether negligible. Between the free energy thus obtained and (6.1), there is a discrepancy which amounts to $4\delta\Delta f$. This illustrates the fact that the terms of order δ are not treated in a completely consistent way. In order to include all terms of order δ in our approach, it would be necessary to include the first-order correction to $\hat{g}_0(r)$ in the functional expansion considered above. This involves the knowledge of the four-body correlation and is quite complicated. Then the term $4\delta\Delta f$ would disappear in (6.2) but a new term of order δ should be included in $\hat{f}_1$, which turns out to have the same sign and order of magnitude as $4\delta\Delta f$. We therefore choose to keep that term in (6.1). We should note, in any case, that this term is very small: $4\beta\delta\Delta f$ is always smaller than 0.05.

In the same way, in order to get the total compressibility factor, we must calculate

$$\hat{Z}_1 = \beta\rho \left(\frac{\partial \hat{f}_1}{\partial \rho}\right)_\beta = \frac{\beta}{1 - 3L} \, \eta_W \left(\frac{d\hat{f}_1}{d\eta_W}\right)_\beta \,, \tag{6.4}$$

with

$$L = \frac{\eta_W}{d_W} \, \frac{\partial d_W}{\partial \eta_W} \,. \tag{6.5}$$

The explicit formulas making it possible to calculate analytically $\hat{Z}_1$ are given in the Appendix.

In Tables VI–IX, the thermodynamic quantities thus obtained are compared with the "exact" Monte

TABLE VI. Compressibility factor, excess free energy, and excess internal energy on the isotherm $T=0.75$. Columns 2–4: exact Monte Carlo Computations (Ref. 21). Columns 5–7: approximate equations (A25), (A34), and (A39).

ρ	Z	βf_i	U_i	$\hat{Z}^A$	$\beta \hat{f}_i^A$	$\hat{U}_i^A$
0.1	0.23	−0.80	−1.15	0.42	−0.55	−0.56
0.2	−0.29	−1.48	−1.90	−0.24	−1.15	−1.19
0.3	−0.78	−2.10	−2.58	−0.93	−1.79	−1.87
0.4	−1.20	−2.68	−3.21	−1.58	−2.43	−2.62
0.5	−1.69	−3.22	−3.73	−2.07	−3.06	−3.40
0.6	−2.05	−3.73	−4.36	−2.24	−3.65	−4.20
0.7	−1.71	−4.17	−5.07	−1.86	−4.12	−5.00
0.8	−0.53	−4.47	−5.78	−0.56	−4.43	−5.75
0.84	+0.37	−4.53	−6.04	+0.32	−4.49	−6.02

Carlo values[24] on the isotherms 0.75, 1.15, 1.35, and 2.74. The agreement is seen to be quite good at high density. Using the basic ideas of the perturbation theory as formulated by WCA, we have succeeded in obtaining quantitatively correct answers which can be obtained with a minimal computational effort.

At low and medium densities the results are only fair and should be improved. For instance, one gets for the critical constants $T_c=1.44$, $\rho_c=0.3$, and $\beta p_c/\rho_c=0.41$, when these constants should be[24,25] $T_c=1.36\pm0.02$, $\rho_c=0.36\pm0.03$, and $\beta_c p_c/\rho_c=0.31\pm0.03$ for a Lennard-Jones system with enforced large scale density homogeneity.

A first idea[14] in order to improve the situation in the low-density region is to subtract from the free energy its low-density expansion and to add the exact low-density expansion of the Lennard-Jones system.[26] The results become evidently exact at low density, but the theory breaks down at high density. Making a Padé approximant with the correcting series does not improve the situation.

We then try to use some approximation for the remainder of the perturbation series for the free energy. By (3.2) it is equal to

$$\tfrac{1}{2}\rho\int_0^1 d\lambda \int d\vec{r}\,[g_\lambda(r)-g_0(r)]\,w(r),$$

where $g_\lambda(r)$ is the rdf for the potential $v_0(r)+\lambda\, w(r)$. We may first try a simple approximation proposed by Stell.[14] It consists in writing

$$g_\lambda(r)=\exp\{-\beta[v_0(r)+\lambda\, S_{\rm HS}^2(0)\ w(r)]\}y_{\rm HS}(r). \quad (6.6)$$

This approximation incorporates the correct asymptotic form for large distances and the right behavior at small separations. It leads to an exact second virial coefficient. It appears, unfortunately, that the screening of the potential tail yielded by (6.6) is too effective, so that the correction term is too small, except at very low density. For instance, at $T=1.35$, the correction to $\beta\hat{f}_i^A$ is -0.04 for $\rho=0.1$, when it should be -0.07; this is fairly satisfactory. But at the same temperature, for $\rho=0.4$, a correction of -0.02 is obtained instead of the -0.09 which is required.

A technically more complicated method appears to be quite successful. It consists in calculating $g_\lambda(r)$ by solving the Percus-Yevick equation and in calculating the remainder of the series in that approximation. There we work again in the spirit of Stell's mixed perturbation expansion. λ expansion is used and its first two terms are calculated exactly; the remainder of the series is treated through a method of integral equations which amounts to a ρ expansion. The results, shown in Tables VIII and IX for the isotherms $T=1.35$ and $T=2.74$, appear to be very good. For $T=0.75$ and $\rho=0.84$, the remainder calculated in the PY approximation gives practically zero. Thus one does not get the small correction which should come in at high density, but at least the very good agreement so far obtained is not spoiled by our treatment of the remainder of the perturbation series. We have therefore succeeded in giving a theory of liquids which provides a value of the free energy with a precision of about 1/100 for all densities in a temperature region ranging from triple point to twice or three times the critical temperature. There is however at the present time a very great inhomogeneity in the ingredients of that theory. The high-density and low-density parts of the theory are obtained through simple formulas; the medium-density range requires a substantial computational effort. We hope to simplify this part of the theory.

VII. WCA APPROXIMATION

As we have said above, WCA make two further assumptions which we have shown to be separately inadequate. The first approximation consists in using the PY approximation for the hard-sphere correlation function; the second consists in approximating the total system rdf by that of the reference system. As these authors have shown by numerical computations that the equation of state and the in-

TABLE VII. Compressibility factor, excess free energy, and excess internal energy on the isotherm $T=1.15$. Columns 2–4: exact Monte Carlo computations (Ref. 21). Columns 5–7: approximate equations (A25), (A34), and (A39).

ρ	Z	βf_i	U_i	$\hat{Z}^A$	$\beta \hat{f}_i^A$	$\hat{U}_i^A$
0.1	0.61	−0.38	−0.86	0.70	−0.29	−0.55
0.2	0.35	−0.73	−1.55	0.37	−0.61	−1.17
0.3	0.12	−1.05	−2.24	0.05	−0.92	−1.84
0.4	−0.09	−1.34	−2.85	−0.19	−1.23	−2.55
0.5	−0.13	−1.59	−3.47	−0.27	−1.51	−3.29
0.6	0.07	−1.78	−4.14	−0.08	−1.73	−4.03
0.65	0.31	−1.84	−4.45	0.17	−1.81	−4.40
0.75	1.17	−1.89	−5.13	1.10	−1.87	−5.09
0.85	2.86	−1.78	−5.67	2.83	−1.76	−5.68
0.92	4.72	−1.56	−5.96	4.69	−1.54	−5.99

TABLE VIII. Compressibility factor, excess free energy, and excess internal energy on the isotherm $T=1.35$. Columns 2–4: exact Monte Carlo results (Ref. 16). Columns 5–7: approximate equations (A25), (A34), and (A39). Column 8: remainder of the series (3.2)

$$\beta\int_0^1 d\lambda \frac{\langle W\rangle_\lambda - \langle W\rangle_0}{N}$$

calculated in the PY approximation. The last column is obtained by adding the values of column 8 to those of the free excess energy of column 6.

ρ	Z	βf_i	U_i	$\hat{Z}^A$	$\beta\hat{f}_i^A$	$\hat{U}_i^A$	Δ	$\beta\hat{f}_i^{\text{tot}}$
0.1	0.72	−0.29	−0.78	0.77	−0.22	−0.55	−0.07	−0.29
0.2	0.50	−0.56	−1.51	0.53	−0.46	−1.16	−0.11	−0.56
0.3	0.35	−0.80	−2.09	0.32	−0.69	−1.82	−0.11	−0.80
0.4	0.27	−1.00	−2.75	0.18	−0.91	−2.52	−0.09	−1.00
0.5	0.30	−1.16	−3.37	0.20	−1.09	−3.24	−0.07	−1.15
0.55	0.41	−1.22	−3.70	0.30	−1.16	−3.60	−0.05	−1.21
0.70	1.17	−1.29	−4.68	1.15	−1.25	−4.64	−0.03	−1.27
0.80	2.42	−1.19	−5.25	2.42	−1.15	−5.24	0.00	−1.15
0.90	4.58	−0.91	−5.66	4.53	−0.87	−5.70	0.00	−0.87
0.95	6.32	−0.67	−5.71	5.97	−0.64	−5.84	0.00	−0.64

ternal energy obtained in this way are quite good, this means[27] that they have found a very good semiempirical way of representing the rdf of dense fluid, by writing for it

$$\hat{g}_{\text{WCA}}(r)=e^{-\beta v_0(r)}\, y_W(r/a,\eta) \tag{7.1}$$

with

$$\eta=\tfrac{1}{6}\pi\rho a^3 \ . \tag{7.2}$$

This form of the correlation where the screening of the tail of the potential is complete, clearly entails a hard-sphere-like structure factor with a diameter a, which will be given by the condition (4.8). We can follow the same line of argument as in Secs. IV and V. We have for the hard-sphere diameter

$$a=d_B\left(1+\frac{\sigma_1}{2\sigma_0}\,\delta\right) \ , \tag{7.3}$$

where d_B and δ are given by (4.15) and (4.16), respectively, and where $\sigma_1/2\sigma_0$, as calculated in the PY approximation, is expressed in the Appendix [Eq. (A40)]. The WCA equation of state is obtained as

$$\hat{Z}_{\text{WCA}}=\zeta_1+\zeta_2 \ , \tag{7.4}$$

with

$$\zeta_1=1-\frac{2\pi\rho}{3kT}\int r^3\,\frac{dv_0(r)}{dr}\,\hat{g}_{\text{WCA}}(r)\,dr \ . \tag{7.5}$$

Using the techniques of Sec. IV, one obtains, for ζ_1, the approximation

$$\zeta_1^A=\frac{1+2\eta+3\eta^2}{(1-\eta)^2}+4\eta\delta\left(\frac{\tau_2}{2}-\frac{\tau_1\sigma_1}{2\sigma_0}\right) \ , \tag{7.6}$$

where τ_1 and τ_2 are coefficients of the expansion of $x^3 g_W(x,\eta)$ around $x=1$ (see Eq. (4.19) and Appendix), and with

$$\zeta_2=-\frac{2\pi\rho}{3kT}\int r^3\,\frac{dw(r)}{dr}\,\hat{g}_{\text{WCA}}(r)\,dr \ . \tag{7.7}$$

Using the methods of Sec. V, we obtain the following approximation for ζ_2:

$$\zeta_2^A=96\beta\eta\left[\frac{2I_1^{12}(\eta)-2I_2^{12}(\eta)}{a^{12}}-\frac{I_1^{6}(\eta)-I_2^{6}(\eta)}{a^{6}}\right] \ , \tag{7.8}$$

where $I_1^n(\eta)$ and $I_2^n(\eta)$ have been defined by (5.5) and (5.7), respectively, and calculated in the Appendix. In Table X, we have compared the compressibility factor $\hat{Z}_{\text{WCA}}$ obtained numerically by WCA using (7.5) and (7.7) with the value $\hat{Z}_{\text{WCA}}^A$ obtained using the approximations (7.6) and (7.8). It is seen that the approximations leading to the analytical equation of state are outstandingly good. The comparison of the WCA equation of state with the one presently derived shows a very slight superiority of the latter one, especially in the low-density region (where both equations are inadequate anyhow). For instance, the critical constants obtained with the WCA equation are $T_c=1.55$, $\rho_c=0.27$, and $\beta_c p_c/\rho_c=0.36$.

WCA have also shown by a direct comparison with molecular-dynamics calculations that their theory provides a good rdf and structure factor in the neighborhood of the triple point. It is unfortunate that this simple semiempirical representation of the rdf turns out to have a rather narrow range of validity. It fails at lower density for the obvious reason that the tail of the potential is entirely neglected. It can be shown also to be unsatisfactory when the density is larger than the triple-point density. An illustration of this inadequacy is provided when one tries to apply the freezing criterion

TABLE IX. Compressibility factor, excess free energy, and excess internal energy on the isotherm $T=2.74$. Columns 2–4: exact Monte Carlo results (Ref. 16). Columns 5–7: approximate equations (A25), (A34), and (A39). Column 8: remainder of the series (3.2)

$$\beta\int_0^1 d\lambda \frac{\langle W\rangle_\lambda - \langle W\rangle_0}{N}$$

calculated in the PY approximation. The last column is obtained by adding the values of column 8 to those of the excess free energy of column 6.

ρ	Z	βf_i	U_i	$\hat{Z}^A$	$\beta\hat{f}_i^A$	$\hat{U}_i^A$	Δ	$\beta\hat{f}_i^{\text{tot}}$
0.1	0.97	−0.03	−0.61	0.98	−0.02	−0.52	−0.02	−0.03
0.2	0.99	−0.05	−1.21	0.99	−0.03	−1.08	−0.02	−0.05
0.3	1.04	−0.05	−1.78	1.05	−0.02	−1.67	−0.02	−0.05
0.4	1.20	−0.01	−2.37	1.19	0.01	−2.28	−0.02	−0.01
0.55	1.65	0.06	−3.21	1.65	0.07	−3.16	−0.01	0.06
0.70	2.64	0.37	−3.90	2.62	0.39	−3.92	0.01	0.38
0.80	3.60	0.65	−4.28	3.70	0.67	−4.27	0.00	0.67
0.90	5.14	1.04	−4.41	5.24	1.07	−4.43	0.00	1.07
1.00	7.39	1.58	−4.18	7.35	1.63	−4.31	0.00	1.63
1.08	9.58	2.16	−3.80	9.46	2.19	−3.97	0.00	2.19

presented in Ref. 4. There it was stated that freezing should occur in a liquid when the underlying hard-sphere gas, yielded by the hard-sphere model,[5] solidifies, that is, when the maximum of the structure factor $S(k_0)$ reaches the value 2.85. This occurs[28,24] when $\eta_S = 0.491$, which, by (2.9), corresponds to the value $\eta_W^S = 0.476$ if the PY approximation is used. Using (7.2), (7.3), and (A40) one obtains at solidification

$$\rho_S = [0.91/d_B^3(\beta_S)][1 + 13.25\delta(\beta_S)] \qquad (7.9)$$

which gives the density at freezing ρ_S as a function of β_S, the inverse of the solidification temperature. Table XI shows that this relation is not so well verified and this shows that the structure factor yielded by (7.1) is not good enough along the freezing line.

VIII. CONCLUSION

We have examined the validity of the various approximations introduced by Weeks, Chandler, and Andersen in their version of the perturbation theory and shown that these authors have introduced some very interesting and fruitful new ideas. Using these ideas with an improved solution of the hard-sphere problem, we have derived a successfully analytical equation of state for liquids. Such an equation can and will be used to determine effective potentials for real dense liquids.

TABLE X. Compressibility factor and excess internal energies for various states tabulated in Ref. 12. Columns 3 and 6: exact molecular dynamics results (Ref. 15). Columns 4 and 7: compressibility factor and excess internal energy obtained by WCA (cf. Table III of Ref. 12). Columns 5 and 8: approximate compressibility factor and excess internal energy as given by Eqs. (A34) and (A39).

ρ	T	Z	$\hat{Z}_{\text{WCA}}$	$\hat{Z}^A$	U_i	$\hat{U}_{\text{WCA}i}$	$\hat{U}_i^A$
0.88	1.095	3.48	3.42	3.38	−5.85	−5.92	−5.88
	0.94	2.77	2.87	2.74	−6.04	−6.08	−6.05
	0.591	−0.18	0.18	−0.46	−6.53	−6.47	−6.46
0.85	2.889	4.36	4.27	4.43	−4.25	−4.35	−4.27
	2.202	4.20	4.11	4.25	−4.76	−4.85	−4.78
	1.214	3.06	3.05	3.02	−5.60	−5.65	−5.62
	1.128	2.78	2.82	2.76	−5.69	−5.73	−5.70
	0.88	1.64	1.82	1.59	−5.94	−5.96	−5.95
	0.782	0.98	1.20	0.86	−6.04	−6.06	−6.05
	0.76	0.82	1.03	0.67	−6.07	−6.08	−6.07
	0.658	−0.20	0.09	−0.45	−6.19	−6.19	−6.18
	0.591	−1.20	−0.75	−1.43	−6.26	−6.26	−6.26
0.75	2.849	3.10	3.05	3.14	−4.07	−4.09	−4.05
	1.304	1.61	1.63	1.58	−5.02	−4.99	−4.99
	1.069	0.90	0.90	0.77	−5.19	−5.15	−5.15
	1.071	0.89	0.91	0.78	−5.17	−5.15	−5.15
	0.881	−0.12	−0.02	−0.26	−5.31	−5.28	−5.29
	0.827	−0.54	−0.38	−0.66	−5.38	−5.32	−5.33
0.65	2.557	2.14	2.08	2.14	−3.78	−3.78	−3.76
	1.585	1.25	1.21	1.23	−4.23	−4.20	−4.20
	1.036	−0.11	−0.23	−0.29	−4.52	−4.46	−4.46
	0.90	−0.74	−0.91	−1.01	−4.61	−4.52	−4.53

TABLE XI. Solidification densities for the temperatures $T = 2.74$, 1.35, 1.15, 0.75, using exact Monte Carlo computations (Ref. 4) (column 2), the criterion (Ref. 4) $S(k_0) = 2.85$ (column 3), and expression (7.9) (column 4).

T	ρ_S^{MC}	ρ_S^{HV}	ρ_S
2.74	1.113	1.118	1.018
1.35	0.964	0.966	0.921
1.15	0.936	0.935	0.902
0.75	0.871	0.866	0.857

The extension of the present study to liquid mixture is now under way.

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APPENDIX: TECHNICAL DETAILS OF CALCULATION OF THERMODYNAMIC PROPERTIES OF LENNARD-JONES FLUID

1. *Calculation of Diameter d*

d_B, given by the integral (4.15) and tabulated below, can be approximated by

$$d_B = \frac{\alpha_1 + \alpha_3 \beta}{\alpha_2 + \beta} , \qquad (\text{A1})$$

with $\alpha_1 = 0.3837$, $\alpha_2 = 0.4293$, $\alpha_3 = 1.068$. For $0.7 \leq T \leq 1.6$, the error is less than 2×10^{-4}. This entails an error of less than 0.02 on the compressibility factor $\hat{Z}_0$ of the reference state. For $1.6 < T < 4.5$ the error may reach 8×10^{-4} which may yield an error of 0.08 on $\hat{Z}_0$ near the solidification line. This error decreases very rapidly with the density.

In the same way δ may be approximated by

$$\delta = \frac{1}{\alpha_4 + \alpha_5 \beta} , \qquad (\text{A2})$$

with $\alpha_4 = 210.31$ and $\alpha_5 = 404.6$. The precision of that fit is of order 8×10^{-5}, which is quite sufficient for our purpose.

If we know d, we calculate the packing fractions

$$\eta = \tfrac{1}{6}\pi\rho d^3 \qquad (\text{A3})$$

and

$$\eta_W = \eta - \tfrac{1}{16}\eta^2 . \qquad (\text{A4})$$

It is convenient to introduce the following approximant [see following Eqs. (A12) and (A14)]:

$$\frac{\sigma_1}{2\sigma_0} = \frac{1 + S_1\eta_W + S_2\eta_W^2 + S_3\eta_W^3}{(1-\eta_W)^2} , \qquad (\text{A5})$$

TABLE XII. Values of d_B and δ and their derivatives d_B' and δ_B' with respect to the inverse temperature β for temperatures going from the triple point temperature up to $T=5$.

T	d_B	d_B'	δ	δ_β'
0.65	1.030 61	0.021 48	0.001 26	−0.000 50
0.70	1.028 14	0.023 56	0.001 32	−0.000 56
0.75	1.025 79	0.025 67	0.001 37	−0.000 62
0.80	1.023 57	0.027 81	0.001 43	−0.000 68
0.85	1.021 44	0.029 97	0.001 48	−0.000 74
0.90	1.019 42	0.032 16	0.001 53	−0.000 80
0.95	1.017 47	0.034 36	0.001 58	−0.000 86
1.00	1.015 61	0.036 59	0.001 62	−0.000 92
1.05	1.013 81	0.038 84	0.001 67	−0.000 99
1.10	1.012 08	0.041 10	0.001 71	−0.001 05
1.15	1.010 41	0.043 38	0.001 76	−0.001 12
1.20	1.008 80	0.045 68	0.001 80	−0.001 18
1.25	1.007 24	0.047 99	0.001 84	−0.001 25
1.30	1.005 73	0.050 32	0.001 88	−0.001 32
1.35	1.004 26	0.052 66	0.001 92	−0.001 39
1.40	1.002 84	0.055 01	0.001 95	−0.001 46
1.50	1.000 11	0.059 75	0.002 02	−0.001 60
1.60	0.997 52	0.064 54	0.002 09	−0.001 74
1.70	0.995 06	0.069 37	0.002 16	−0.001 88
1.80	0.992 72	0.074 24	0.002 22	−0.002 03
1.90	0.990 47	0.079 15	0.002 28	−0.002 17
2.00	0.988 33	0.084 09	0.002 34	−0.002 32
2.20	0.984 29	0.094 05	0.002 46	−0.002 62
2.40	0.980 54	0.104 13	0.002 56	−0.002 93
2.60	0.977 04	0.114 31	0.002 66	−0.003 24
2.80	0.973 77	0.124 57	0.002 75	−0.003 55
3.00	0.970 68	0.134 90	0.002 84	−0.003 87
3.50	0.963 67	0.161 04	0.003 04	−0.004 67
4.00	0.957 46	0.187 52	0.003 22	−0.005 49
4.50	0.951 37	0.214 29	0.003 39	−0.006 31
5.00	0.946 85	0.241 28	0.003 53	−0.007 14

where $S_1=-17/4$, $S_2=1.362$, and $S_3=-0.8751$. Then

$$d=d_B\left[1+(\sigma_1/2\sigma_0)\,\delta\right] \tag{A6}$$

and

$$d_W=d(\eta_W/\eta)^{1/3}\ . \tag{A7}$$

As we do not know d beforehand, we use d_B as a trial value and eventually iterate through the preceding equations.

2. *Calculation of Compressibility Factor $\hat{Z}_0^A$ of Reference System*

$[xy_W(x,d_W)]$ and its first derivatives with respect to x at $x=1$ are given by

$$\alpha_0=\frac{1+\frac{1}{2}\eta_W}{(1-\eta_W)^2}\ , \tag{A8}$$

$$\alpha_1=\frac{1-5\eta_W-5\eta_W^2}{(1-\eta_W)^3}\ , \tag{A9}$$

$$\alpha_2=-\frac{3\eta_W(2-4\eta_W-7\eta_W^2)}{(1-\eta_W)^4}\ . \tag{A10}$$

From the compressibility factor of the hard-sphere system

$$Z_{\text{HS}}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\ , \tag{A11}$$

we obtain, by applying the virial theorem, the value of $y(1,\eta)$ that we have called σ_0:

$$\sigma_0=(1-\tfrac{1}{2}\eta)/(1-\eta)^3\ . \tag{A12}$$

We shall find it convenient to use for the combination $A\mu$ [A and μ are defined by Eqs. (2.10) and (2.17), respectively] the expression

$$A\mu=\frac{27}{2}\,\frac{\eta_W^3}{(1-\eta_W)^6}\,\frac{(1-0.7117\eta_W-0.114\eta_W^2)^2}{1+\frac{1}{2}\eta_W}\ , \tag{A13}$$

which is not difficult to calculate using (2.10) and (2.12). We then have for the coefficients of the expansions (4.10) and (4.19)

$$\sigma_1=\sigma_0+\alpha_1-A\mu\ , \tag{A14}$$

$$\tau_1=2\sigma_0+\alpha_1-A\mu\ , \tag{A15}$$

$$\tau_2=2\sigma_0+4\alpha_1+\alpha_2-4A\mu\ . \tag{A16}$$

As stated in Sec. IV [Eq. (4.20)], $\hat{Z}_0^A$ is given by

$$\hat{Z}_0^A=Z_{\text{HS}}(\eta)=4\eta\delta\,(\tfrac{1}{2}\tau_2-\tau_1\sigma_1/2\sigma_0)\ . \tag{A17}$$

3. *Calculation of First-Order Contribution $\hat{f}_1^A$ to Free Energy*

A first part of the perturbed free energy is given by

$$\hat{f}_1^1=48\eta_W\,(I_1^{12}/d_W^{12}-I_1^6/d_W^6)\ . \tag{A18}$$

We have built approximants for the integrals $I_1^n(n_W)$ [Eq. (5.5)] by noting that use may be made of the known virial expansion of $y_W(x,\eta_W)$ on the one hand and that it may be supposed that I_1^n behaves like $(1-\eta_W)^{-2}$ as $y_W(1,\eta_W)$ does. We thus write

$$I_1^n=\mu_0^n\,\frac{1+\mu_1^n\eta_W+\mu_2^n\,\eta_W^2+\mu_3^n\eta_W^3}{(1-\eta_W)^2} \tag{A19}$$

and find that

$$\mu_0^{12}=\tfrac{1}{9},\quad \mu_1^{12}=0,\quad \mu_2^{12}=-0.797,\quad \mu_2^{12}=-0.480\ ,$$
$$\mu_0^6=\tfrac{1}{3},\quad \mu_1^6=-0.691,\quad \mu_2^6=-1.169,\quad \mu_3^6=0.751\ . \tag{A20}$$

The error is of order 1×10^{-3}.

In order to evaluate the next contribution $\hat{f}_1^2$, we need to calculate the integrals I_2^n defined by (5.7).

Putting $\theta=r_m/d_W-1$ and $n'=n-2$, we have

$$I_2^n=\sum_{m=0}^{2}J_m^n\ , \tag{A21}$$

with

$$J_m^n = \frac{\alpha_m}{n'(n'-1)\cdots(n'-m)}\left(1 - \frac{1+n'\theta+[n'(n'-1)/2!]\,\theta^2+\cdots+[n'(n'-1)\cdots(n'-m+1)/m!]\theta_n}{(1+\theta)^{n'}}\right) \tag{A22}$$

and

$$I_2^0 = \sum_{n=0}^{\infty}\left(\frac{\alpha_n}{n!} + \frac{\alpha_{n-1}}{(n-1)!}\right)\frac{\theta_{n+1}}{n+1}\ , \tag{A23}$$

with $\alpha_{-1} = 0$. Then, as noted in Sec. V,

$$\hat{f}_1^{\,2} = 48\eta_W\left(-\frac{I_2^{12}}{d_W^{12}} + \frac{I_2^6}{d_W^6} - \frac{I_2^0}{4}\right) \tag{A24}$$

and

$$\hat{f}_1^A = \hat{f}_1^1 + \hat{f}_1^2\ . \tag{A25}$$

Using the preceding formulas, we can cast $\hat{f}_1^A$ in the form

$$\hat{f}_1^A = 48\eta_W\left[\frac{1}{d_W^{12}}\left(I_1^{12} - \frac{\alpha_0}{10} - \frac{\alpha_1}{90} - \frac{\alpha_2}{720}\right) - \frac{1}{d_W^6}\left(I_1^6 - \frac{\alpha_0}{4} - \frac{\alpha_1}{12} - \frac{\alpha_2}{24}\right) - \frac{9}{64}\frac{r_m^4}{d_W^4}\alpha_2\right.$$
$$\left. - \frac{2}{9}\left(\frac{r_m}{d_W}\right)^3(\alpha_1 - \alpha_2) - \frac{9}{40}\left(\frac{r_m}{d_W}\right)^2\left(\alpha_0 - \alpha_1 + \frac{\alpha_2}{2}\right) + \frac{1}{8}\left(\alpha_0 - \frac{\alpha_1}{3} + \frac{\alpha_2}{12}\right)\right]\ . \tag{A26}$$

4. *Free Energy for Reference System*

The free energy for the reference system is given by (6.1) with

$$\beta\Delta f = \int_0^\eta d\eta\left[\frac{\tau_2}{2} - \frac{\tau_A\sigma_1}{2\sigma_0} - 3\sigma_0\eta\frac{\partial}{\partial\eta}\left(\frac{\sigma_1}{2\sigma_0}\right)\right]$$
$$\simeq \frac{3\eta^2(1+1.759\eta-5.249\eta^3)}{(1-\eta)^3}\ . \tag{A27}$$

5. *Calculation of First-Order Contribution $\hat{Z}_1^A$ to Compressibility Factor*

$\hat{f}_1^A$ as given above depends explicitly on η_W, d_W, and θ. We can easily see that

$$\frac{\partial\hat{f}_1^A}{\partial\theta} = 0\ . \tag{A28}$$

We have

$$d_W\frac{\partial\beta\hat{f}_1^A}{\partial d_W} = -3\zeta_2^A\ , \tag{A29}$$

with

$$\zeta_2^A = 96\,\eta_W\,\beta\left(\frac{2I_1^{12} - 2I_2^{12}}{d_W^{12}} - \frac{I_1^6 - I_2^6}{d_W^6}\right)\ . \tag{A30}$$

$\partial\beta\hat{f}_1^A/\partial\eta_W$ is easily calculated using (A18), (A19), (A24), and (A25), with the α_m given by (A8)–(A10).

We still need to know

$$\frac{\eta_W}{d_W}\frac{\partial d_W}{\partial\eta_W} = L$$
$$= \lambda - \tfrac{1}{48}\eta(1-\tfrac{1}{8}\eta)^{-1}, \tag{A31}$$

where

$$\lambda = \eta_W\frac{\partial}{\partial\eta_W}\left(\frac{\sigma_1}{2\sigma_0}\right)\delta \tag{A32}$$

is calculated with the help of (A5).

We then have

$$\hat{Z}_1^A = \frac{1}{1-3L}\left(\eta_W\frac{\partial\beta\hat{f}_1^A}{\partial\eta_W} - 3L\zeta_2^A\right)\ . \tag{A33}$$

The total compressibility factor of the total system is then

$$\hat{Z}^A = \hat{Z}_0^A + \hat{Z}_1^A\ . \tag{A34}$$

6. *Total Excess Internal Energy*

Using

$$\hat{U}_i^A = \frac{\partial\beta(\hat{f}_0^A + \hat{f}_1^A)}{\partial\beta}\ , \tag{A35}$$

we obtain

$$\hat{U}_i^A = \hat{f}_1^A + 4\delta_\beta'\,\Delta f + (\hat{Z}^A - 1 - \zeta_2^A)(1 - 3\lambda\nu)\frac{1}{\eta}\frac{\partial\eta}{\partial\beta}\ , \tag{A36}$$

where

$$\nu = \frac{\eta}{\eta_W}\frac{d\eta_W}{d\eta}$$
$$= \frac{1-\frac{1}{8}\eta}{1-\frac{1}{16}\eta} \tag{A37}$$

and

$$\frac{1}{\eta}\frac{\partial\eta}{\partial\beta} = 3\frac{d_B'}{d_B}(1+3\lambda\nu) + \frac{3\sigma_1}{2\sigma_0}\delta_\beta'\ . \tag{A38}$$

Then

$$\hat{U}_i^A = \hat{f}_1^A + 4\delta_\beta'\,\Delta f + 3(\hat{Z}^A - 1 - \zeta_2^A)(d_B'/d_B + \sigma_1/2\sigma_0\,\delta_\beta')\ . \tag{A39}$$

7. *Equation of State in* WCA *Approximation*

In order to calculate the hard-sphere diameter, the value of $\sigma_1/2\sigma_0$ is needed, which in the PY approximation is simply given by

$$\frac{\sigma_1}{2\sigma_0}=\frac{1-\frac{11}{2}\eta-\frac{11}{2}\eta^2}{(1+\frac{1}{2}\eta)(1-\eta)} . \tag{A40}$$

In the PY approximation τ_1 and τ_2 are given by (A15) and (A16) with $A\mu=0$ and $\sigma_0=\alpha_0$.

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*Laboratory associated with the Centre National de la Recherche Scientifique.

[1] R. W. Zwanzig, J. Chem. Phys. 22, 1420 (1954).

[2] J. A. Barker and D. Henderson, J. Chem. Phys. 47, 2856 (1967); 47, 4714 (1967).

[3] G. A. Mansoori and F. B. Canfield, J. Chem. Phys. 51, 4958 (1968).

[4] J. Rasaiah and G. Stell, Mol. Phys. 18, 249 (1970).

[5] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).

[6] N. F. Carnahan and K. E. Starling, J. Chem. Phys. 51, 635 (1969).

[7] B. J. Alder and T. E. Wainwright, J. Chem. Phys. 33, 1439 (1960).

[8] M. S. Wertheim, Phys. Rev. Letters 10, 321 (1963).

[9] E. J. Thiele, J. Chem. Phys. 38, 1959 (1963).

[10] B. J. Alder and C. E. Hecht, J. Chem. Phys. 30, 2032 (1969).

[11] D. Schiff and L. Verlet (unpublished).

[12] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. 54, 5237 (1971). A summary of the results is given in D. Chandler and J. D. Weeks, Phys. Rev. Letters 25, 149 (1970).

[13] S. Kim, Phys. Fluids 12, 2046 (1969).

[14] G. Stell, SUNY Engineering Report No. 182, 1970 (unpublished).

[15] L. Verlet, Phys. Rev. 165, 201 (1968).

[16] D. Levesque and L. Verlet, Phys. Rev. 182, 307 (1969).

[17] A misprint in Fig. 1 of Ref. 16 has been corrected.

[18] J. A. Barker and D. Henderson, J. Chem. Phys. 52, 2315 (1970).

[19] D. A. McQuarrie and J. L. Katz, J. Chem. Phys. 44, 2393 (1966).

[20] J. L. Lebowitz, Phys. Letters 28A, 569 (1969).

[21] J. P. Hansen, Phys. Rev. A 2, 221 (1970).

[22] J. J. Kozac and S. A. Rice, J. Chem. Phys. 48, 1226 (1968).

[23] H. C. Andersen, J. D. Weeks, D. Chandler (unpublished).

[24] J. P. Hansen and L. Verlet, Phys. Rev. 184, 151 (1969).

[25] L. Verlet and D. Levesque, Physica 36, 254 (1967).

[26] J. A. Barker, D. J. Leonard, and A. Pompe, J. Chem. Phys. 44, 4266 (1966).

[27] We owe this remark to J. Lebowitz.

[28] W. G. Hoover and F. H. Ree, J. Chem. Phys. 49, 3609 (1968).