PHYSICAL REVIEW A VOLUME 8, NUMBER 5 NOVEMBER 1973

Perturbation Correction for the Free Energy and Structure of Simple Fluids

F. Lado
Department of Physics, North Carolina State University, Raleigh, North Carolina 27607

(Received 25 June 1973)

Separation of an arbitrary potential φ into a short-range, repulsive part φ_0 and a weak correction φ_1 affords the possibility of describing the φ-system properties as corrections to the assumed-known φ_0 reference system. We derive here an expression for such a correction of the classical Helmholtz free energy that is the analog of a result familiar from the development of the hypernetted-chain integral equation. Other corrections are obtained therefrom, including a corrected pair-distribution function proposed earlier. All results are easily adapted for numerical calculation.

I. INTRODUCTION

The advantages accruing from possession of a simple ideal model of bulk matter are well evidenced by the practical successes of solid- and gaseous-state theories, where the ideal crystal and ideal gas provide a unique point of departure for the systematic application of perturbation theory. For want of a unique "ideal liquid," such advantages are not available in the statistical theory of dense fluids. In recent years, however, as its properties were extensively studied, the hard sphere model has *faute de mieux* moved more and more into such a role. This development has been accompanied by an increased interest in perturbation theories applicable to the fluid state, either to the thermodynamic functions directly or to the intervening pair-distribution function.

In these theories, one treats the weak, possibly long-range, part $\varphi_1(r)$ of an intermolecular potential

$$\varphi(r)=\varphi_0(r)+\varphi_1(r) \tag{1}$$

as a perturbation added to the short-range repulsive potential $\varphi_0(r)$; the properties of the reference system described by $\varphi_0(r)$ alone are assumed known. Such a separation was first used by Kirkwood *et al.*[1] in calculating the first two terms of a power series in inverse temperature for the perturbation correction to the pair-distribution function. A similar series expansion for the Helmholtz free energy was given by Zwanzig,[2] who evaluated the lowest-order term. Higher terms quickly become intractable, but a novel truncation scheme for this series has been proposed by Barker and Henderson.[3] Avoiding the use of a series expansion, Broyles *et al.*[4] employed a collective coordinate integration to obtain a perturbation correction to the pair-distribution function $g(r)$.

The specific manner of accomplishing the separation in Eq. (1) is a sensitive question which affects the final results.[3,5] In this paper, we shall merely assume that a suitable separation has been made and shall be concerned with obtaining a computable perturbation expression for the free energy and other thermodynamic quantities of the perturbed system. This work extends earlier results[6] on a perturbation correction to the pair-distribution function. In particular, it is shown in Sec. II that an analysis of the free energy[7,8] familiar from the development of the hypernetted-chain (HNC) integral equation[7-9] can be applied to the corresponding perturbed differences, yielding an expression for the corrected free energy in terms of a corrected $g(r)$ obtained in Ref. 6 (subsequently referred to as I) by what was called an "HNC-type approximation."

The Percus-Yevick[10] (PY) and HNC integral equations offer relatively uncomplicated paths to the determination of the structure and thermodynamic properties of simple fluids, given the intermolecular potential. For potentials with a sharp repulsive core, the PY equation provides the more accurate results.[11] The situation is less clear, and may be reversed,[12] in the case of potentials lacking such a core. These considerations suggest that, for a calculation from first principles, one could use a PY approximation to study the reference system and an HNC approximation for the correction. We discuss in Sec. III how the latter calculation can be carried out.

As in the work of Broyles *et al.*,[4] the results obtained here are not in the form of a series expansion. By comparison with such expansions, an infinite number of selected terms is in effect summed. This should make the present results less sensitive to the details of the potential separation of Eq. (1).

II. CORRECTION FOR HELMHOLTZ FREE ENERGY

Canonical-ensemble formalism, describing an N-particle system in thermal contact with a heat reservoir at temperature T and contained in the volume V, will be used. For mathematical purposes, we generalize Eq. (1) by the common artifice of inserting a "charging" parameter ξ, so that the intermolecular potential is

$$\varphi(r;\xi)=\varphi_0(r)+\xi\varphi_1(r)\,. \tag{2}$$

The value $\xi=0$ then pertains to the reference system, whose properties are assumed known. Except for the fact that ξ is associated only with the perturbing part of the potential, the subsequent development follows that of Morita and Hiroike[7] and Green.[8]

The configurational part of the free energy is

$$A^c(\xi)=-k_BT\ln Q(\xi)\,, \tag{3}$$

where

$$Q(\xi)=V^{-N}\int d^{3N}r\exp\Big(-\beta\sum_{i<j}\varphi(r_{ij};\xi)\Big) \tag{4}$$

and $\beta\equiv(k_BT)^{-1}$. Evidently, the difference in free energy between the system with arbitrary ξ and the reference system can be written

$$\begin{aligned}A(\xi)-A_0&=\int_0^\xi d\xi\frac{dA^c(\xi)}{d\xi}\\&=\frac{1}{2}\Big(\frac{N\rho}{\beta}\Big)\int_0^\xi d\xi\int d\vec{r}\,g(r;\xi)\beta\varphi_1(r)\,,\end{aligned} \tag{5}$$

where ρ is the number density N/V and

$$\begin{aligned}g(r_{12};\xi)=\frac{N(N-1)}{\rho^2Q(\xi)}&\int d\vec{r}_3\cdots d\vec{r}_N\\&\times\exp\Big(-\beta\sum_{i<j}\varphi(r_{ij};\xi)\Big)\,.\end{aligned} \tag{6}$$

In Eq. (5) and hereafter, the subscript 0 labels quantities pertaining to the reference system, where $\xi=0$.

Now, from the graphical analysis of the pair-distribution function,[7-9,13] it is known that $g(r;\xi)$ may be written

$$g(r;\xi)e^{\beta\varphi(r;\xi)}=e^{S(r;\xi)+B(r;\xi)}\,, \tag{7}$$

where S is the sum of all diagrams of the series type and B the sum of bridge-type diagrams, and furthermore that

$$S(r;\xi)=\rho\int d\vec{r}'\,G(r';\xi)C(|\vec{r}-\vec{r}'|;\xi)\,, \tag{8}$$

where

$$G(r;\xi)\equiv g(r;\xi)-1 \tag{9}$$

and

$$C(r;\xi)=G(r;\xi)-S(r;\xi) \tag{10}$$

is the direct-correlation function. Similar equations can be written for the reference system and, in particular, we have

$$g_0(r)e^{\beta\varphi_0(r)}=e^{S_0(r)+B_0(r)}\,, \tag{11}$$

so that dividing Eq. (7) by Eq. (11) yields

$$g(r;\xi)=g_0(r)\exp[-\xi\beta\varphi_1(r)+\Delta S(r;\xi)+\Delta B(r;\xi)]\,, \tag{12}$$

where

$$\Delta S(r;\xi)\equiv S(r;\xi)-S_0(r)\,, \tag{13a}$$

$$\Delta B(r;\xi)\equiv B(r;\xi)-B_0(r)\,. \tag{13b}$$

Differentiation of Eq. (12) gives

$$\begin{aligned}g(r;\xi)\beta\varphi_1(r)&=-\frac{\partial g(r;\xi)}{\partial\xi}+g(r;\xi)\frac{\partial[\Delta S(r;\xi)+\Delta B(r;\xi)]}{\partial\xi}\\&=-\frac{\partial}{\partial\xi}\Big[g(r;\xi)-g(r;\xi)\ln\Big(\frac{g(r;\xi)e^{\xi\beta\varphi_1(r)}}{g_0(r)}\Big)\Big]\\&\quad-[\Delta S(r;\xi)+\Delta B(r;\xi)]\frac{\partial g(r;\xi)}{\partial\xi}\,.\end{aligned} \tag{14}$$

The left-hand side of Eq. (14) is of course the integrand of Eq. (5). Recalling the definition of $C(r;\xi)$, Eq. (10), we may write

$$\begin{aligned}\Delta S(r;\xi)\frac{\partial g(r;\xi)}{\partial\xi}&=\Delta S(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}\\&=\frac{\partial[\frac{1}{2}\Delta G(r;\xi)^2]}{\partial\xi}-\Delta C(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}\,,\end{aligned} \tag{15}$$

with ΔC and ΔG defined similarly as in (13). With (15), Eq. (14) becomes

$$\begin{aligned}g(r;\xi)\beta\varphi_1(r)=-\frac{\partial}{\partial\xi}\Big[&\tfrac{1}{2}\Delta G(r;\xi)^2+g(r;\xi)\\&-g(r;\xi)\ln\Big(\frac{g(r;\xi)e^{\xi\beta\varphi_1(r)}}{g_0(r)}\Big)\Big]\\&+\Delta C(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}\\&-\Delta B(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}\,,\end{aligned} \tag{16}$$

which, inserted into (5), yields

$$\begin{aligned}\beta[A(\xi)-A_0]/N=&-\tfrac{1}{2}\rho\int d\vec{r}\Big[\tfrac{1}{2}\Delta G(r;\xi)^2+\Delta G(r;\xi)-g(r;\xi)\ln\Big(\frac{g(r;\xi)e^{\xi\beta\varphi_1(r)}}{g_0(r)}\Big)\Big]\\&+\tfrac{1}{2}\rho\int_0^\xi d\xi\int d\vec{r}\,\Delta C(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}-\tfrac{1}{2}\rho\int_0^\xi d\xi\int d\vec{r}\,\Delta B(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}\,.\end{aligned} \tag{17}$$

We shall use a tilde to denote a Fourier transform. It can be readily verified that in the penultimate term of (17) we may put

$$\int d\vec{r}\,\Delta C(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}=(2\pi)^{-3}\int d\vec{k}\,\Delta\tilde{C}(k;\xi)\frac{\partial\Delta\tilde{G}(k;\xi)}{\partial\xi}$$
$$=\frac{1}{\rho^2(2\pi)^3}\frac{\partial}{\partial\xi}\int d\vec{k}\left[\frac{\rho\Delta\tilde{G}(k;\xi)}{1+\rho\tilde{G}_0(k)}-\ln\left(1+\frac{\rho\Delta\tilde{G}(k;\xi)}{1+\rho\tilde{G}_0(k)}\right)\right], \tag{18}$$

where in the second equality we have used

$$1+\rho\tilde{G}(k;\xi)=[1-\rho\tilde{C}(k;\xi)]^{-1}, \tag{19}$$

which follows from Eqs. (8) and (10). Equation (18) may be inserted in (17) and the integration over ξ carried out, yielding finally for the difference in free energy between the fully perturbed ($\xi=1$) and reference systems

$$\beta(A-A_0)/N=-\tfrac{1}{2}\rho\int d\vec{r}\,\{\tfrac{1}{2}\Delta G(r)^2+\Delta G(r)-g(r)\ln[g(r)e^{\beta\varphi_1(r)}/g_0(r)]\}$$
$$-\frac{1}{2\rho(2\pi)^3}\int d\vec{k}\left[\ln\left(1+\frac{\rho\Delta\tilde{G}(k)}{1+\rho\tilde{G}_0(k)}\right)-\frac{\rho\Delta\tilde{G}(k)}{1+\rho\tilde{G}_0(k)}\right]-\tfrac{1}{2}\rho\int_0^1 d\xi\int d\vec{r}\,\Delta B(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}. \tag{20}$$

Equation (20) is the analog of the expression for the free energy obtained by Morita and Hiroike[7] and Green.[8] If we chose the ideal gas as the reference system, it would be identical.

With $g_0(r)$ assumed known, there remain two additional steps that must be taken to render (20) usable. These deal with the calculations of ΔG and ΔB. The former is discussed in Sec. III. With respect to the latter, we note that there is no simple functional known which expresses the bridge set in terms of G, and the same lack holds for their differences ΔB and ΔG. The most straightforward approximation for ΔB is to neglect it altogether as in the HNC equation. It is not the same as the HNC approximation, however, in that one neglects only the effect of the perturbing potential φ_1 on the bridge-diagram set, rather than the entire bridge set, and hence we call it an "HNC-type" approximation. Our usable result is then

$$\frac{\beta(A-A_0)}{N}\approx-\tfrac{1}{2}\rho\int d\vec{r}\left[\tfrac{1}{2}\Delta G(r)^2+\Delta G(r)-g(r)\ln\left(\frac{g(r)e^{\beta\varphi_1(r)}}{g_0(r)}\right)\right]-\frac{1}{2\rho(2\pi)^3}\int d\vec{k}\left[\ln\left(1+\frac{\rho\Delta\tilde{G}(k)}{1+\rho\tilde{G}_0(k)}\right)-\frac{\rho\Delta\tilde{G}(k)}{1+\rho\tilde{G}_0(k)}\right]. \tag{21}$$

The equilibrium condition for the canonical ensemble is that the free energy be minimum. Variation of Eq. (20) with respect to $g(r)$, holding $g_0(r)$ fixed, then yields our point of departure, Eq. (12) (with $\xi=1$), as the condition for minimum difference in $A-A_0$. (See Appendix.) Similarly, variation of the approximate Eq. (21) yields

$$g(r)\approx g_0(r)e^{-\beta\varphi_1(r)+\Delta S(r)}, \tag{22}$$

which was used in I and will be taken up again in Sec. III.

It is of interest to examine the thermodynamic quantities obtainable from the free energy, because an inconsistency appears when using the approximations (21) and (22). The last term in (20) will warrant special attention, so we put

$$\frac{\beta\Delta A'}{N}\equiv-\tfrac{1}{2}\rho\int_0^1 d\xi\int d\vec{r}\,\Delta B(r;\xi)\frac{\partial\Delta G(r;\xi)}{\partial\xi}. \tag{23}$$

For the energy difference per particle due to this term we get

$$\frac{\partial}{\partial\beta}\left(\frac{\beta\Delta A'}{N}\right)=\int d\vec{r}\,\frac{\delta(\beta\Delta A'/N)}{\delta g(r)}\frac{\partial g(r)}{\partial\beta}$$
$$+\int d\vec{r}\,\frac{\delta(\beta\Delta A'/N)}{\delta g_0(r)}\frac{\partial g_0(r)}{\partial\beta}=-\tfrac{1}{2}\rho\int d\vec{r}\,\Delta B(r)\frac{\partial g(r)}{\partial\beta}+\tfrac{1}{2}\rho\int d\vec{r}\,\Delta G(r)\frac{\partial B_0(r)}{\partial\beta}, \tag{24}$$

having again used the results in the Appendix. Differentiation of (20) then yields

$$
\begin{aligned}
(E-E_0)/N &= \frac{\partial[\beta(A-A_0)/N]}{\partial\beta} \\
&= \tfrac{1}{2}\rho\int d\vec{r}\, g(r)\varphi_1(r) + \tfrac{1}{2}\rho\int d\vec{r}\,\Delta G(r)\frac{\partial[G_0(r)-C_0(r)+B_0(r)-\ln g_0(r)]}{\partial\beta} \\
&\quad + \tfrac{1}{2}\rho\int d\vec{r}\left[\ln\left(\frac{g(r)e^{\beta\varphi_1(r)}}{g_0(r)}\right)-\Delta G(r)+\Delta C(r)-\Delta B(r)\right]\frac{\partial g(r)}{\partial\beta}. \qquad (25)
\end{aligned}
$$

The last term in (25) vanishes because of (12), while from (11) the derivative in the second term is just $\varphi_0(r)$. Thus we get the expected result:

$$
\begin{aligned}
\frac{E-E_0}{N} &= \tfrac{1}{2}\rho\int d\vec{r}\,[g(r)\varphi_1(r)+\Delta G(r)\varphi_0(r)] \\
&= \tfrac{1}{2}\rho\int d\vec{r}\,[g_0\varphi_1(r)+\Delta G(r)\varphi(r)]. \qquad (26)
\end{aligned}
$$

An inconsistency appears when the approximation (21) is used instead of (20). Because *both* terms in Eq. (24) are then neglected, not only does the approximate $g(r)$ [Eq. (22)] appear in (26), but also an additional term, the wanted second term of (24). This means that energy differences calculated by β differentiation of Eq. (21) and from Eq. (26), with the approximate $g(r)$, will not be the same.

A similar situation obtains for the pressure difference

$$
\begin{aligned}
p-p_0 &= \rho^2\frac{\partial[(A-A_0)/N]}{\partial\rho} \\
&= -\tfrac{1}{6}\rho^2\int d\vec{r}\, r[g_0(r)\varphi_1'(r)+\Delta G(r)\varphi'(r)]. \qquad (27)
\end{aligned}
$$

Here the first equality, using Eq. (21), will not give the same result as the second equality, using Eq. (22). We omit the details.

Such breakdowns in consistency are common features of approximate theories.

The third derivative of (20), with respect to number, for the change in the chemical potential, can be expressed in terms of quantities already given:

$$
\mu-\mu_0 = \frac{\partial(A-A_0)}{\partial N} = \frac{A-A_0}{N}+\frac{p-p_0}{\rho}. \qquad (28)
$$

III. CORRECTION FOR THE PAIR-DISTRIBUTION FUNCTION

In Sec. II, the problem of calculating the free energy, internal energy, etc., of a given system was reduced to knowledge of the corresponding quantities for a related reference system and calculation of the difference in the respective pair-distribution functions. Here we take up this latter question.

By combining Eqs. (7) and (10), one gets, for $\xi=1$,

$$
C(r) = G(r) - \ln[g(r)e^{\beta\varphi(r)}] + B(r), \qquad (29)
$$

and subtraction of the similar equation for the reference system yields

$$
\Delta C(r) = -\beta\varphi_1(r) + \Delta G(r) - \ln\left(\frac{g(r)}{g_0(r)}\right) + \Delta B(r). \qquad (30)
$$

A similar use of Eq. (19) gives a second relation between the transforms of ΔG and ΔC:

$$
\Delta\tilde{G}(k) = \frac{[1+\rho\tilde{G}_0(k)]^2\Delta\tilde{C}(k)}{1-\rho[1+\rho\tilde{G}_0(k)]\Delta\tilde{C}(k)}. \qquad (31)
$$

Equations (30) and (31) were used in I to produce a simple noniterative approximation to the perturbed $g(r)$. This was to neglect ΔB in (30) and approximate ΔC by its lowest-order term $-\beta\varphi_1$, whence (30) yields

$$
g(r) \approx g_0(r)e^{\Delta G(r)}, \qquad (32)
$$

and from (31),

$$
\Delta\tilde{G}(k) \approx -\frac{[1+\rho\tilde{G}_0(k)]^2\beta\tilde{\varphi}_1(k)}{1+\rho[1+\rho\tilde{G}_0(k)]\beta\tilde{\varphi}_1(k)}. \qquad (33)
$$

This approximation has proved reasonably accurate in a variety of applications[14] and is above all convenient.

We are, however, not forced into a second approximation after neglect of ΔB. Instead, it is possible to treat Eqs. (30) and (31) as in the HNC equation itself, i.e., neglect ΔB and solve the resulting pair of nonlinear equations for ΔG by iterating to a self-consistent solution. To avoid possible numerical difficulties in computing $\ln(g/g_0)$ in a hard-core region, it will be preferable to solve for the unknown in the form

$$
H(r) = \ln[g(r)/g_0(r)] + \beta\varphi_1(r). \qquad (34)
$$

Equations (30) (with ΔB neglected) and (31) are then rearranged to read

$$
\Delta C(r) = g_0(r)\{\exp[H(r)-\beta\varphi_1(r)]-1\} - H(r), \qquad (35)
$$

$$
\tilde{H}(k) = \frac{[1+\rho\tilde{G}_0(k)]^2\Delta\tilde{C}(k)}{1-\rho[1+\rho\tilde{G}_0(k)]\Delta\tilde{C}(k)} - \Delta\tilde{C}(k). \qquad (36)
$$

The solution is begun by guessing $H(r)$. With a given iterate $H^{(j)}$, Eq. (35) produces $\Delta C^{(j)}$, whose Fourier transform yields, from (36), a new iterate $H^{(j+1)}$. The iterations can be continued until the solution is self-consistent.

If the perturbing potential possesses a Fourier transform, we may take as the initial guess $H^{(0)}(r) = \beta\varphi_1(r)$; in this case, it is easy to show that the approximation in Eqs. (32) and (33) is simply the output of the first iteration of Eqs. (35) and (36).

APPENDIX

The functional derivatives of $\beta\Delta A'/N$, the last term of Eq. (20), were needed at several points in Sec. II. They are obtained in this Appendix.

We first simplify the term by writing

$$\frac{\beta\Delta A'}{N} = -\tfrac{1}{2}\rho\int_0^1 d\xi \int d\vec{r}\, \Delta B(r;\xi)\frac{\partial g(r;\xi)}{\partial\xi}$$

$$= -\tfrac{1}{2}\rho\int_0^1 d\xi \int d\vec{r}\, B(r;\xi)\frac{\partial g(r;\xi)}{\partial\xi}$$

$$+\tfrac{1}{2}\rho\int d\vec{r}\, B_0(r)\Delta G(r)\,. \tag{A1}$$

Then assuming $B(r;\xi)$ and $B_0(r)$ to be functionals of $g(r;\xi)$ and $g_0(r)$, respectively, and letting these latter functions vary, we get the variation

$$\delta\frac{\beta\Delta A'}{N} = -\tfrac{1}{2}\int_0^1 d\xi\int d\vec{r}\left(B(r;\xi)\frac{\partial\delta g(r;\xi)}{\partial\xi} + \delta B(r;\xi)\frac{\partial g(r;\xi)}{\partial\xi}\right) + \tfrac{1}{2}\rho\int d\vec{r}\, B_0(r)[\delta g(r) - \delta g_0(r)] + \tfrac{1}{2}\rho\int d\vec{r}\,\delta B_0(r)\Delta G(r)$$

$$= \tfrac{1}{2}\rho\int d\vec{r}\left(\Delta G(r)\frac{\delta B_0(r)}{\delta g_0(r)}\delta g_0(r) - \Delta B(r)\delta g(r)\right) + \tfrac{1}{2}\rho\int_0^1 d\xi\int d\vec{r}\left(\frac{\partial B(r;\xi)}{\partial\xi} - \frac{\delta B(r;\xi)}{\delta g(r;\xi)}\frac{\partial g(r;\xi)}{\partial\xi}\right)\delta g(r;\xi)\,, \tag{A2}$$

after an integration by parts. The bracketed integrand in the second term of (A2) vanishes and so we have immediately

$$\frac{\delta(\beta\Delta A'/N)}{\delta g(r)} \; -\tfrac{1}{2}\rho\Delta B(r), \tag{A3}$$

$$\frac{\delta(\beta\Delta A'/N)}{\delta g_0(r)} = \tfrac{1}{2}\rho\,\Delta G(r)\frac{\delta B_0(r)}{\delta g_0(r)}\,. \tag{A4}$$

---

[1] J. G. Kirkwood, V. A. Lewison, and B. J. Alder, J. Chem. Phys. 20, 929 (1952).

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

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

[4] A. A. Broyles, H. L. Sahlin, and D. D. Carley, Phys. Rev. Lett. 10, 319 (1963).

[5] E. B. Smith and B. J. Alder, J. Chem. Phys. 30, 1190 (1959); J. S. Rowlinson, Mol. Phys. 8, 107 (1964); D. A. McQuarrie and J. L. Katz, J. Chem. Phys. 44, 2393 (1966); J. Rasaiah and G. Stell, Mol. Phys. 18, 249 (1970); H. C. Anderson, D. Chandler, and J. D. Weeks, J. Chem. Phys. 57, 2626 (1972), and references therein.

[6] F. Lado, Phys. Rev. 135, A1013 (1964).

[7] T. Morita and K. Hiroike, Prog. Theor. Phys. 23, 1003 (1960).

[8] M. S. Green, J. Chem. Phys. 33, 1403 (1960).

[9] J. M. J. van Leeuwen, J. Groeneveld, and J. DeBoer, Physica (Utr.) 25, 792 (1959); E. Meeron, J. Math. Phys. 1, 192 (1960); G. S. Rushbrooke, Physica (Utr.) 26, 259 (1960); L. Verlet, Nuovo Cimento 18, 77 (1960).

[10] J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958).

[11] A. A. Broyles, S. U. Chung, and H. L. Sahlin, J. Chem. Phys. 37, 2462 (1962); D. Levesque, Physica (Utr.) 32, 1985 (1966).

[12] D. D. Carley, Phys. Rev. 136, A127 (1964); J. F. Springer, M. A. Pokrant, and F. A. Stevens, Jr., J. Chem. Phys. 58, 4863 (1973).

[13] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Wiley, New York, 1965), Chap. 2.

[14] D. D. Carley, J. Chem. Phys. 43, 3489 (1965); T. Dunn and A. A. Broyles, Phys. Rev. 157, 156 (1967); M. A. Pokrant, Phys. Rev. A 6, 1588 (1972).