PHYSICAL REVIEW VOLUME 108, NUMBER 3 NOVEMBER 1, 1957

Equation of State of Gases and Liquids at Low Temperatures*

W. B. RIESENFELD† AND K. M. WATSON††
Department of Physics, University of Wisconsin, Madison, Wisconsin

(Received March 14, 1957)

Application of a quantum-mechanical many-particle perturbation method is made to the determination of the equation of state of gases and liquids at low temperatures. The method utilizes the "nearest neighbor" expansion, which is a special case of Brueckner's "linked cluster" expansion. A description is given of condensation, mixed phases, the critical point and the critical temperature. It is shown that even the lowest-order approximation, which involves a relatively simple calculation, yields a physically reasonable theory of these phenomena, as well as the equation of state of the liquid phase. Specific calculations are presented for a system both above and below the critical temperature, and a description of collective phenomena in a quantum-mechanical system is given. The physical basis of the approach rests in a technique for interchanging the order in which averages are taken, and putting "fluctuations" into higher-order terms, which in turn may be handled by the same method. At low temperatures, when the thermal de Broglie wavelength of the particles is large so that they are effectively "spread over large distances," such fluctuations due to particle-particle encounters are expected to be small.

I. INTRODUCTION

In a previous paper,[1] which will hereafter be referred to as I, we described a perturbation method for calculating the energy of a quantum-mechanical system composed of N identical particles ($N\gg1$), contained in a box of volume $\mathcal{V}$. The particles were assumed to interact through two-body potentials

$$V_{ij}=V_{ij}(\mathbf{r}_i-\mathbf{r}_j), \tag{1}$$

where the subscripts "i" and "j" refer to individual particles, and $\mathbf{r}_i$ is the coordinate of particle "i". The energy of the system was expressed in the form of an expansion which was called the "nearest-neighbor expansion." This method represented a specific example of the proposal of Brueckner[2] to expand in "linked clusters."

As a perturbation method, the object in I was to calculate the energy $E_{\lambda0}$ corresponding to that eigenstate "λ_0" of the complete Hamiltonian which is associated with an unperturbed state "p_0". For our present discussion it will suffice to suppose the unperturbed state p_0 to be an eigenstate for N non-interacting particles in the volume $\mathcal{V}$, so that

$$p_0=(\mathbf{p}_{01}S_1,\mathbf{p}_{02}S_2,\cdots,\mathbf{p}_{0N}S_N). \tag{2}$$

Here $\mathbf{p}_{0i}$ ($i=1, 2, \cdots N$) represents the momentum vector of the ith particle and S_i its spin coordinate. Equation (2) simply indicates a scheme for labelling unperturbed states in terms of a complete set of independent-particle quantum numbers. Thus the assumption of pairing of states enables us to write

$$E_{\lambda0}=E(\mathbf{p}_{01}S_1,\cdots\mathbf{p}_{0N}S_N). \tag{3}$$

We now wish to discuss applications of this perturbation method to quantum statistical mechanics. In particular, we shall consider the calculation of the equation of state for gases and liquids, the nature of the phase transition between gas and liquid states, and the properties of the system at the critical point. The discussion of the wave function of the system (and its relation to particle correlation functions) is given in a separate publication.[3]

For simplicity we shall suppose that the N particles which comprise our system are identical, and that the interactions between them, i.e., the V_{ij}'s of Eq. (1), depend only on $(\mathbf{r}_i-\mathbf{r}_j)$ and the spins S_i and S_j. Our formal argument remains valid if the S_i are generalized to describe all internal degrees of freedom when the "particles" are complex systems.

To develop the thermodynamic properties of the system we shall use the canonical[4] ensemble for an N-particle system, and therefore must evaluate the partition function

$$Z=\sum_{\lambda_0}\exp(-\beta E_{\lambda0})$$
$$=\frac{1}{N!}\frac{\mathcal{V}^N}{h^{3N}}\sum_S\int\prod_{i=1}^N d^3p_{0i}\times\exp[-\beta E(\mathbf{p}_{01}S_1,\cdots\mathbf{p}_{0N}S_N)]. \tag{4}$$

Here

$$1/\beta\equiv\theta\equiv kT \tag{5}$$

is the temperature of the system in energy units. The index λ_0 runs over all quantum-mechanically distinct states, and the factor $(N!)^{-1}$ arises in the explicit repre-

---

* This work was supported by a grant from the National Science Foundation.

† Now at Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

†† Now at the Department of Physics, University of California, Berkeley.

[1] W. B. Riesenfeld and K. M. Watson, Phys. Rev. **104**, 492 (1956). This paper will be referred to as I.

[2] Brueckner, Levinson, and Mahmoud, Phys. Rev. **95**, 217 (1954); K. A. Brueckner, Phys. Rev. **96**, 508 (1954); **97**, 1353 (1955).

[3] R. Karplus and K. M. Watson, Phys. Rev. **107**, 1205 (1957).

[4] D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954).

sentation of the partition function in the form of an integral over momenta and a sum over spins as a consequence of the indistinguishability requirement placed on the N particles.

For later reference we express several thermodynamic functions in terms of Z, which is considered to be a function of N, $\beta=\theta^{-1}$, and $\mathcal{V}$:

$$\begin{aligned} U&=-\frac{\partial}{\partial\beta}\ln Z &&=\text{internal energy},\\ P&=\theta\frac{\partial}{\partial\mathcal{V}}\ln Z &&=\text{pressure},\\ S&=k\ln Z-k\beta\frac{\partial}{\partial\beta}\ln Z &&=\text{entropy},\\ F&=U-TS=-\theta\ln Z &&=\text{Helmholtz free energy},\end{aligned} \tag{6}$$

where the normalization of Z as given by Eq. (4) ensures that thermodynamic functions like entropy and free energy are properly extensive quantities.

In the next two sections we discuss the problem of evaluating Z once the energies $E(\mathbf{p}_{01}S_1,\cdots\mathbf{p}_{0N}S_N)$ have been found. In the course of the discussion it will be necessary to anticipate some properties of the $E(\mathbf{p}_{01}\cdots S_N)$ which are physically plausible—but which must actually be justified by detailed calculations for specific physical systems. For this reason we emphasize that the discussion of Secs. II and III is not presented as a *theory* of the equation of state or of condensation, but rather as a method for evaluating Z (and thus the thermodynamic properties of the system) once the spectrum $E(\mathbf{p}_{01}\cdots S_N)$ has been obtained. In Secs. IV and V we shall give examples by calculating E and the equation of state for gaseous, mixed, and liquid phases in the vicinity of the critical point, for systems having specified potentials V_{ij}. In the remainder of this section we review the quantum-mechanical perturbation method which was described in I.

The first step in obtaining the energies $E_{\lambda 0}$ was the elimination of the potentials V_{ij} in terms of two-body *scattering matrices* R_{ij}. This is the technique introduced by Brueckner *et al.*[5] in their studies of nuclear structure, and which also had been used in studying multiple scattering by quantum-mechanical systems.[6] On physical grounds this appears very reasonable, since in principle one now starts from exact solutions to the two-body problem in studying the many-body problem. From the standpoint of obtaining a rapidly converging N-particle perturbation theory, the use of the R_{ij}'s has a particular advantage in that regions of coordinate space corresponding to large values of $|V_{ij}|$ tend to become "smeared out" and weakened in the R_{ij}'s. For example, if the V_{ij}'s have "infinite repulsive cores," there is no perturbation theory possible in terms of the V_{ij}'s. The R_{ij}'s remain finite in this case, however, and are suitable for use in a perturbation theory.

This feature of the R_{ij}'s results from the principle of complementarity, according to which particles having momenta within a restricted range of values cannot be precisely localized in coordinate space. Indeed, one of the principal physical reasons for using a momentum-space representation is that we thus automatically exploit this quantum-mechanical "smearing" of interactions. We expect that for an essentially "random medium" such as a gas or liquid, the interactions will be "smoother" functions of the momenta $\mathbf{p}_i$ than of the coordinates $\mathbf{r}_i$. This simplification is expected to be especially important at low temperatures.

We may restate this point by saying that the energy of each particle, expressed as a function of its momentum, is that of a particle traveling in a dispersive medium—a medium consisting of the remaining $(N-1)$ particles. The total energy $E_{\lambda 0}$ represents a self-consistent summation over these single-particle energies. The calculation of the energy of a particle in a dispersive medium is that of finding the index of refraction for a wave propagation through a medium, or that of finding the "optical model" potential. Here the "suddenness" of particle-particle encounters may be largely lost in the wave-number (or momentum) description.

To continue, the "nearest neighbor" expansion[1] expresses the energy in the form

$$E_{\lambda 0}=K(p_0)+\delta E, \tag{7}$$

where

$$K(p_0)=\sum_{i=1}^{N}\frac{p_{0i}^2}{2M} \tag{8}$$

is the kinetic energy, M is the particle mass, and δE is given by the expectation value

$$\delta E=\sum_{n=2}^{N}\sum_{i_1<i_2<\cdots<i_n} v_n(i_1\cdots i_n). \tag{9}$$

The quantity $v_n(i_1\cdots i_n)$ represents the interaction energy of particles $i_1\cdots i_n$. Its perturbation expansion[7] is

$$v_n(i_1\cdots i_n) =\left\langle p_0\left|\sum_l \sum_{\alpha_1,\alpha_2,\cdots\alpha_l} R_{\alpha_1}\frac{1}{d}R_{\alpha_2}\cdots\frac{1}{d}R_{\alpha_l}\right|p_0\right\rangle. \tag{10}$$

Here (and in the following) Greek subscripts such as α refer to *pairs* of interacting particles, and R_α is the two-

---

[5] K. A. Brueckner and C. A. Levinson, Phys. Rev. **97**, 1344 (1955); R. J. Eden and N. C. Francis, Phys. Rev. **97**, 1366 (1955); R. J. Eden, Phys. Rev. **99**, 1418 (1955); K. A. Brueckner, Phys. Rev. **100**, 36 (1955); **103**, 1121 (1956); K. A. Brueckner and W. Wada, Phys. Rev. **103**, 1008 (1956).

[6] N. C. Francis and K. M. Watson, Phys. Rev. **92**, 291 (1953); K. M. Watson, Phys. Rev. **89**, 575 (1953).

[7] An integral equation representation for v_n is possible. See reference 1.

particle scattering operator R_{ij} mentioned above. The summation over $(\alpha_1\cdots\alpha_l)$ runs over all combinations of pairs of particles belonging to the set $(i_1\cdots i_n)$ in such a manner that *every* member of the entire set $(i_1\cdots i_n)$ is "linked" to *each* other member in the sense of Brueckner.[2] That is, two particles such as "a" and "b" are linked in Eq. (10) if for each term in the sum either "a' and "b" scatter directly, or there exists at least one set of particles $a_1, a_2, \cdots a_r$ such that "a" and a_1 scatter, a_1 and a_2 scatter, $\cdots$, a_{r-1} and a_r scatter, and finally a_r and "b" scatter. The sum l runs over all numbers of scattering consistent with the requirement that the set $(i_1\cdots i_n)$ be "linked." Finally, no pair of particles scatters twice in succession in Eq. (10).

The energy denominators d in Eq. (10) are defined as

$$d=\sum_{l=1}^{n}[\epsilon(\mathbf{p}_{0il})-\epsilon(\mathbf{p}_{il})], \tag{11}$$

where $\epsilon(\mathbf{p}_i)$ is the "dispersive" energy of the ith particle in the medium. This is given by

$$\epsilon(\mathbf{p}_i)=\frac{p_i^2}{2M}+\delta\epsilon(\mathbf{p}_i), \tag{12}$$

with

$$\delta\epsilon(\mathbf{p}_i)=\sum_{l=1,(l\neq i)}^{N} R_{il}F_{il},$$

$$F_{il}=1+\sum_{r=1,(r\neq l,i)}^{N}\frac{1}{d}R_{ir}F_{ir} \tag{13}$$

evaluated as an expectation value for particle "i" in the excited state $\mathbf{p}_i$. Thus $\delta\epsilon(\mathbf{p}_i)$ is just the "optical model potential" for particle "i."

Finally, the two-body scattering operators are defined as solutions to the integral equations

$$R_{ij}=V_{ij}+V_{ij}\frac{1}{d}R_{ij}. \tag{14}$$

The evaluation of these was described in I. In the appendix we give a somewhat expanded discussion of Eqs. (12) and (13).

For degenerate Fermi-Dirac or Bose-Einstein systems it may be convenient to write Eq. (10) in second-quantized form. Following Brueckner and Levinson,[5] we may set

$$R_\alpha=\eta_i^\dagger\eta_j^\dagger\langle\mathbf{p}_iS_i,\mathbf{p}_jS_j|R|\mathbf{p}_mS_m,\mathbf{p}_nS_n\rangle\eta_m\eta_n,$$

where the $\eta_i^\dagger$ and η_i are creation and absorption operators, respectively, for particles in the momentum state $\mathbf{p}_i$, S_i. In this case, we use the terminology "connected Feynman graph" rather than "linked cluster" in describing the terms in Eq. (10). To use this terminology, we may think of "p_0" as the "vacuum state." A pair of particles is "created" when the particles scatter out of the "p_0" state. The scattering of two particles may be represented by two intersecting particle lines, etc. Equation (9) then represents a "vacuum expectation value." A more detailed description of this terminology is given in Sec. V. When Eqs. (9) and (10) are interpreted in this manner, the development of reference 1 is unchanged.

Boundary conditions at the walls of the volume $\mathcal{V}$ will be consistently ignored.[8] This means that we shall calculate only the volume energy (and not the surface energy) of the system. For most systems of interest in statistical mechanics this seems a quite satisfactory approximation.

We anticipate that some of the states λ_0 of the N-particle system may contain "bound states" of smaller groups of particles. For instance, there may be bound states of pairs of particles, triplets, etc. These "bound states" are characterized by the fact that the "bound particles" are confined about their center of mass to a region of space with volume less than $\mathcal{V}$. Such states are "degenerate" in the sense that the centers of mass associated with them may be moved about within the volume $\mathcal{V}$. In particular there may be "bound states" containing very large numbers of particles. We shall call one of these a "droplet" substate of the system when it contains enough particles that its surface energy may be ignored compared to its volume energy.

On this basis we shall classify the "bound states" as either "droplet states" or "cluster states," depending upon whether or not the number of particles involved is large enough that the surface energy may be neglected. This separation appears somewhat arbitrary, but becomes precise once we have specified the error which can be accepted in the "surface energies." As we shall see, the "droplet states" become important only at the condensation point. Thus *large* "droplets" appear sud-

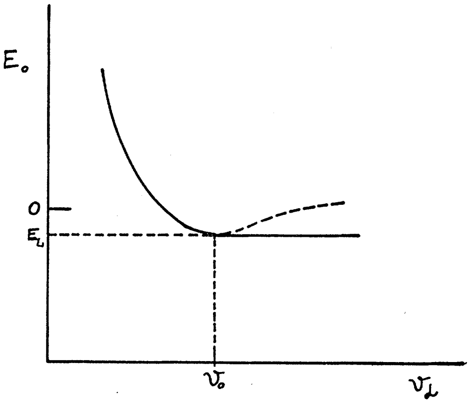

FIG. 1. The energy of a "droplet" as a function of the volume to which it is confined. When the walls pull away from the droplet, its energy remains constant. The dashed curve shows the failure of perturbation methods to yield constant energy for $\mathcal{V}_d > \mathcal{V}_0$.

---

[8] H. A. Bethe, Phys. Rev. **103**, 1353 (1956), has described a method by which boundary conditions can be handled in principle.

denly, and a precise definition of a "droplet" appears unnecessary in practice.

To identify and obtain the energy of these "droplet states" we argue as follows: the actual volume $\mathcal{V}$ of the system is replaced by a variable volume $\mathcal{V}_d$, and the number of particles N is replaced by N_d. Let us suppose that we have found the energy E_0 of the lowest state as a function of $\mathcal{V}_d$. If the forces between the particles lead to *saturation*, then E_0 should become very large for small $\mathcal{V}_d$. As we increase $\mathcal{V}_d$, E_0 may fall to a value E_L at a volume $\mathcal{V}_d=\mathcal{V}_0$ and then remain constant for $\mathcal{V}_d>\mathcal{V}_0$. This will happen if $E_L<0$, and means that for $\mathcal{V}_d>\mathcal{V}_0$ the confining walls have moved away from the system which then occupies its *natural volume* $\mathcal{V}_0$. Such a situation is shown by the solid curve in Fig. 1.

In actual practice, calculation is more likely to yield a result such as is indicated by the dashed curve in Fig. 1 for $\mathcal{V}_d>\mathcal{V}_0$. This is anticipated because we expect any perturbation method to converge much more slowly (if at all) when the system has been put into the wrong volume in the unperturbed stated p_0. This need cause us no difficulty, since we only need to locate the minimum value of E_0 (i.e., E_L) at the volume $\mathcal{V}_0$. This value we know to be the actual value of E_0 for $\mathcal{V}_d>\mathcal{V}_0$, which permits us to obtain the complete solid curve in Fig. 1 without further calculation.

In general, of course, there will also be excited states of the N_d particle subsystem, which are confined to a volume $\mathcal{V}_d\simeq\mathcal{V}_0$. These states must be obtained in the same manner (i.e., the first excited, second excited, etc. states will show a similar behavior as a function of energy—the number of states actually "bound" presumably being finite).

For an actual state λ_0 of the N-particle system, we may count all the particles in droplet states to obtain a total number N_L. Thus,

$N_L=$ total number of particles in "droplet states,"

$N_G=N-N_L=$ number of particles in "gas-like states." (15)

Here N_G is the number of all single particles and all particles in "cluster states." Since we are calculating only the volume energy of the droplet states, it follows that the total energy E_d of these will be proportional to N_L:

$$E_d=N_L\mathcal{U}_d, \tag{16}$$

where the "energy per droplet particle" $\mathcal{U}_d$ is independent of N_L. The total volume associated with all droplets will be

$$\mathcal{V}_0=N_L\tau_0, \tag{17}$$

where τ_0 is independent of N_L. As was shown in I, Eqs. (16) and (17) hold for every term in the sum over n of Eq. (9). That these equations hold for the sum itself must be verified for each specific problem.

There is a flaw in the argument given above, because the medium may also have "crystal-like" states. Such states would probably be missed in our perturbation calculation, since it was designed for media which are essentially "random" rather than "ordered" in coordinate space. Here we appeal to physical plausibility, arguing that for a system in either its gaseous or liquid phase the "crystal-like" states play a negligible role in determining its thermodynamic properties. In other words, these states will have a negligible statistical weight in the evaluation of Z for a liquid or gas. In this sense our theory is incomplete, since we do not expect to obtain liquid-solid phase transitions from it.

We close this section by summarizing its contents: it is proposed to calculate the energy of the many-particle system in such a manner as to treat *fluctuations* associated with particle encounters as perturbations. This is done first of all by using a momentum-space description, which for the lowest states exploits the expected quantum-mechanical "smearing of particle positions." The quantum-mechanical "smearing" is particularly emphasized in the use of the R_{ij}'s rather than the V_{ij}'s. Finally, retaining the energies $\delta\epsilon$ in the propagators d means that complex cooperative interactions are kept even in a lowest-order calculation, but that fluctuations in these interactions have been "averaged out."

II. EVALUATION OF THE PARTITION FUNCTION—CONDENSATION

In this and the following section we shall suppose the eigenenergies E_λ to have been obtained and shall consider the purely formal problem of evaluating the partition function Z. The momentum-space representation which we are using has some novel features which appear to be quite helpful in carrying out this evaluation.

For a given volume $\mathcal{V}$, a given number of particles N, and a given state λ, let us write Eq. (15) in greater detail by assuming that there are N_s single particles, N_p particles bound as pairs, N_t particles bound as triplets, $\cdots N_L$ particles bound in droplets. Then

$$N_G=N_s+N_p+\cdots;\quad N_G+N_L=N. \tag{18}$$

We formally write E_λ as

$$E_\lambda=E_{\lambda s}+E_{\lambda p}+\cdots+E_{\lambda D}, \tag{19}$$

where $E_{\lambda s}$ is the energy associated with the single particles, $E_{\lambda p}$ is the energy associated with bound pairs of particles, $\cdots$, and $E_{\lambda D}$ is the energy associated with droplet states. $E_{\lambda D}$ is well-defined because we have agreed to keep only the volume energy of the droplets. A more precise definition of $E_{\lambda s}$, $E_{\lambda p}$, $\cdots$ will be given in Sec. III.

As a consequence of Eqs. (18) and (19), Eq. (4) can be written in the form

$$Z=\sum_{\substack{N_G=0\\(N_G+N_L=N)}}^{N} Z_L(N_L)Z_G(N_G), \tag{20}$$

with

$$Z_L(N_L)=\sum_{\substack{\lambda_D\\(N_L\ \text{fixed})}}\exp(-\beta E_{\lambda_D}),$$

$$Z_G(N_G)=\sum_{\substack{\lambda_s,\lambda_p,\cdots\\N_s,N_p,\cdots(N_s+N_p+\cdots=N_G)}}\times\exp[\beta(E_{\lambda_s}+E_{\lambda_p}+\cdots)].\qquad(21)$$

In carrying out the above sum over states λ_D in Z_L, one must in principle sum over the number of "droplets," say D, and the possible positions of the droplets within $\mathcal{V}$. The statistical weight of these states is negligible, however, since it is roughly given by

$$[\mathcal{V}\delta^3p/h^3]^D,$$

which by Eq. (17) is to be compared with

$$[N_L\tau_0\delta^3p/h^3]^{N_L}.$$

Here δ^3p is the appropriate volume element in momentum space. Since the droplets have been assumed "big," the first factor is negligible compared to the second. Thus the droplets may be treated as if they were all "coalesced" into a single large "droplet" which, for instance, may rest on the "bottom of the container."

We shall henceforth refer to Z_G as "the partition function of the gaseous phase" and to Z_L as "the partition function of the liquid phase"—a terminology for which the justification will become evident. Once Z_L and Z_G are individually known, the evaluation of Z in Eq. (20) is easily accomplished by a saddle-point method.[9] In the remainder of this section we illustrate this technique in some detail because of its importance to the following discussion. In Sec. III we consider the evaluation of Z_L and Z_G.

We first observe that Z_L and Z_G may generally be written in the form

$$\begin{aligned}Z_L&=\frac{1}{N_L!}[N_L\tau Q_L(\tau,\theta)]^{N_L},\\ Z_G&=\frac{1}{N_G!}[\mathcal{V}_GQ_G(\mathcal{V}_G/N_G,\theta)]^{N_G}.\end{aligned}\qquad(22)$$

Here τ is interpreted as the "volume per particle" in the liquid phase, so that

$$\mathcal{V}_L\equiv N_L\tau\qquad(23)$$

is the volume occupied by the liquid phase. The actual value of τ will be determined in the following discussion; we anticipate, however, that τ will be approximately equal to the τ_0 of Eq. (17). Then $\mathcal{V}_G$ is defined as

$$\mathcal{V}_G\equiv\mathcal{V}-\mathcal{V}_L.\qquad(24)$$

Finally, Q_L and Q_G are functions of the indicated variables, the evaluation of which we shall consider in Sec. III.

According to Eq. (6), the pressures of the two phases are, respectively,

$$\begin{aligned}\frac{P_G}{\theta}&=\frac{\partial}{\partial\mathcal{V}_G}\ln Z_G=\frac{1}{\nu}+\frac{\partial}{\partial\nu}\ln Q_G,\\ \frac{P_L}{\theta}&=\frac{\partial}{\partial\mathcal{V}_L}\ln Z_L=\frac{1}{\tau}+\frac{\partial}{\partial\tau}\ln Q_L,\end{aligned}\qquad(25)$$

where we have introduced

$$\nu\equiv\mathcal{V}_G/N_G.\qquad(26)$$

To obtain Z, and thus the equation of state, let us start the system in a volume $\mathcal{V}$ large enough to ensure that the system is purely gaseous. We shall then suppose it to be compressed isothermally, and shall calculate the equation of state at each stage of the compression.

Equation (20) may be rewritten as

$$Z=\sum_{N_L=0}^{N}\frac{1}{N_L!}[N_L\tau Q_L(\tau,\theta)]^{N_L}\frac{1}{(N-N_L)!}\times[\mathcal{V}_GQ_G(\nu,\theta)]^{N-N_L}.\qquad(27)$$

When $\mathcal{V}$ is sufficiently large we may consider $N_L\ll N$, and expand $\mathcal{V}_G$, Q_G to first order in N_L:

$$\begin{aligned}\mathcal{V}_GQ_G(\nu,\theta)&=(\mathcal{V}-N_L\tau)Q_G\left(\frac{\mathcal{V}-N_L\tau}{N-N_L},\theta\right)\\ &\cong\mathcal{V}Q_G(\nu_G,\theta)\left[1-\frac{N_L\tau}{\mathcal{V}}+\frac{N_L}{N}\left(1-\frac{\tau}{\nu_G}\right)\right.\\ &\qquad\left.\times\nu_G\frac{\partial}{\partial\nu_G}\ln Q_G(\nu_G,\theta)\right]\\ &=\mathcal{V}Q_G(\nu_G,\theta)\left\{1-\frac{N_L}{N}\left[\frac{P_G}{\theta}(\tau-\nu_G)+1\right]\right\}.\end{aligned}\qquad(28)$$

Here we have defined

$$\nu_G\equiv\mathcal{V}/N\qquad(29)$$

and have eliminated $(\partial/\partial\nu_G)\ln Q_G$ by means of Eq. (25). We have considered τ to be a parameter and used Eqs. (23) and (24) in expanding $\mathcal{V}_G$.

For very large N we have

$$\left\{1-\frac{N_L}{N}\left[\frac{P_G}{\theta}(\tau-\nu_G)+1\right]\right\}^N\cong\exp\left\{-N_L\left[\frac{P_G}{\theta}(\tau-\nu_G)+1\right]\right\}.$$

---

[9] Considerably more complicated sums than that of Eq. (20) are handled by this or related methods, of course. See, for instance, reference 4.

Substituting Eq. (28) into Eq. (27) and using both this result and Stirling's approximation for the factorials, we obtain

$$Z=\frac{1}{N!}[\mathcal{V}Q_G(\nu_G,\theta)]^N \sum_{N_L=0}^{N}\left(\frac{eN}{N_L}\right)^{N_L}\left[\frac{N_L\tau Q_L(\tau,\theta)}{\mathcal{V}Q_G(\nu_G,\theta)}\right]^{N_L}$$

$$\times\exp\left\{-N_L\left[\frac{P_G}{\theta}(\tau-\nu_G)+1\right]\right\}$$

$$\equiv\frac{1}{N!}[\mathcal{V}Q_G(\nu_G,\theta)]^N \sum_{N_L=0}^{N} R^{N_L}$$

$$=\frac{1}{N!}[\mathcal{V}Q_G(\nu_G,\theta)]^N\left(\frac{1-R^{N+1}}{1-R}\right), \tag{30}$$

where

$$R\equiv\frac{N\tau Q_L(\tau,\theta)}{\mathcal{V}Q_G(\nu_G,\theta)}\exp\left[\frac{P_G}{\theta}(\nu_G-\tau)\right]. \tag{31}$$

Since N is assumed to be very large, it is evident that for

$$R<1 \tag{32}$$

only values of N_L are important in the sum of Eq. (30) for which $N_L \ll N$. Thus, our approximation that $N_L \ll N$, made in Eq. (28), is justified. It also is evident that in this case we may replace Eq. (30) by

$$Z=Z_G(\mathcal{V},N,\theta)$$

$$=\frac{1}{N!}[\mathcal{V}Q_G(\nu_G,\theta)]^N, \tag{33}$$

From Eqs. (6) and (25) we obtain the pressure of the systems as

$$P=P_G, \tag{34}$$

and the resulting equation of state is that of the gaseous phase.

It is clear that for $R=1$, or for

$$N\tau Q_L(\tau,\theta)e^{-P_G\tau/\theta}=\mathcal{V}Q_G(\nu_G,\theta)e^{-P_G\nu_G/\theta}, \tag{35}$$

the properties of the system show a discontinuous change. This occurs, as we compress isothermally, at the first (i..e, largest) value of $\mathcal{V}$, say $\mathcal{V}_c$, which satisfies Eq. (35). (We have not yet shown how to obtain τ, of course.) As we shall see, Eq. (35) defines the condensation point.

When $R>1$, the approximate evaluation of Z as given by Eq. (30) fails. For $\mathcal{V}<\mathcal{V}_c$ we therefore evaluate Z by means of a conventional saddle-point method.

We return to Eq. (27) and write it in the form

$$Z=\sum_{N_G=0}^{N}\frac{1}{(N-N_G)!}[(N-N_G)\tau Q_L(\tau,\theta)]^{N-N_G}$$

$$\times\frac{1}{N_G!}[\mathcal{V}_GQ_G(\nu,\theta)]^{N_G}$$

$$=\sum_{N_G=0}^{N}[e\tau Q_L(\tau,\theta)]^{N-N_G}\left[e\frac{\mathcal{V}_G}{N_G}Q_G\left(\frac{\mathcal{V}_G}{N_G},\theta\right)\right]^{N_G}$$

$$\equiv[e\tau Q_L(\tau,\theta)]^N\sum_{N_G=0}^{N}\Gamma(N_G), \tag{36}$$

where

$$\ln\Gamma(N_G)\equiv N_G\ln\left[\frac{\mathcal{V}_GQ_G(\nu,\theta)}{N_G\tau Q_L(\tau,\theta)}\right]. \tag{37}$$

To derive Eqs. (36) and (37) we have again used Stirling's approximation for the factorials. A Taylor expansion of $\ln\Gamma$ about the value N_{G0} of N_G which maximizes $\ln\Gamma$ will yield an expression of the form

$$\ln\Gamma(N_G)=\ln\Gamma(N_{G0})-\frac{\alpha}{2N_{G0}}(N_G-N_{G0})^2+\cdots, \tag{38}$$

with α given by

$$\alpha=-N_G\frac{\partial^2\ln\Gamma}{\partial N_G{}^2}\bigg|_{N_G=N_{G0}}.$$

To calculate $\ln\Gamma(N_{G0})$, N_{G0}, and α, we still treat τ as an undetermined constant parameter, and write

$$\mathcal{V}_G=\mathcal{V}-N_L\tau=\mathcal{V}-N\tau+N_G\tau, \tag{39}$$

so that

$$\partial\mathcal{V}_G/\partial N_G=\tau,$$

$$\frac{\partial\nu}{\partial N_G}=\frac{\partial}{\partial N_G}\left(\frac{\mathcal{V}_G}{N_G}\right)=-\frac{1}{N_G}(\nu-\tau). \tag{40}$$

Consequently N_{G0} is determined by the equation

$$\frac{\partial}{\partial N_G}\ln\Gamma(N_G)=\ln\frac{\mathcal{V}_GQ_G(\nu,\theta)}{N_G\tau Q_L(\tau,\theta)}+\frac{\tau}{\nu}-1-(\nu-\tau)\frac{\partial}{\partial\nu}\ln Q_G$$

$$=0. \tag{41}$$

Since this equation depends only upon $\nu=\mathcal{V}_G/N_G$ and not upon N_G or $\mathcal{V}_G$ separately, it has a solution of form

$$\nu_0\equiv\mathcal{V}_{G0}/N_{G0}, \tag{42}$$

which is *independent* of the volume $\mathcal{V}$ as long as

$$0<N_{G0}<N;\quad \mathcal{V}_{G0}>0. \tag{43}$$

Combining Eqs. (37) and (41), we obtain

$$\ln\Gamma(N_{G0})=N_{G0}\left[-\frac{\tau}{\nu_0}+1+(\nu_0-\tau)\frac{\partial}{\partial\nu}\ln Q_G\bigg|_{\nu=\nu_0}\right]$$

$$=(\mathcal{V}_{G0}-N_{G0}\tau)\frac{P_{G0}}{\theta}, \tag{44}$$

where we have used Eq. (25) to define

$$\frac{P_{G0}}{\theta}\equiv\frac{1}{\nu_0}+\frac{\partial}{\partial\nu_0}\ln Q_G(\nu_0,\theta). \tag{45}$$

When the conditions of Eq. (43) are satisfied, P_{G0} is evidently a constant, independent of the volume $\mathcal{V}$.

To find the parameter α of Eq. (38) we differentiate Eq. (41) with respect to N_G, set $N_G=N_{G0}$, and use Eq. (45):

$$\left.\frac{\partial^2\ln\Gamma}{\partial N_G^2}\right|_{N_G=N_{G0}}=-\frac{1}{N_{G0}}(\nu_0-\tau)\left[\frac{1}{\nu_0}-\frac{\tau}{\nu_0^2}-(\nu_0-\tau)\frac{\partial^2}{\partial\nu_0^2}\ln Q_G(\nu_0,\theta)\right]$$

$$=\frac{1}{\theta N_{G0}}(\nu_0-\tau)^2\frac{\partial P_{G0}}{\partial\nu_0}.$$

Thus

$$\alpha=-(\nu_0-\tau)^2\frac{1}{\theta}\frac{\partial P_{G0}}{\partial\nu_0}. \tag{46}$$

Physical considerations make it clear that in general P_{G0} is a decreasing function of ν_0, so that α is a positive quantity. If, furthermore, α is not of order $1/N_{G0}$, then the summand in Eq. (36) will be sharply peaked about $N_G=N_{G0}$.

Equations (38) and (44)) may now be used in Eq. (36), so that the sum becomes

$$Z=[e\tau Q_L]^N\exp\left[\frac{P_{G0}}{\theta}(\mathcal{V}_{G0}-N_{G0}\tau)\right]$$

$$\times\sum_{N_G=0}^{N}\exp\left[-\frac{\alpha}{2N_{G0}}(N_G-N_{G0})^2\right]. \tag{47}$$

We exploit the sharp peaking of the summand by retaining only the term with $N_G=N_{G0}$, the remaining terms giving negligible contributions to Z. There results

$$Z=[e\tau Q_L]^N\exp\left[\frac{P_{G0}}{\theta}(\mathcal{V}_{G0}-N_{G0}\tau)\right]. \tag{48}$$

We now determine τ by demanding that when the conditions of Eq. (43) hold, we must have pressure equilibrium between the two phases:

$$P_L=P_G=P_{G0}.$$

By use of Eq. (25) this becomes

$$\frac{1}{\tau}+\frac{\partial}{\partial\tau}\ln Q_L=\frac{P_{G0}}{\theta}, \tag{49}$$

which, as we have seen, in a constant independent of $\mathcal{V}$ when Eq. (43) is valid. Therefore in the "mixed phase" region given by Eq. (43), and by continuity at the condensation point given by Eq. (35), τ is determined by Eq. (49).

As we compress the system isothermally in the "mixed phase" region, the pressure is determined from Eq. (48) to be

$$\frac{P}{\theta}=\frac{\partial}{\partial\mathcal{V}}\ln Z$$

$$=\frac{P_{G0}}{\theta}\left(1-\frac{\tau}{\nu_0}\right)\frac{\partial\mathcal{V}_{G0}}{\partial\mathcal{V}}.$$

But by combining Eqs. (39) and (42) we obtain

$$\frac{\partial\mathcal{V}_{G0}}{\partial\mathcal{V}}=\left(1-\frac{\tau}{\nu_0}\right)^{-1},$$

so that

$$P/\theta=P_{G0}/\theta. \tag{50}$$

The pressure thus remains constant as long as Eq. (43) is satisfied. However, as we continue compressing the system, we shall eventually reach a volume $\mathcal{V}$ such that

$$\mathcal{V}=N\tau, \tag{51}$$

and consequently

$$\mathcal{V}_{G0}=0,\quad N_{G0}=0. \tag{52}$$

As we compress further, Eq. (51) obviously remains valid so that τ no longer remains constant; it is, in fact, directly determined by Eq. (51). Equations (52) also remain valid, and the partition function as given by Eq. (48) becomes

$$Z=[e\tau Q_L(\tau,\theta)]^N. \tag{53}$$

The equation of state is

$$\frac{P}{\theta}=\frac{P_L}{\theta}=\frac{1}{\tau}+\frac{\partial}{\partial\tau}\ln Q_L(\tau,\theta), \tag{54}$$

with τ given by Eq. (51).

Equation (35) does not necessarily have a solution, of course, and in this case we do not expect condensation to occur. When it has a solution, comparison with Eq. (41) shows that

$$\nu_G=\nu_0,$$

as must be the case. We also expect that Eq. (35) will in general have solutions for θ less than some θ_c, where θ_c is the "critical temperature." To see this qualitatively, we set

$$Q_L\cong e^{\beta\Delta\epsilon}Q_G,$$

where $\Delta\epsilon$ may be interpreted roughly as the "binding energy" of a particle in the "droplet states." Also, we may take

$$\exp\left[-\frac{P_G}{\theta}(\nu_G-\tau)\right]\cong 1.$$

Then Eq. (35) becomes

$$e^{\beta\Delta\epsilon}=\frac{\mathcal{V}}{N_T}. \tag{55}$$

As we raise the temperature $\beta\rightarrow 0$ and $\mathcal{V}/N_T\rightarrow 1$. However, as $\mathcal{V}/N_T\rightarrow 1$, $\Delta\epsilon\rightarrow 0$ because the distinction between "droplet" and "gaseous" states is lost as $\nu\rightarrow\tau$. Consequently Eq. (55) will in general have the solution $\nu_0=\tau$ at some finite temperature θ_c. This determines the *critical point*, above which condensation does not occur. Reference to Eq. (46) shows that fluctuations in the system become arbitrarily large close to the critical point—which is to be expected, of course. In Secs. IV and V we shall illustrate these remarks with specific calculations.

Let us emphasize again that the foregoing is not presented as a "theory" of condensation, since the evaluation of the quantities Q_G and Q_L has not yet been described. Some comment on the relation to theories of condensation is in order, however.

Our "droplet states" are certainly related physically to the "liquid droplets" of the liquid drop model.[10] We have not had to make simplifying assumptions, however, concerning the properties of the droplets. Closely related, also, are the theories based on "dissociating systems" of Band[11] and Frenkel.[12] Less closely related is the theory of Mayer.[13] Indeed, the present use of "linked clusters" is not at all the same as the use of "clusters" by Mayer.[13]

III. EVALUATION OF THE QUANTITY Z_G

The determination of Z_G presents far more formidable problems than those encountered in Sec. II. We are therefore forced to find approximate methods applicable to special systems. A simplifying assumption, for instance, presents itself quite naturally as a consequence of the smallness of the relative fluctuations known to prevail in gaseous systems. Thus the actual interaction energies of bound groups of particles, such as pairs, with single particles and other bound groups may be replaced, approximately, by an "average" interaction of the pairs, etc., with a statistical medium composed of the other bound groups.

Let us now assume that Eq. (21) for Z_G may be written in the form

$$Z_G(N_G)=\sum_{\substack{N_s,\,N_p,\,\cdots\\(N_s+N_p+\cdots=N_G)}} Z_s(N_s)Z_p(N_p)\cdots, \tag{56}$$

where Z_s, Z_p, $\cdots$ are considered to be partition functions for the "single particles," "pairs of particles," etc.

Comparing Eqs. (21) and (56), we are led to

$$\begin{aligned}Z_s(N_s)&=\sum_{\lambda_s}\exp(-\beta E_{\lambda_s}),\\ Z_p(N_p)&=\sum_{\lambda_p}\exp(-\beta E_{\lambda_p}),\\ &\cdots\cdot\end{aligned} \tag{57}$$

An energy such as E_{λ_p} contains, of course, not only the "binding energy" of the pairs, but also the interaction energy of the pairs with single particles, with each other, and with all other bound-particle configurations. The factorization of Eq. (21) made in Eq. (57) implies that we replace the interactions of the "pairs" with "single particles in the state λ_s" by an interaction with "single particles in an average (or most probable) state λ_s," etc. This approximation is in accordance with the assumption made above, and appears to be valid for many physical situations. In any case, we shall accept Eqs. (56) and (57) as the basis for most of the discussion in this section.

Following an argument similar to that of Sec. II, we may replace Eq. (56) by

$$Z_G(N_G)=Z_s(N_{s0})Z_p(N_{p0})\cdots, \tag{58}$$

where N_{s0}, N_{p0}, $\cdots$ maximize the summand of Eq. (56) as given by Eq. (57), subject to the restriction that

$$N_{s0}+N_{p0}+\cdots=N_G. \tag{59}$$

In the particular case that only single particles and pairs need be considered, we write in analogy with Eqs. (22)

$$\begin{aligned}Z_s&=\frac{1}{N_s!}\left[\mathcal{V}_GQ_s\left(\frac{\mathcal{V}_G}{N_s},\theta\right)\right]^{N_s},\\ Z_p&=\frac{1}{(\tfrac{1}{2}N_p)!}\left[\mathcal{V}_GQ_p\left(\frac{2\mathcal{V}_G}{N_p},\theta\right)\right]^{\frac{1}{2}N_p},\end{aligned} \tag{60}$$

maximize

$$\ln\Gamma(N_s)=N_s\ln\left[\frac{e}{N_s}\mathcal{V}_GQ_s\right]+\tfrac{1}{2}(N_G-N_s)\ln\left[\frac{2e}{N_G-N_s}\mathcal{V}_GQ_p\right]$$

with respect to N_s, and obtain

$$\frac{N_{p0}}{2N_{s0}^2}=\frac{Q_p}{\mathcal{V}_GQ_s^2}. \tag{61}$$

Here Q_s and Q_p are functions yet to be determined.

We next consider the problem of calculating Q_s or Z_s. A method of doing this for low temperatures was given in I. This assumed that E_{λ_s} could be expanded in a power series in the particle momenta $\mathbf{p}_{0i}$. Terms no

---

[10] R. Becker and W. Doering, Ann. Physik 24, 719 (1935); H. Wergeland, Avhandl. Norske Videnskaps-Akad. Oslo I. Mat-Naturv. Kl. No. 11 (1943).

[11] W. Band, J. Chem. Phys. 7, 324, 927, 1114 (1939).

[12] J. Frenkel, J. Chem. Phys. 7, 200 (1939).

[13] J. E. Mayer, J. Chem. Phys. 5, 67 (1937).

higher than quadratic were kept, giving

$$E_{\lambda s}=\sum_{i=1}^{N_s}\frac{p_{0i}^2}{2M^*}+\text{“extra terms.”} \tag{62}$$

Here $M^*=M^*(N_s/\mathcal{V}_G)$ is an “effective mass” and the “extra terms” were shown to be negligible. The existence of an expansion such as Eq. (62) will have to be verified in any special case. It always appears possible, however, to obtain the correct second virial coefficient at low temperatures from Eq. (62), at least for two-body forces having finite range.

Using Eq. (62), we obtain

$$\begin{aligned}Q_s&=\frac{1}{h^3}\int d^3p\,\exp\left(-\frac{\beta}{2M^*}p^2\right)\\&=\frac{1}{h^3}[2\pi M^*\theta]^{\frac{3}{2}}.\end{aligned} \tag{63}$$

We shall now describe a general method, involving a sequence of approximations, for obtaining Q_s. This makes use of our observation that in the momentum representation each particle “moves in an effective potential due to the other particles.” Rapid convergence is expected when the finite wavelength of the particles “smooths out” the uneven interactions in coordinate space.

We consider the “single particle” density function in phase space given by

$$\rho_{\lambda s}\equiv\exp\left(\frac{\psi-E_{\lambda s}}{\theta}\right), \tag{64}$$

which is normalized so that

$$\sum_{\lambda_s}\rho_{\lambda s}=1,$$

or

$$\frac{1}{N_s!}\frac{\mathcal{V}_G{}^{N_s}}{h^{3N_s}}\sum_S\int d^3p_{01}\cdots d^3p_{0N}\rho(\mathbf{p}_{01}S_1,\cdots\mathbf{p}_{0N}S_N)=1.$$

Thus $\rho_{\lambda s}$ depends upon the variables $(\mathbf{p}_{01}S_1,\cdots\mathbf{p}_{0N}S_N)$ introduced in Eq. (2). Our *first approximation* involves replacing Eq. (64) by

$$\rho_{\lambda s}=\prod_{i=1}^{N}\rho_1(\mathbf{p}_{0i}S_i), \tag{65}$$

with the ρ_1 normalized to unity:

$$\eta\equiv\sum_{S_i}\int d\omega_{pi}\rho_1(\mathbf{p}_{0i},S_i)=1, \tag{66}$$

where

$$d\omega_p=\frac{e}{N_s}\frac{\mathcal{V}_G}{h^3}d^3p. \tag{67}$$

The physical meaning of the first approximation as given by Eq. (65) is that each particle moves in an “average potential” due to the other particles. In contrast to the effective potential in the *dynamical* problem, this represents a *statistical* potential averaged over λ_s states.

To simplify notation, we shall omit the subscripts “0” on p_{0i}, “s” on N_s, and “G” on $\mathcal{V}_G$ in the remainder of this discussion. For the same reason we also shall not write explicitly the spin variables S_i, which may be included formally in the symbols “p_i”.

To determine the ρ_1 and the average potential, we use the entropy principle (or H theorem) as a *variational principle*. Indeed, it is well-known that

$$-\mathrm{H}\equiv-\sum_{\lambda_s}\rho_{\lambda s}\ln\rho_{\lambda s} \tag{68}$$

satisfies a maximal principle subject to the conditions that

$$\sum_{\lambda_s}\rho_{\lambda s}=1,\quad\sum_{\lambda_s}E_{\lambda s}\rho_{\lambda s}\equiv U=\text{constant}. \tag{69}$$

We can use this maximal principle as a variational principle to determine the “best” densities ρ_1.

For example, let us expand, in accordance with Eqs. (9) and (10), the energy as

$$E_{\lambda s}=\sum_{i=1}^{N}K_s(p_i)+\sum_{i<j}v_2(\mathbf{p}_i,\mathbf{p}_j)+\sum_{i<j<k}v_3(\mathbf{p}_i,\mathbf{p}_j,\mathbf{p}_k)+\cdots \tag{70}$$

We have written

$$K_s\equiv p_i^2/2M, \tag{71}$$

and have expanded the energy in terms of “linked clusters.” It is often desirable to sum the series (9) formally by means of integral equations. In this event a different expansion than Eq. (70) might be desirable, which would lead to minor modifications of the following development.

Using Eqs. (65) and (70), we find that the expressions (66), (68), and (69) become:

$$\begin{aligned}\eta&=\int d\omega_p\rho_1(p)=1,\\\mathrm{H}&=N\int d\omega_p\rho_1(\mathbf{p})\ln\rho_1(\mathbf{p}),\\U&=N[\bar{K}_s+\tfrac{1}{2}\langle v_2\rangle+\tfrac{1}{6}\langle v_3\rangle+\cdots],\end{aligned} \tag{72}$$

where

$$\bar{K}_s\equiv\int d\omega_p\rho_1(\mathbf{p})K_s(p),$$

$$\langle v_2\rangle\equiv(N-1)\int d\omega_p d\omega_{p'}\rho_1(\mathbf{p})\rho_1(\mathbf{p}')v_2(\mathbf{p},\mathbf{p}'),$$

$$\langle v_3\rangle \equiv (N-1)(N-2)\int d\omega_p d\omega_{p'} d\omega_{p''} \times \rho_1(\mathbf{p})\rho_1(\mathbf{p}')\rho_1(\mathbf{p}'')v_3(\mathbf{p},\mathbf{p}',\mathbf{p}'').$$

$$\cdots .$$

By varying the functional form of ρ_1, we obtain the first variations $\delta\mathrm{H}$, δU, and $\delta\eta$. Introducing $1/\theta$ and ψ_1/θ as the customary Lagrangian multipliers, we obtain the minimum value of H subject to the constraints that $\delta U=\delta\eta=0$ by solving the equation

$$\delta\mathrm{H}+\frac{1}{\theta}[\delta U-N\psi_1\delta\eta]=0.$$

On substituting from Eq. (72) this becomes

$$\int d\omega_p \delta\rho_1(\mathbf{p})\left\{\ln\rho_1-\frac{1}{\theta}[\psi_1-K_s(p)-\bar{v}_2(\mathbf{p}) -\tfrac{1}{2}\bar{v}_3(\mathbf{p})-\cdots]\right\}=0, \tag{73}$$

where

$$\bar{v}_2(\mathbf{p})\equiv(N-1)\int d\omega_{p'}\rho_1(\mathbf{p}')v_2(\mathbf{p},\mathbf{p}'),$$

$$\bar{v}_3(\mathbf{p})\equiv(N-1)(N-2)\int d\omega_{p'}d\omega_{p''}\rho_1(\mathbf{p}') \times\rho_1(\mathbf{p}'')v_3(\mathbf{p},\mathbf{p}',\mathbf{p}'') \tag{74}$$

$$\cdots .$$

Since the left-hand side of Eq. (73) is to vanish for arbitrary $\delta\rho_1$, we obtain

$$\rho_1(\mathbf{p})=\exp\{-\beta[-\psi_1+K_s(p)+\bar{v}_2(\mathbf{p})+\tfrac{1}{2}\bar{v}_3(\mathbf{p})+\cdots]\}. \tag{75}$$

This provides a nonlinear integral equation to determine ρ_1.

It would be incorrect to calculate the partition function Z_s directly from the ρ_1's. Instead we must use $S=-k\mathrm{H}$, which is stationary at its correct value. Using Eq. (6) we get

$$F=U-TS=U+\theta\mathrm{H},$$

which becomes, after substitution from Eqs. (72) and (75),

$$F=N\left[\bar{K}_s+\tfrac{1}{2}\langle v_2\rangle+\tfrac{1}{6}\langle v_3\rangle+\cdots+\psi_1-\int d\omega_p\rho_1(\mathbf{p}) \times(K_s(p)+\bar{v}_2(\mathbf{p})+\tfrac{1}{2}\bar{v}_3(\mathbf{p})+\cdots)\right]$$
$$=N[\psi_1-\tfrac{1}{2}\langle v_2\rangle-\tfrac{1}{3}\langle v_3\rangle-\cdots]. \tag{76}$$

Furthermore, from the normalization of ρ_1 it follows that

$$e^{-\psi_1/\theta}=\frac{e}{N}\frac{\mathcal{V}}{h^3}\int d^3p\exp\{-\beta[K_s(p)+\bar{v}_2(\mathbf{p}) +\tfrac{1}{2}\bar{v}_3(\mathbf{p})+\cdots]\}. \tag{77}$$

Finally, by Eqs. (60) and (6) we have

$$Z_s=\frac{1}{N!}[\mathcal{V}Q_s]^N=\exp(-F/\theta), \tag{78}$$

so that substituting Eqs. (76) and (77) into Eq. (78) we obtain

$$Q_s=\frac{1}{h^3}\int d^3p\exp\left\{-\beta\left[\frac{p^2}{2M}+\bar{v}_2(\mathbf{p})-\tfrac{1}{2}\langle v_2\rangle +\tfrac{1}{2}\bar{v}_3(\mathbf{p})-\tfrac{1}{3}\langle v_3\rangle+\cdots\right]\right\}. \tag{79}$$

A similar technique may be applied to the calculation of Q_p, etc.

It is possible to generalize the assumption of Eq. (65) systematically by including "pair correlations" $\rho_2(\mathbf{p}_i,\mathbf{p}_j)$, "triplet correlations" $\rho_3(\mathbf{p}_i,\mathbf{p}_j,\mathbf{p}_k)$, etc. in the density function $\rho_{\lambda s}$. A discussion of these is given later in this section.

We emphasize, however, that the omitted correlations in Eq. (65) are in *momentum space* rather than in *coordinate space*. It is quite clear from Eqs. (75) and (79) that complex correlations between clusters of particles are already included in our first approximation. Indeed, as we shall see in Sec. IV, even our first approximation can lead to a description of condensation.

We now calculate the second virial coefficient in order to illustrate the technique described and also to show that particle-particle correlations are included in the trial form of Eq. (65).

To calculate the second virial coefficient we need consider only the limit of very low density. Thus, only v_2 need be kept in Eq. (9), and Eq. (70) for $E_{\lambda s}$ becomes

$$E_{\lambda s}=\sum_{i=1}^{N_s}\frac{p_i^2}{2M}+\sum_{i<j}R_{ij}(\mathbf{p}_i,\mathbf{p}_j), \tag{80}$$

since $v_2(\mathbf{p}_i,\mathbf{p}_j)=\langle p|R_{ij}|p\rangle=R_{ij}(\mathbf{p}_i,\mathbf{p}_j)$, and $v_3=v_4=\cdots\cong 0$. For simplicity we neglect spin interactions. Then, as was shown in I [Eq. (136)], the diagonal elements of R_{ij} may be expressed in the form

$$R_{ij}(\mathbf{p}_i,\mathbf{p}_j)=-\frac{8\pi\hbar^3}{\mathcal{V}Mk_{ij}}\sum_l(2l+1)\delta_l(k_{ij}), \tag{81}$$

where $\mathbf{k}_{ij}\equiv\frac{1}{2}(\mathbf{p}_i-\mathbf{p}_j)$ is the relative momentum, δ_l is the scattering phase shift for a pair of particles interacting in a state of orbital angular momentum l, and the sum runs over even or odd values of l depending upon whether the particle statistics is Bose-Einstein or Fermi-Dirac.

In general, the particle pairs may have bound states. Let us assume that there is only one such state with binding energy ϵ_B, the generalization to many bound states being straightforward. Then, in the low density limit, the "pair energy" is

$$E_{\lambda p}=-\tfrac{1}{2}N_p\epsilon_B+\sum_{r\,(\text{pairs})}\frac{p_r^{\,2}}{4M}. \tag{82}$$

Here p_r is the center-of-mass momentum of the rth pair.

To obtain Q_s in the low density limit, we may take

$$\rho_1=\exp\left[-\beta\left(-\psi_1+\frac{p^2}{2M}\right)\right];\quad e^{\beta\psi_1}=\frac{N}{\mathcal{V}}\frac{h^3}{e}\left[\frac{2\pi M}{\beta}\right]^{-\frac{3}{2}}$$

in Eq. (75), and expand the exponential of Eq. (79) to first order in v_2. Thus

$$\begin{aligned}Q_s&\cong\frac{1}{h^3}\int d^3p\,\exp\left(-\frac{\beta}{2M}p^2\right)\{1-\beta[\bar{v}_2(\mathbf{p})-\tfrac{1}{2}\langle v_2\rangle]\}\\&=\frac{1}{h^3}\left[\frac{2\pi M}{\beta}\right]^{\frac{3}{2}}-\frac{\beta N}{2h^3}\left[\frac{2\pi M}{\beta}\right]^{-\frac{3}{2}}\int d^3p_1d^3p_2\\&\qquad\times\exp\left[-\frac{\beta}{2M}(p_1^2+p_2^2)\right]R_{12}(k_{12}).\end{aligned}\tag{83}$$

By letting $\mathbf{k}_{12}$ and $\mathbf{P}=\mathbf{p}_1+\mathbf{p}_2$ be the independent variables, we may integrate over the latter to obtain

$$\begin{aligned}Q_s=\frac{1}{h^3}\left[\frac{2\pi M}{\beta}\right]^{\frac{3}{2}}&+\frac{4\sqrt{2}}{\pi}\frac{N}{\mathcal{V}}\frac{\beta}{M}\int_0^\infty dk\,k\\&\times\exp\left(-\frac{\beta}{M}k^2\right)\sum_l(2l+1)\delta_l(k).\end{aligned}\tag{84}$$

Similarly, from Eq. (82) we obtain

$$Q_p=\frac{e^{\beta\epsilon_B}}{h^3}\left[\frac{4\pi M}{\beta}\right]^{\frac{3}{2}}. \tag{85}$$

To first order in $1/\mathcal{V}$, Eq. (61) gives

$$\tfrac{1}{2}N_p=N(N/\mathcal{V})e^{\beta\epsilon_B}2^{\frac{3}{2}}[2\pi\beta\hbar^2/M]^{\frac{3}{2}}, \tag{86}$$

since now $\mathcal{V}_G=\mathcal{V}$.

Finally, by combining Eqs. (6), (60), (84), (85), and (86), and dropping terms of higher than quadratic power in $1/\mathcal{V}$, the equation of state is obtained in the form

$$\begin{aligned}\frac{P}{\theta}&=\frac{\partial}{\partial\mathcal{V}}\ln Z=\left[\frac{\partial\ln Z_s}{\partial\mathcal{V}}+\frac{\partial\ln Z_p}{\partial\mathcal{V}}\right]_{N_s,N_p}\\&=\frac{N}{\mathcal{V}}\left\{1-\frac{N}{\mathcal{V}}\left[-2^{\frac{3}{2}}e^{\beta\epsilon_B}\left(\frac{2\pi\beta\hbar^2}{M}\right)^{\frac{3}{2}}\right.\right.\\&\qquad+16\pi^{\frac{1}{2}}\hbar^3\left(\frac{\beta}{M}\right)^{\frac{5}{2}}\int_0^\infty dk\,k\\&\qquad\left.\left.\times\exp\left(-\frac{\beta}{M}k^2\right)\sum_l(2l+1)\delta_l(k)\right]\right\}.\end{aligned}\tag{87}$$

The coefficient of $1/\mathcal{V}$ in the second term within the curly brackets is the exact second virial coefficient.[14]

The above calculation was made to illustrate a somewhat trivial example of the methods developed in this section. In general, our technique of developing ρ in terms of correlated densities in momentum space is not simply related to the virial expansion. Indeed, our method is intended primarily to describe systems at low temperatures and high densities.

We shall now generalize the assumed form for $\rho_{\lambda s}$ given by Eq. (65). There are various possible ways of doing this, such as developing $\rho_{\lambda s}$ and Z_s in a "cluster expansion" in momentum space. We prefer, however, to continue using the variational principle by improving our trial form (65).

We illustrate the generalization of our method by making the special and simple assumption

$$\begin{aligned}\rho_{\lambda s}=\prod_{i=1}^{N-n}\rho_1(\mathbf{p}_i)\rho_2(\mathbf{p}_{N-n+1},\mathbf{p}_{N-n+2})\cdots\rho_2(\mathbf{p}_{N-1},\mathbf{p}_N);\\\rho_2(\mathbf{p},\mathbf{p}')=\rho_2(\mathbf{p}',\mathbf{p}).\end{aligned}\tag{65'}$$

To keep our expressions simple, we neglect v_3, v_4, etc. in Eq. (70). We consider the functional forms of ρ_1 and ρ_2 and the value of n, as quantities to be varied.

Repeating the steps taken in connection with Eqs. (72), (73), and (74), we obtain

$$\begin{aligned}\eta_1&\equiv\int d\omega_p\rho_1(\mathbf{p})=1,\\\eta_2&\equiv\int d\omega_pd\omega_{p'}\rho_2(\mathbf{p},\mathbf{p}')=1,\\\mathrm{H}&=(N-n)\int d\omega_p\rho_1(\mathbf{p})\ln\rho_1(\mathbf{p})\\&\qquad+\frac{n}{2}\int d\omega_pd\omega_{p'}\rho_2(\mathbf{p},\mathbf{p}')\ln\rho_2(\mathbf{p},\mathbf{p}'),\\U&=(N-n)\bar{K}_s+n\bar{K}_s^{\,p}+\frac{1}{N}\left[\frac{(N-n)(N-n-1)}{2}\langle v_2\rangle\right.\\&\qquad\left.+\frac{n(n-1)}{2}\langle v_2\rangle^p+n(N-n)\langle v_2\rangle^{s,p}\right],\end{aligned}\tag{72'}$$

where

$$\begin{aligned}\bar{K}_s&\equiv\int d\omega_pK_s(p)\rho_1(\mathbf{p}),\\\bar{K}_s^{\,p}&\equiv\int d\omega_pd\omega_{p'}K_s(p)\rho_2(\mathbf{p},\mathbf{p}'),\\\langle v_2\rangle&\equiv N\int d\omega_pd\omega_{p'}v_2(\mathbf{p},\mathbf{p}')\rho_1(\mathbf{p})\rho_1(\mathbf{p}'),\end{aligned}$$

---

[14] G. E. Uhlenbeck and E. Beth, Physica 3, 729 (1936).

$$\langle v_2\rangle^p\equiv N\int d\omega_p d\omega_{p'} v_2(\mathbf{p},\mathbf{p}')\rho_2(\mathbf{p},\mathbf{p}'),$$

$$\langle v_2\rangle^{s,p}\equiv N\int d\omega_p d\omega_{p'} d\omega_{p''} v_2(\mathbf{p},\mathbf{p}')\rho_1(\mathbf{p})\rho_2(\mathbf{p}',\mathbf{p}'').$$

The variational principle becomes

$$\delta\mathrm{H}+\frac{1}{\theta}\left[\delta U-(N-n)\psi_1\delta\eta_1-\frac{n}{2}\psi_2\delta\eta_2\right]=0.$$

Carrying out the variations, and defining the quantities

$$\begin{aligned}\bar{v}_2(\mathbf{p})&\equiv N\int d\omega_{p'} v_2(\mathbf{p},\mathbf{p}')\rho_1(\mathbf{p}'),\\ \bar{v}_2{}^p(\mathbf{p})&\equiv N\int d\omega_{p'} d\omega_{p''} v_2(\mathbf{p},\mathbf{p}')\rho_2(\mathbf{p}',\mathbf{p}''),\\ \mu&\equiv n/N,\end{aligned}\tag{74'}$$

we get a modified form of Eq. (73):

$$\begin{aligned}&(N-n)\int d\omega_p\delta\rho_1(\mathbf{p})\Big\{\ln\rho_1(\mathbf{p})\\ &\quad+\frac{1}{\theta}[K_s(p)+(1-\mu)\bar{v}_2(\mathbf{p})+\mu\bar{v}_2{}^p(\mathbf{p})-\psi_1]\Big\}\\ &+\frac{n}{2}\int d\omega_p d\omega_{p'}\delta\rho_2(\mathbf{p},\mathbf{p}')\Big\{\ln\rho_2(\mathbf{p},\mathbf{p}')\\ &\quad+\frac{1}{\theta}[K_s(p)+K_s(p')+(1-\mu)\bar{v}_2(\mathbf{p})\\ &\quad+(1-\mu)\bar{v}_2(\mathbf{p}')+\mu N v_2(\mathbf{p},\mathbf{p}')-\psi_2]\Big\}\\ &+\delta n\Big\{\frac{1}{2}\int d\omega_p d\omega_{p'}\rho_2(\mathbf{p},\mathbf{p}')\ln\rho_2(\mathbf{p},\mathbf{p}')\\ &\quad-\int d\omega_p\rho_1(\mathbf{p})\ln\rho_1(\mathbf{p})+\frac{1}{\theta}[\bar{K}_s{}^p-K_s\\ &\quad+(1-2\mu)\langle v_2\rangle^{s,p}+\mu\langle v_2\rangle^p-(1-\mu)\langle v_2\rangle]\Big\}=0.\end{aligned}\tag{73'}$$

When the coefficients of $\delta\rho_1$, $\delta\rho_2$, and δ_n in Eq. (73′) are separately equated to zero, and the normalization conditions on ρ_1 and ρ_2 are written down, we obtain a complete set of equations. To exhibit these, it is convenient to define a parameter G by means of

$$\psi_2\equiv 2\psi_1+\theta G-\mu\langle v_2\rangle.$$

There results

$$\begin{aligned}\rho_1(\mathbf{p})&=\exp\Big\{-\frac{1}{\theta}[-\psi_1+K_s(p)+(1-\mu)\bar{v}_2(\mathbf{p})\\ &\qquad+\mu\bar{v}_2{}^p(\mathbf{p})]\Big\},\\ \rho_2(\mathbf{p},\mathbf{p}')&=\exp\Big\{-\frac{1}{\theta}[-2\psi_1-\theta G+\mu\langle v_2\rangle+K_s(p)\\ &\qquad+K_s(p')+(1-\mu)(\bar{v}_2(\mathbf{p})+\bar{v}_2(\mathbf{p}'))\\ &\qquad+\mu N v_2(\mathbf{p},\mathbf{p}')]\Big\},\\ &=\rho_1(\mathbf{p})\rho_1(\mathbf{p}')\exp\Big\{G+\frac{\mu}{\theta}[\bar{v}_2{}^p(\mathbf{p})+\bar{v}_2{}^p(\mathbf{p}')\\ &\qquad-Nv_2(\mathbf{p},\mathbf{p}')-\langle v_2\rangle]\Big\}.\end{aligned}\tag{88}$$

The parameter G must be chosen to normalize ρ_2 to unity according to the second equation of Eqs. (72′).

An equation to determine n is obtained from the last term of Eq. (73′). The explicit indication of a correction due to "fluctuations" is evident from the form of Eq. (88) for ρ_2. A variety of possible forms for ρ_{λ_s} other than that of Eq. (65′) are feasible, of course. In particular, three-particle correlations ρ_3, etc. may be kept.

Furthermore we observe that the zeroth-order approximation to ρ_{λ_s} of Eq. (65) [leading to Eq. (75)] becomes *exact* in the limit of *zero temperature* if the power-series expansion of Eq. (62) for the energy is valid. This is consistent with our point of view that fluctuations should become small at low temperatures.

Finally, the methods for obtaining Z_s which we have described are expected to be applicable to the calculation of Z_L. Also, it appears possible to improve the approximate Eq. (56) if necessary. That is, "fluctuations" associated with the dependence of $E_{\lambda p}$ on λ_s, etc., may in principle be handled by the techniques used in connection with Eq. (88). Thus we feel justified in describing our method as providing a systematic means for evaluating the partition function for a low-temperature system.

IV. APPLICATIONS—THE "EFFECTIVE MASS" APPROXIMATION

In this section we shall discuss the energy spectrum, and give thermodynamic applications, in the approximation that only two-particle scatterings are kept. We recognize that this approximation may be quite inadequate, in general. On the other hand, we shall see that it can give qualitatively correct results even for the liquid state.[15] In Sec. V we shall study many-scattering contributions to the energy.

---

[15] This is the approximation used by Brueckner *et al.* in their theory of nuclear structure, references 2 and 5.

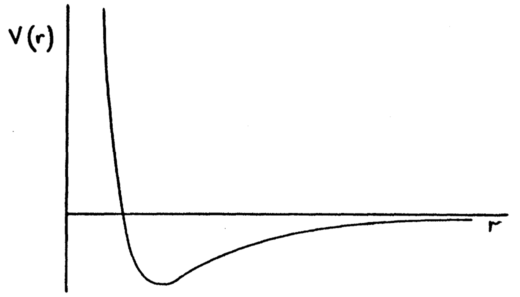

FIG. 2. A typical intermolecular potential, with long-range attraction and a repulsive core.

To provide a simple model, we shall neglect exchange corrections, treating the particles as equivalent but distinguishable. The investigation of degenerate Fermi-Dirac[16] and Bose-Einstein systems by the methods which we describe is of considerable interest, but must await a subsequent publication. To simplify notation, we shall also assume that the particles have no spin.

Our approximation implies that we keep only the terms involving v_2 in Eq. (9), so that

$$\delta E=\langle p_0|\sum_{i<j} R_{ij}|p_0\rangle$$

$$=\sum_{i<j}\langle \mathbf{p}_{0i},\mathbf{p}_{0j}|R|\,\mathbf{p}_{0i},\mathbf{p}_{0j}\rangle. \tag{89}$$

The F_{il}'s in Eq. (13) become unity, and hence the dispersive energy of a single particle is given by

$$\epsilon(\mathbf{p}_i)=\frac{p_i^2}{2M}+\sum_{j(j\neq i)}\langle \mathbf{p}_i,\mathbf{p}_{0j}|R|\,\mathbf{p}_i,p_{0j}\rangle. \tag{90}$$

The second term is our present approximation to $\delta\epsilon(\mathbf{p}_i)$ in Eq. (12). The scattering matrix R is defined by the integral Eq. (14).

For small values of $\mathbf{p}_i$ let us assume that the second term in Eq. (90) may be expanded in the form

$$\delta\epsilon(\mathbf{p}_i)=\epsilon_0+\tfrac{1}{2}ap_i^2+\cdots, \tag{91}$$

the higher power terms in the momentum variable being neglected. The coefficients ϵ_0 and a are of course functions of the volume $\mathcal{V}$ and the parameters describing the interactions. By use of Eq. (91), Eq. (90) becomes

$$\epsilon(\mathbf{p}_i)=\epsilon_0+\frac{p_i^2}{2M}+\frac{a}{2}p_i^2$$

$$=\epsilon_0+\frac{1}{2M^*}p_i^2, \tag{92}$$

where

$$M^*/M=1/(1+aM). \tag{93}$$

M^* is thus an "effective mass." [5]

Use of this approximation in calculating the propagator d of Eq. (11) enables us to write the integral equation (14) for R in the form

$$\langle\mathbf{k}'|R|\mathbf{k}\rangle=\langle\mathbf{k}'|V|\mathbf{k}\rangle$$

$$+\frac{\mathcal{V}}{h^3}M^*\int d^3k''\frac{\langle\mathbf{k}'|V|\mathbf{k}''\rangle\langle\mathbf{k}''|R|\mathbf{k}\rangle}{k_0''^2-k''^2}. \tag{94}$$

Here $\mathbf{k}$ is the relative momentum $\frac{1}{2}(\mathbf{p}_i-\mathbf{p}_j)$ of the two colliding particles.

When the expansion (91) is valid, the use of the effective mass simplifies our calculation considerably. This approximation is of course completely independent of that of keeping only the terms v_2 in Eq. (9). With use of both approximations, the problem is completely defined by Eqs. (89), (91), (93), and (94).

The appearance of the dispersive energy shift in the equation for the R_{ij}'s means that complex cooperative phenomena are included to some extent even in the first approximation of keeping only the v_2's in Eq. (9). For instance, saturation would not take place in a nondegenerate gas or liquid in an approximation in which only two-body correlations occur. As we shall see, however, saturation may be accounted for in the approximation just described.

For example, let us suppose the two-body force to be attractive at large distances, but very strongly repulsive at short distances. The potential corresponding to such a force is illustrated in Fig. 2. In this case we may expect the energy ϵ_0 to be negative. The shift $\delta\epsilon$, however, might be expected to increase with p, becoming *positive*[5] for large p (i.e., small "impact parameters"). With a "smooth" p dependence, such as indicated in Fig. 3, the effective mass approximation should be valid.

For the case illustrated in Fig. 3 the coefficient a of Eq. (91) is *positive*. This quantity is expected to vary roughly as $\mathcal{V}^{-1}$, so that the effective mass as given by Eq. (93) will *decrease* as $\mathcal{V}$ decreases. Decreasing M^* *reduces* the effective strength of the potential, as is clear from Eq. (94). Thus compressing the gas (or liquid) will "reduce" the strength of the interactions between particles. In particular, the effect of the attractive

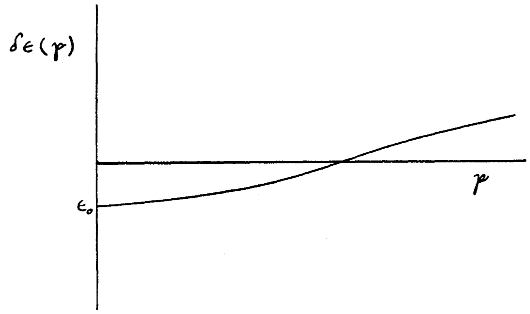

FIG. 3. The expected dependence of the energy $\delta\epsilon$ of Eq. (91) on p.

---

[16] The degenerate Fermi-Dirac system is, of course, that originally studied by Brueckner and his collaborators, references 2 and 5.

part of the potential (Fig. 2) is thereby reduced. The R matrix is, however, little affected by the actual "height" of the "repulsive core," so that the repulsive part of the interaction is not much influenced by compression. Consequently, when the system is compressed, the forces may change from being *effectively attractive* to being *effectively repulsive* as a result of the "effective mass" correction.

To illustrate these remarks, let us carry through an explicit calculation. We choose a potential having the properties of that of Fig. 2. We shall actually use a potential that is "factorable" in momentum space, since this will permit us to find an analytic solution to Eqs. (94), (93), etc.[17]:

$$\langle k|V|q\rangle = G_1\varphi_1(k)\varphi_1(q) + G_2\varphi_2(k)\varphi_2(q). \tag{95}$$

Here $G_1<0$ and $G_2\gg 0$ are constants, and we choose

$$\begin{aligned} \varphi_1(k) &= (1-bk^2)\exp(-ak^2),\\ \varphi_2(k) &= \exp(-\alpha_2 k^2),\\ b &= 2(a+\alpha_2),\quad \alpha_2 \cong a. \end{aligned} \tag{96}$$

If we evaluate the expectation value of the potential of Eq. (95) for wave packets separated by a distance r, we obtain an energy with spatial dependence similar to that of Fig. 2. To reduce the number of terms in the solution (97), we have chosen φ_1 and φ_2 to make the integral $\int_0^\infty dk\varphi_1(k)\varphi_2(k)$ vanish.

With this choice of V, Eq. (94) may be solved rigorously. We are interested in the system only at "low temperatures," which implies that only energies near the ground-state energy are important. Adopting the conventional continuum normalization, we therefore obtain

$$\langle k|R|k\rangle = \frac{(2\pi)^3}{\mathcal{V}}\left[\frac{G_1\varphi_1^2(k)}{1-4\pi M^*G_1I_1} + \frac{G_2\varphi_2^2(k)}{1-4\pi M^*G_2I_2}\right],$$

with

$$\begin{aligned} I_1 &= -\int_0^\infty dk\varphi_1^2(k) = -\frac{1}{2}\left(\frac{\pi}{2a}\right)^{\frac{1}{2}}\left[1-\frac{1}{2}\frac{b}{a}+\frac{3}{16}\left(\frac{b}{a}\right)^2\right],\\ I_2 &= -\int_0^\infty dk\varphi_2^2(k) = -\frac{1}{2}\left(\frac{\pi}{2\alpha_2}\right)^{\frac{1}{2}}. \end{aligned} \tag{97}$$

In obtaining this solution we have replaced the actual[1] boundary condition on the pole of Eq. (94) by that of taking the principal value of the integral. The *correct* value of R is just a simple algebraic function of that given in Eq. (97), as was discussed in I. When the scattering phase shift δ is less than $\pi/2$, Eq. (97) gives a fair approximation to R; this will be the case in our example.

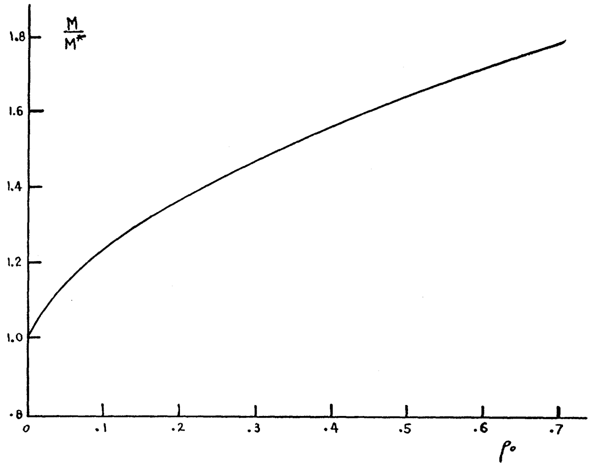

FIG. 4. Variation of the effective mass with volume for the system described by Eq. (100).

For a strong "repulsive core," we may set $G_2=\infty$ in Eq. (97), and obtain

$$\langle k|R|k\rangle = \frac{(2\pi)^3}{\mathcal{V}}\left[\frac{G_1\varphi_1^2(k)}{1-4\pi M^*G_1I_1} + \frac{\varphi_2^2(k)}{4\pi M^*|I_2|}\right]. \tag{98}$$

In the limit of very low temperatures, Eq. (90) becomes

$$\epsilon(p_i) = \frac{p_i^2}{2M} + N\langle \tfrac{1}{2}p_i|R|\tfrac{1}{2}p_i\rangle, \tag{99}$$

since then $\mathbf{k}=\frac{1}{2}\mathbf{p}_i$ in Eq. (98). An expansion in powers of p_i, as in Eq. (91), then leads to an explicit expression for M^*. The quantity δE is finally obtained from Eq. (89).

For the purpose of carrying through a specific numerical example, we have taken

$$\begin{aligned} \alpha_1 &\equiv \tfrac{1}{2}[3a+2\alpha_2],\\ G_1 &= -\alpha_1^{\frac{3}{2}}U_1,\\ \eta &\equiv U_1M_{\alpha 1} = 0.78,\\ r &\equiv (\alpha_2/\alpha_1)^{\frac{3}{2}} = 0.20,\\ U_1 &= 0.1\text{ ev},\\ \hbar(4\pi\alpha_1)^{\frac{1}{2}} &= 10^{-8}\text{ cm},\\ \rho_0 &\equiv (N/\mathcal{V})\alpha_1^{\frac{3}{2}}\hbar^3,\\ \mathcal{V}_0 &\equiv \mathcal{V}\rho_0. \end{aligned} \tag{100}$$

The evaluation is straightforward and will not be shown in detail. The effective mass M^* and the energy ϵ_0 of Eq. (91) are shown as functions of the density ρ_0 in Figs. 4 and 5, respectively. The "droplet states" were identified from Fig. 5, as described at the close of Sec. I. The effective-mass approximation of Eq. (63) was used to evaluate the partition functions Q_L and Q_G

---

[17] Applications of such potentials to statistical mechanics have been suggested by K. M. Watson, Phys. Rev. **103**, 489 (1956). The use of variational techniques for solving Eq. (94) was also described there.

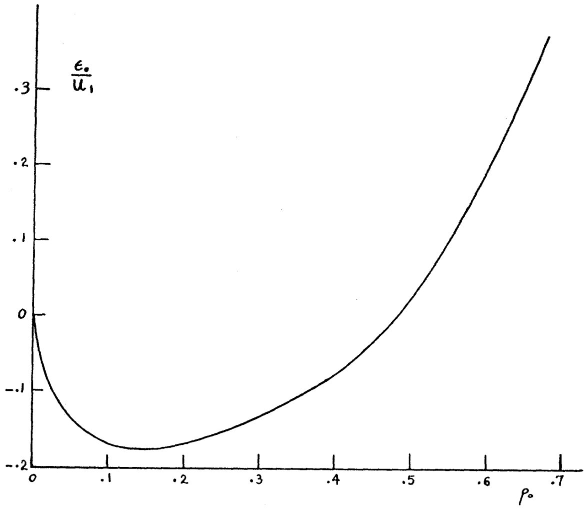

FIG. 5. Variation of the energy ϵ_0 with volume for the system described by Eq. (100).

(in the present case $Q_s = Q_G$), so from Eq. (63) we obtain

$$e^{\beta(\epsilon_0/2)}Q_L = Q_G = \frac{1}{h^3}\left[\frac{2\pi M^*}{\beta}\right]^{\frac{3}{2}}. \tag{101}$$

The equation of state was obtained exactly as described in Sec. II. In our specific example, the critical temperature was found to be $T_c = 40$°K. Several calculated isotherms are shown in Fig. 6.

The simple example just given suggests that a qualitative, or semiquantitative, description of a low-temperature system may be obtained even in a first-order calculation. To get detailed quantitative results, we must investigate higher order terms in Eq. (9), as will be done in the next section. We may now note, however, that an effective mass which decreases with decreasing $\mathcal{V}$ will help to reduce the importance of the higher order terms in Eq. (9).

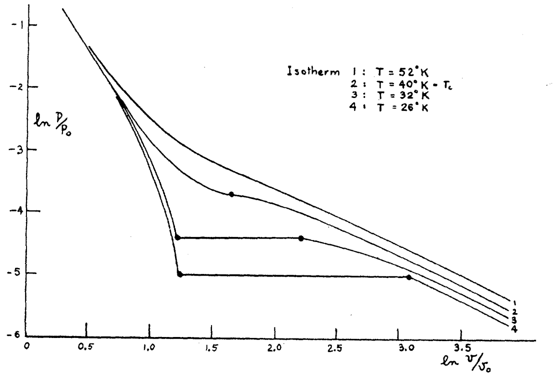

FIG. 6. Calculated isotherms for the system described by Eq. (100). Here P_0 is a constant scaling parameter, the value of which may be obtained from the curves in the large volume region, where they approach ideal gas isotherms. The critical temperature is $T_c = 40$°K, and the critical point is shown on the diagram as a dot. Phase-transition points are also indicated by dots.

It appears that the approximation involved in Eqs. (89) and (90) amounts to treating "fluctuations" as small. That is, $\epsilon(\mathbf{p}_i)$ in Eq. (90) is an *average energy*, whereas the actual energy of a particle shows fluctuations. These fluctuations appear as higher order terms in Eq. (9).

V. COOPERATIVE INTERACTIONS

In this section we discuss more generally the nearest-neighbor expansion given by Eq. (9). In I it was observed that the terms in the series had rather simple topological properties and, in particular, could be easily represented by graphical constructions. Let us first review and extend this description.

It is convenient to draw an analogy to quantum field theory. As described in Sec. I, the "reference state" (or "unperturbed state") $p_0 = (\mathbf{p}_{01}S_1 \cdots \mathbf{p}_{0N}S_N)$ may be considered as analogous to the "vacuum state." A particle which by virtue of a scattering is excited out of the p_0 state, may be considered to have been "created." Since according to Eq. (10) the terms in Eq. (9) are expectation values with respect to the p_0 state, every particle which has been "created" must be "annihilated" by the time the final scattering has occurred. Thus Eq. (9) represents a "vacuum expectation value."

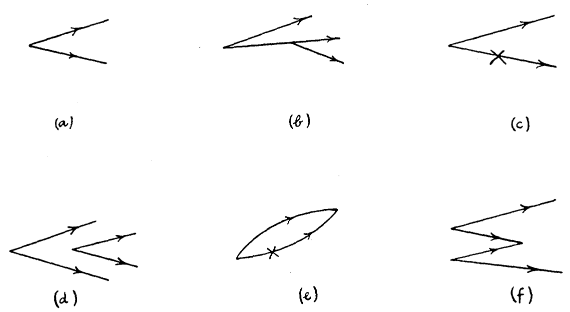

FIG. 7. Several typical "Feynman graphs," as discussed in the development of Sec. V.

The scattering of a pair of particles from the p_0 state represents "pair creation." The scattering of an "excited particle" by one in the p_0 state may leave both particles "excited." These processes are illustrated in Figs. 7(a) and 7(b) by means of "Feynman diagrams." In the latter type of scattering the original particle may drop back to the p_0 state. In this case the new particle continues as if it were the original particle, but with a different momentum in general. This type of scattering is represented by an "x" drawn on the particle line, as in Fig. 7(c). In a topological sense, no scattering has occurred, so that we may describe this process as "particle exchange" scattering. (It is to be recalled that we must never return the system to the p_0 state as a virtual intermediate state.[1])

Let us now consider in detail Eqs. (9) and (10). To excite the system out of the p_0 state, the first interaction must in any case "create" a pair of particles, and therefore we may write δE in the form

$$\delta E=\langle p_0|\sum_{i<j} R_{ij}|p_0\rangle+\left\langle p_0\left|\sum_{i<j} F_{ij}\frac{1}{d}R_{ij}\right|p_0\right\rangle -\left\langle p_0\left|\sum_{i<j} R_{ij}\frac{1}{d}R_{ij}\right|p_0\right\rangle. \quad (102)$$

Here F_{ij} is a "two-particle amplitude" which describes all possible scatterings taking place between the "creation" of the initial pair and the ultimate return of the system to the p_0 state. This amplitude can be represented by the following set of coupled integral equations[18]:

$$F_{ij}=\sum_{\substack{l=1\\ l\neq i,j}}^{N}\left[F_{ijl}\frac{1}{d}R_{lj}+F_{ijl}\frac{1}{d}R_{li}\right] +\sum_{\substack{l=1\\ l\neq i,j}}^{N}\left[F_{il}\frac{1}{d}R_{lj}+F_{jl}\frac{1}{d}R_{li}\right] +\sum_{\substack{k<l\\ k,l\neq i,j}} F_{ijkl}\frac{1}{d}R_{kl}+R_{ij}. \quad (103)$$

In this equation F_{ijl} is a "three-particle amplitude" and F_{ijkl} is a "four-particle amplitude." The first term above represents the creation of a third particle l, as is shown in Fig. 7(b). The second term is of the "particle-exchange" type as shown in Fig. 7(c); here one of the particles (i,j) is "annihilated," i.e., returned to the p_0 state. The third term describes the "creation of a new pair" (k,l), as in Fig. 7(d). The last term annihilates the single-particle pair on which F_{ij} operates. This is illustrated in Fig. 7(e). The annihilation must be consistent with the "linkage" requirement as well as the restriction that the same two particles not scatter twice in succession.[1] The last term of Eq. (102) is necessary to subtract out the direct "closed loop" contribution furnished by the integral Eq. (103).

To complete Eq. (103), we must define the amplitudes F_{ijl}, F_{ijkl}, etc. This may be achieved by means of an infinite set of coupled equations. Let us consider the n-particle amplitude $F_{i_1\cdots i_n}$ which satisfies

$$\begin{aligned}F_{i_1\cdots i_n}= &\sum_{\substack{l=1\\ l\neq i_1\cdots i_n}}^{N}\sum_{\rho=1}^{n} F_{i_1\cdots i_n l}\frac{1}{d}R_{li_\rho}\\ &+\sum_{\substack{\nu=1\\ \nu\neq\rho}}^{n}\sum_{\rho=1}^{n} F_{i_1\cdots i_{\rho-1}i_{\rho+1}\cdots i_n}\frac{1}{d}R_{i_\nu i_\rho}\\ &+\sum_{\substack{l=1\\ l\neq i_1\cdots i_n}}^{N}\sum_{\rho=1}^{n} F_{i_1\cdots i_{\rho-1}li_{\rho+1}\cdots i_n}\frac{1}{d}R_{li_\rho}\\ &+\sum_{\substack{l<k\\ l,k\neq i_1\cdots i_n}}^{N} F_{i_1\cdots i_n lk}\frac{1}{d}R_{lk}\\ &+\sum_{\rho,\,\nu=1}^{n}{}' F_{i_1\cdots i_{\nu-1}i_{\nu+1}\cdots i_{\rho-1}i_{\rho+1}\cdots i_n}\frac{1}{d}R_{i_\nu i_\rho}. \quad (104)\end{aligned}$$

The terms here are the same as the corresponding ones in Eq. (103). Again we emphasize that in both equations the sums over interactions must be consistent with the requirement that the same pair of particles not act twice in succession. The first two terms of Eq. (104) describe single-particle creation and annihilation, respectively; the third term, annihilation of particle i_ρ and creation of particle l; the fourth term, creation of the pair (l,k); the last term, annihilation of the pair (i_ν,i_ρ). The prime on the last summation of Eq. (104) means that this sum must be carried out in such a manner as to leave no "unlinked clusters." A properly linked pair-annihilation diagram is illustrated in Fig. 7(f). In a topological sense, the annihilation diagram may be "straightened out" to correspond to Fig. 7(a), just as if neither annihilation nor creation had occurred in the intermediate states.

The similarity to Feynman diagrams is quite evident, and suggests that Eqs. (103) and (104) may be formally simplified by the use of second quantization. A more detailed development of this approach will be published separately in connection with a discussion of degenerate Bose-Einstein systems.[19]

An interesting approximation to Eqs. (104) results if we omit the first two terms on the right hand side. This amounts to dropping graphs of the form shown in Fig. 7(b). As was noted in I, in this case all graphs may be deformed into simple loops in view of the nonoccurrence of "unlinked" diagrams. Also, for *each* scattering the momentum imparted to *each* particle is always $\pm\mathbf{q}$, where $\mathbf{q}$ is a variable. Integration over this variable $\mathbf{q}$ is performed as the last step in the second term of Eq. (102). The system of equations (104) therefore reduces to a set of *algebraic equations*.

---

[18] Equation (103) represents an extension of a technique suggested by W. Macke, Z. Naturforsch. **5A**, 192 (1950). We are indebted to Professor K. A. Brueckner and Professor M. Gell-Mann for calling Macke's work to our attention, and also for the suggestion that it might be extended in generality by means of integral equations. These equations are precisely those used in I to determine δE, written out in greater detail, and, as was noted in I, the terms treated by this method can be made to furnish a starting point for a perturbation expansion. In the meantime, a detailed development of the technique has been carried out independently by Professor Brueckner and Professor Gell-Mann and by ourselves. See also reference 19.

[19] M. A. Ruderman and K. M. Watson (to be published). Also, K. A. Brueckner and K. Sawada, Phys. Rev. **106**, 1117 (1957).

In this approximation, the solution of the set of Eqs. (104) for the ground-state energy of a system of distinguishable, spinless particles becomes almost trivial (we shall use the effective-mass approximation of Sec. IV). The handling of excited states may also be illustrated by simple methods, and we shall do so at the end of this section.

Our approximation enables us to write $R=R(\mathbf{q})$ as a function of the momentum transfer $\mathbf{q}$ only, and the propagator as given by Eq. (11) becomes

$$d=-(n/2M^*)q^2\equiv(n/2)D, \qquad (105)$$

where n is the number of particles excited above the p_0 state ($\mathbf{p}_{01}=0, \cdots \mathbf{p}_{0N}=0$). We define

$$\sum_{i_1\cdots i_{2m}} F_{i_1\cdots i_{2m}}\equiv N^{2m}F_{2m}; \quad m=1,2,\cdots, \qquad (106)$$

and sum Eq. (104) over $(i_1\cdots i_{2m})$ to obtain

$$N^{2m}F_{2m}=N^{2m+1}2mF_{2m}\frac{1}{mD}R+N^{2m+2}F_{2m+2}\frac{1}{(m+1)D}R$$
$$+N^{2m}m(m-1)F_{2m-2}\frac{1}{(m-1)D}R; \quad m>1. \qquad (107)$$

In a similar manner we may sum Eq. (103) over (i,j), getting

$$F_2=2N\frac{1}{D}RF_2+N^2\frac{1}{2D}RF_4+R.$$

Comparing this result with Eq. (107), we obtain the identification

$$F_0=D(\mathbf{q}). \qquad (108)$$

The solution to the set of difference Eqs. (107) subject to the boundary condition of Eq. (108) is

$$F_{2m}=m!r^mF_0, \qquad (109)$$

where r is that root of the quadratic equation

$$\left(\frac{N^2R}{D-2NR}\right)r^2-r+\frac{R}{D-2NR}=0, \qquad (110)$$

which remains finite as R approaches zero.

To simplify notation, we write

$$R(\mathbf{q})\equiv\frac{r_0^3}{\mathcal{V}}U(\mathbf{q}), \quad \rho\equiv\frac{Nr_0^3}{\mathcal{V}}, \qquad (111)$$

where r_0 is a distance, presumably of the order of the range of the two-body force, and U is an "effective interaction energy." Equation (102) for δE becomes

$$\delta E=\tfrac{1}{2}N\rho U(0)+\tfrac{1}{2}N^2\frac{\mathcal{V}}{h^3}\int d^3q[F_2(\mathbf{q})-R(\mathbf{q})]\frac{1}{D}R(\mathbf{q}). \qquad (112)$$

Solving Eq. (110) for r and using Eq. (109) for F_2, we obtain

$$r=\mp\frac{1}{2N\rho M^*U}\{|A|-[A^2-(2\rho M^*U)^2]^{\frac{1}{2}}\}$$

$$F_2=rD,$$

$$\delta E=\tfrac{1}{2}N\rho U(0)\mp\frac{\mathcal{V}}{4h^3M^*}\int d^3q$$
$$\times\left\{|A|-[A^2-(2\rho M^*U)^2]^{\frac{1}{2}}\mp\frac{2}{q^2}(\rho M^*U)^2\right\}, \qquad (113)$$

where

$$A\equiv q^2+2\rho M^*U, \qquad (114)$$

and the upper or lower signs are used when $A>0$ or $A<0$, respectively.

The expression for the energy shift given by Eq. (113) seems physically reasonable. It exhibits saturation for repulsive-core interactions, and can lead to a description of condensation and the liquid state even when one sets $M^*=M$. The result agrees with that obtained by Lee and Yang[20] for the ground-state energy shift of a system of Bose particles interacting through hard-sphere potentials of radius a. In that case, we may set

$$\begin{aligned}&R=4\pi a/(M\mathcal{V}), \quad \rho U=4\pi Na/(m\mathcal{V}),\\ &\rho_0\equiv N/\mathcal{V}, \quad b\equiv 8\pi Na/\mathcal{V},\end{aligned} \qquad (115)$$

and obtain

$$\delta E=\frac{2\pi N\rho_0a}{M}-\frac{\pi\mathcal{V}}{h^3M}\int_0^\infty dqq^2$$
$$\times\{q^2+b-[(q^2+b)^2-b^2]^{\frac{1}{2}}-\tfrac{1}{2}(b^2/q^2)\} \qquad (116)$$
$$=\frac{2\pi N\rho_0a}{M}\left[1+\frac{128(\rho_0a^3)^{\frac{1}{2}}}{15\pi^{\frac{1}{2}}\hbar^3}\right].$$

This result for Bose-Einstein systems was also obtained by Brueckner and Sawada,[19] using a different method.

Inspection of Eq. (113) shows that for *attractive* potentials care must be exercised in fixing the lower limit of the magnitude of q in the integration, because the integrand should be restricted to those values of q for which the energy is real. We conjecture that values of q less than the minimum value q_{min} have a connection with the "condensed sub-states" discussed in Sec. I, but it appears that a definite answer to this question depends upon a more detailed quantitative evaluation of the scattering matrices. In any case, restriction of the integral to the range $\int_{q_{\mathrm{min}}}^{\infty}dq$ seems a valid approximation.

It also appears likely that our approximate solution (109) to Eqs. (104) may provide a starting point for

---

[20] T. D. Lee and C. N. Yang, Phys. Rev. **105**, 1119 (1957).

further calculations. The possibility of applying the "Tamm-Dancoff" or "Tomonaga" techniques from field theory is suggested—indeed, our equations look very much like those of a "cutoff field theory." [21]

The handling of excited states may be illustrated by the following simple calculation:

Neglecting the amplitudes F_{ijkl}, and retaining only "closed loop" terms, Eq. (103) for the two-particle amplitude may be written in the form

$$F_{ij}=\sum_l\left[F_{il}\frac{1}{d_{il}}R_{jl}+F_{jl}\frac{1}{d_{jl}}R_{il}\right]+R_{ij},\tag{117}$$

where, by Eqs. (11) and (92),

$$d_{ij}=D-(1/M^*)\mathbf{q}\cdot(\mathbf{p}_{0i}-\mathbf{p}_{0j}),\quad D=-q^2/M^*.\tag{118}$$

Since the reference p_0 state is considered to be an excited state in this discussion, we define

$$R_{ij}\equiv R+R_{ij}',\quad F_{ij}\equiv F_2+F_{ij}',\tag{119}$$

where F_2 is given by Eq. (106), and R is the scattering operator as specified in the development preceding Eq. (105). We also expand the propagators in the form

$$\frac{1}{d_{ij}}R=\frac{1}{D}R+\Delta_{ij},\quad \Delta_{ij}=-\frac{R}{D}\frac{\mathbf{q}\cdot(\mathbf{p}_{0i}-\mathbf{p}_{0j})}{q^2+\mathbf{q}\cdot(\mathbf{p}_{0i}-\mathbf{p}_{0j})}.\tag{120}$$

We treat the Δ_{ij}, R_{ij}', and F_{ij}' as small perturbations in Eq. (117), and keep only first-order terms in these quantities. Substitution of Eqs. (119) and (120) into Eq. (117) then yields

$$\begin{aligned}F_{ij}'=\sum_l[&F_2(\Delta_{il}+\Delta_{jl})+F_2(1/D)(R_{il}'+R_{jl}')\\&+R(1/D)(F_{il}'+F_{jl}')]+R_{ij}'.\end{aligned}\tag{121}$$

We assume a solution of the form

$$\begin{aligned}F_{ij}'=\Gamma_1\sum_k(\Delta_{ik}+\Delta_{jk})&+\Gamma_2\sum_k(R_{ik}'+R_{jk}')\\&+\Gamma_3R_{ij}'+\Gamma_4,\end{aligned}\tag{122}$$

substitute into Eq. (121), and obtain the identifications

$$\begin{aligned}\Gamma_1&=F_2+\frac{NR}{D}\Gamma_1,\\ \Gamma_2&=\frac{F_2}{D}+\frac{NR}{D}\Gamma_2+\frac{R}{D}\Gamma_3,\\ \Gamma_3&=1,\\ \Gamma_4&=\frac{2R}{D}\Gamma_1\sum_{i,j}\Delta_{ij}+\frac{2R}{D}\Gamma_2\sum_{i,j}R_{ij}'+\frac{2NR}{D}\Gamma_4.\end{aligned}\tag{123}$$

The solution is

$$\begin{aligned}\Gamma_1&=\frac{DF_2}{D-NR},\quad \Gamma_2=\frac{F_2+R}{D-NR},\quad \Gamma_3=1,\\ \Gamma_4&=\frac{2RDF_2}{(D-NR)(D-2NR)}\sum_{i,j}\Delta_{ij}\\&\quad+\frac{2R(F_2+R)}{(D-NR)(D-2NR)}\sum_{i,j}R_{ij}',\end{aligned}\tag{124}$$

with

$$\begin{aligned}F_2&=\mp\frac{D}{2N^2R}\{|A|-[A^2-(2NR)^2]^{\frac{1}{2}}\},\\ A&=2NR-D.\end{aligned}\tag{125}$$

Examination of Eq. (120) and Eqs. (122) to (125) shows that F_{ij}' remains finite over the entire range of values that the integration variable q may assume, and in particular as $q\rightarrow 0$. Substitution of Eqs. (119) and (122) into Eq. (102) leads to an expansion of the energy shift in which the dominant term is usually proportional to $\sum_{i<j}(\mathbf{p}_{0i}-\mathbf{p}_{0j})^2$, although the exact form of the expression depends upon the behavior of $R(\mathbf{q})$.

The second-order calculation of the amplitudes F_{ij} proceeds in analogous fashion, but for purposes of illustration it is advantageous to simplify the algebra by setting the R_{ij}' equal to zero. Under this assumption we expand F_{ij} in the form

$$F_{ij}=F_2+F_{ij}'+F_{ij}'',\tag{126}$$

with F_{ij}'' representing the second-order contribution, quadratic in the Δ_{ij}. Substitution into Eq. (117) yields

$$\begin{aligned}F_{ij}'&=\sum_l\left[F_2(\Delta_{il}+\Delta_{jl})+R\frac{1}{D}(F_{il}'+F_{jl}')\right],\\ F_{ij}''&=\sum_l\left[F_{il}'\Delta_{il}+F_{jl}'\Delta_{jl}+R\frac{1}{D}(F_{il}''+F_{jl}'')\right].\end{aligned}\tag{127}$$

The first of Eqs. (127) is a special case of Eq. (121), and the solution is given by Eq. (122) with

$$\begin{aligned}\Gamma_1&=\frac{DF_2}{D-NR},\\ \Gamma_4&=\frac{2RDF_2}{(D-NR)(D-2NR)}\sum_{i,j}\Delta_{ij},\\ \Gamma_2&=\Gamma_3=0.\end{aligned}\tag{128}$$

After substituting this solution into the second of Eqs. (127) we obtain

$$\begin{aligned}F_{ij}''=\sum_{l,k}&[\Gamma_1(\Delta_{ik}\Delta_{il}+\Delta_{jk}\Delta_{jl})+\Gamma_1(\Delta_{il}\Delta_{lk}+\Delta_{jl}\Delta_{lk})]\\&+\sum_l\left[\Gamma_4(\Delta_{il}+\Delta_{jl})+R\frac{1}{D}(F_{il}''+F_{jl}'')\right].\end{aligned}\tag{129}$$

---

[21] Schweber, Bethe, and de Hoffmann, *Mesons and Fields* (Row, Peterson and Company, New York, 1955), Vol. II, Sections 40–44.

We assume a solution of form

$$F_{ij}''=H_1\sum_{m}(\Delta_{im}+\Delta_{jm})+H_2\sum_{m,n}(\Delta_{im}\Delta_{in}+\Delta_{jm}\Delta_{jn})+H_3\sum_{m,n}(\Delta_{im}\Delta_{mn}+\Delta_{jm}\Delta_{mn})+H_4, \quad (130)$$

and insert it into Eq. (129) to get the identifications

$$\begin{aligned} H_1&=\frac{NR}{D}H_1+\Gamma_4,\\ H_2&=\Gamma_1+\frac{NR}{D}H_2,\\ H_3&=\Gamma_1+\frac{NR}{D}H_3,\\ H_4&=\frac{2NR}{D}H_4+\frac{2R}{D}H_1\sum_{i,j}\Delta_{ij}+\frac{2R}{D}(H_2+H_3)\sum_{i,j,k}\Delta_{ij}\Delta_{jk}. \end{aligned} \quad (131)$$

The solution of Eq. (131) is

$$\begin{aligned} H_1&=\frac{2RD^2F_2}{(D-NR)^2(D-2NR)}\sum_{i,j}\Delta_{ij},\\ H_2&=H_3=\frac{D^2F_2}{(D-NR)^2},\\ H_4&=\frac{4RD^2F_2}{(D-NR)^2(D-2NR)}\times\left[\frac{R}{D-2NR}(\sum_{i,j}\Delta_{ij})^2+\sum_{i,j,k}\Delta_{ij}\Delta_{ik}\right]. \end{aligned} \quad (132)$$

This technique can be used to extend the expansion in powers of Δ_{ij} to higher orders.

APPENDIX

We shall describe briefly the physical properties of the "linked clusters" of Brueckner[2] as they appear in our "nearest neighbor" expansion. A more detailed discussion will appear in reference 3.

The basis of the derivation in I was that for an extended medium ($N\gg 1$) the linked clusters behave as if independent of each other. For instance, the wave function of the system may be considered as describing an "ensemble" of all possible different combinations of the particles formed into linked clusters.[3]

The problem of understanding the cluster expansion is complicated by the fact that one uses the kinetic energy of a particle "in the medium," rather than the actual kinetic energy. As will be described in reference 19, there are a variety of ways of defining this "effective kinetic energy" other than in the form given by Eqs. (12) and (13), which is taken from reference 1.

We should emphasize that in reference 1 two different derivations were given of equations having the general form of (12) and (13). In the text of I an approximate, qualitative argument was given for the form of $\delta\epsilon(p_i)$ [see Eq. (12)]. Here the evaluation of $\delta\epsilon$ was described as involving an "average over fluctuations," since the "right cluster" [i.e., the rest of the medium] was treated as remaining in its unperturbed state p_0. This appears to be a very plausible approximation.

On the other hand, in the Appendix C of reference 1 a rigorous development was given. Here a more complicated form for $\delta\epsilon$ was obtained [Eq. (C-25) of I], since $\delta\epsilon$ was expressed as an expectation value with respect to eigenstates φ of the "right-cluster medium"—rather than as an expectation value with respect to the unperturbed state p_0. This latter method is evidently more complicated to use. Recently, however, a straightforward technique for evaluating such expectation values has been developed.[3] When necessary, this makes it possible to avoid the approximation just described.