# On the van der Waals Theory of the Vapor–Liquid Equilibrium.
# II. Discussion of the Distribution Functions

G. E. UHLENBECK, P. C. HEMMER, AND M. KAC

*The Rockefeller Institute, New York, New York*
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For the same one-dimensional fluid model discussed in Part I, we have derived general expressions for the two- and three-particle distribution functions. It is seen that these distribution functions depend on all the eigenvalues and eigenfunctions of the basic Kac integral equation, and the dependence is so transparent that the generalization to $s$ particles is obvious. The fluctuation and virial theorems are discussed and shown to be consequences of our general formula. In the van der Waals limit, the behavior of the two-point distribution function is discussed, both for distances of the order of the hard core and for distances of the order of the range of the attractive force. The long-range behavior is, in first approximation, equivalent to the one-dimensional version of the Ornstein–Zernike theory, but only in the one-phase region and not too near the critical point. In the two-phase region, all distribution functions are linear combinations of the two corresponding distribution functions of the saturated vapor and liquid, with coefficients proportional to the mole fractions of vapor and liquid. This is shown for our model; we also give arguments for our belief that these relations are general, and express the geometrical separation of the two phases. The relation to the Ornstein–Zernike theory is discussed in more detail, especially in connection with a recent formulation of this theory by Lebowitz and Percus. We conclude with some comments on the relevance of our results for the three-dimensional problem.

## I. INTRODUCTION

THE first attempt to go beyond the question of the equation of state of a nonideal gas to the deeper problem of the correlation in position of the molecules in a gas or liquid, was made by Ornstein and Zernike in their well known theory of the critical opalescence.[1] Zernike, Prins and others[2] later used the same ideas to interpret the results of the x-ray scattering in liquids in terms of the so-called two-point correlation function. This correlation function is found to be essentially the Fourier transform of the angular distribution of the scattered rays, and it is therefore directly observable. This cannot be said of the so-called $n$-point correlation functions ($n = 3, 4, \cdots$) but these functions *can* be defined precisely for a system in equilibrium, and with increasing $n$, they describe the structure of the system in more and more detail.

The general theory of these correlation or distribution functions was developed in the forties mainly by Kirkwood, Yvon, de Boer, Mayer,[3] and their collaborators. These authors developed the general expansion theorems for these distribution functions in powers of the fugacity or in powers of the density,[4] which generalize and include the corresponding expansions for the equation of state. They also proposed various approximation schemes, of which Kirkwood's superposition approximation is the best known. This leads to new attempts to discuss the problem of phase transitions, which are of great interest.[5]

So far as we know, no one has tried to relate these general developments with the basic ideas of van der Waals in a systematic way, and it seems to us

[1] L. S. Orsntein and F. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914); Physik. Z. **19**, 134 (1918); **27**, 761 (1926). See also F. Zernike, Dissertation, Groningen, Netherlands 1916, reprinted in Arch. Neerl. Zool., Serie 13A, **4**, 74 (1917). For more recent accounts compare Landau and Lifshitz, *Statistical Physics* (Pergamon Press, London, 1958), p. 366; M. Klein and L. Tisza, Phys. Rev. **76**, 1861 (1949); M. Fierz, Pauli Memorial Volume (Interscience Publishing Co., New York, 1960), p. 175; and especially P. Debye, *Non-Crystalline Solids* (John Wiley & Sons, New York, 1960), pp. 1–20; J. Chem. Phys. **31**, 680 (1959).

[2] F. Zernike and J. A. Prins, Z. Physik. **41**, 184 (1927); P. Debye and H. Menke, Physik. Z. **33**, 593 (1932).

[3] Since the literature is quite extensive, we refer to the reports by J. Yvon, *Fluctuations en densité* (Hermann & Cie., Paris, 1937); by J. de Boer, Rep. Progr. Phys. **12**, 305 (1949); by A. Munster in his book, *Statistische Thermodynamik* (Springer-Verlag, Berlin, Germany, 1956), Chap. 8; and by J. Mayer, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958) Vol. XXII, p. 152.

[4] For a complete discussion of these expansions see J. E. Mayer and E. W. Montroll, J. Chem. Phys. **9**, 2 (1941). Compare also the account given by G. E. Uhlenbeck and G. W. Ford in *Studies in Statistical Mechanics*, (North-Holland Publishing Company, Amsterdam) Vol. I, Part B.

[5] We are thinking especially of the attempts by Kirkwood and his co-workers to derive the liquid–solid phase transition and to show that such a transition even exists for a system of hard spheres. See J. G. Kirkwood and E. Monroe, J. Chem. Phys. **9**, 514 (1941); J. G. Kirkwood, E. K. Mann and B. J. Alder, J. Chem. Phys. **18**, 1040 (1950).

of interest, therefore, to derive the expression for the distribution functions for the one-dimensional gas model described in Part I of this series and to see what these functions become in the van der Waals limit. In Sec. II, the derivation of the two- and three-point distribution function is given, from which the general expression for the $n$-point function can easily be inferred. It is found that the distribution functions depend on *all* eigenvalues and eigenfunctions of the basic Kac integral equation (Part I, Eq. 10), and one may say that this gives a physical interpretation of the eigenvalues and eigenfunctions, although we do not know as yet whether these eigenvalues and eigenfunctions are uniquely determined by the set of distribution functions. Another general expression for the distribution functions, also derived in Sec. II, is in terms of the resolvent of the Kac equation and the eigenfunction $\psi_0(x)$ corresponding to the maximum eigenvalue $\lambda_0(s)$. This expression is especially important for the discussion of the distribution functions in the two-phase region.

In Sec. III we derive the well-known virial and fluctuation theorems. General proofs of these basic theorems are of course available, but it seems worth while to prove them directly from the Kac equation. Since these theorems connect the two-point distribution function with the equation of state, they give valuable checks for any successive-approximation method. Furthermore, they provide a link with the original derivation of the van der Waals equation.

In Secs. IV and V, the van der Waals limit and the successive approximations in powers of $\gamma\delta$ of the two-point distribution function are discussed for the *one-phase region*. It is seen that one must distinguish the case when the distance between the two molecules is of order $\delta$ from the case when this distance is of the order of the range of the attractive force $1/\gamma$. The short-range behavior is, as expected, in zeroth approximation, the same as for a gas of hard rods, since in the van der Waals limit the attractive force is very weak. In first approximation, the attractive force influences somewhat the short-range behavior, but the more interesting effect is on the long-range behavior. We find in this approximation, an exponential dependence on the distance, but with a range which is modified by the compressibility of the gas. This behavior is related to the form predicted by the one-dimensional version of the Ornstein–Zernike theory, and this relation is general (i.e., independent of the form of the long range attractive force) when we approach

the critical region. However *in* the critical region our development breaks down, and deviations from the Ornstein–Zernike theory should be expected to occur. We will come back to this in Part III of this series, where the behavior of the two-point distribution function in the critical region will be discussed in detail.

In Sec. VI, the distribution functions in the van der Waals limit are discussed for the *two-phase region*. We show that *all* distribution functions in this region are linear combinations of the two corresponding distribution functions of the saturated vapor and liquid with coefficients proportional to the mole fractions of vapor and liquid. In our opinion, this shows for the first time that the geometric separation of the two phases follows automatically from the theory. In fact it seems that this property of the distribution functions is a deeper formulation of the condensation problem than the property of the constant vapor pressure (horizontal portion of the isotherm), which it implies. This has already been indicated in a basic paper by Mayer[6] in 1947, and perhaps our results can be looked upon as a strict proof, for a special case, of the general considerations given in that paper, although the precise connection is still dark to us.

In Sec. VII we discuss in detail, the connection of our results with the Ornstein–Zernike theory and especially in respect to a recent, very interesting formulation of this theory given by Lebowitz and Percus.[7] We conclude with some comments on the relevance of our results for the three-dimensional problem.

## II. GENERAL EXPRESSIONS FOR THE DISTRIBUTION FUNCTIONS

First let us recall the general definitions for the distribution functions. For the *canonical ensemble*, the $s$-particle distribution function is defined by

$$n_s(\mathbf{r}_1 \cdots \mathbf{r}_s, N, V) = \frac{N!}{(N-s)!}$$

$$\times \int_V \cdots \int_V d\mathbf{r}_{s+1} \cdots d\mathbf{r}_N D_N(\mathbf{r}_1 \cdots \mathbf{r}_N), \qquad (1)$$

where

[6] J. E. Mayer, J. Chem. Phys. **15**, 187 (1947). Compare also his paper J. Chem. Phys. **16**, 665 (1948) and the account in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1958) Vol. XII, p. 165.

[7] J. L. Lebowitz and J. K. Percus, "Asymptotic behavior of the radial distribution function" (Preprint) (to be published).

$$D_N = \frac{1}{\Lambda^{3N} N!} \frac{1}{Z(V, N)}$$

$$\times \exp\left[-\frac{1}{kT} \sum_{i<j} \varphi(|\mathbf{r}_i - \mathbf{r}_j|)\right]. \quad (2)$$

The corresponding formula for the *grand-canonical ensemble* are

$$\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s, V, z) = \sum_{N \geq s} n_s(\mathbf{r}_1 \cdots \mathbf{r}_s, V, N) P_N, \quad (3)$$

where

$$P_N = (\Lambda z)^N Z(V, N)/G(V, z). \quad (4)$$

In the following we will always have in mind a *single-fluid phase*. In this case one knows that in the thermodynamic limit the distribution functions approach the definite values

$$\lim_{N, V \to \infty} n_s(\mathbf{r}_1 \cdots \mathbf{r}_s, N, V) = \bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v),$$

$$\lim_{V \to \infty} \rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s, V, z) = \bar{\rho}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; z). \quad (5)$$

and these functions differ *only* in the dependence on $v$, and $z$, respectively, which however are uniquely related to each other by the second Mayer relation

$$1/v = z\bar{\chi}'(z). \quad (6)$$

Furthermore one knows that in this case the $\bar{n}_s$ and $\bar{\rho}_s$ are *spatially homogeneous*. Adding a constant vector to $\mathbf{r}_1 \cdots \mathbf{r}_s$ will not change the functions $\bar{n}_s$ and $\bar{\rho}_s$. Therefore $\bar{n}_2(\mathbf{r}_1, \mathbf{r}_2, v)$ depends only on $|\mathbf{r}_1 - \mathbf{r}_2|$, $\bar{n}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, v)$ depends only on the lengths of the sides of the triangle $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, etc. Finally it is known that in this case, the functions $\bar{n}_s$ and $\bar{\rho}_s$ have the *product property*. This means that if the $s$ particles are divided in groups containing $\alpha_1$, $\alpha_2 \cdots$ particles, then for configurations in which these groups are very far apart from each other

$$\bar{n}_s = \bar{n}_{\alpha_1} \cdot \bar{n}_{\alpha_2} \cdots , \quad (7)$$

and similarly for $\bar{\rho}_s$. Note that the meaning of "far" depends on the value of $v$ or $z$. The product property implies that if all particles are far apart from each other, then $\bar{n}_s \to (1/v)^s$ and $\bar{\rho}_s \to \bar{\rho}_1^s$. Note that this product property is the only direct relation between the $\bar{n}_s$ or $\bar{\rho}_s$ and the lower distribution functions. One cannot find the lower distribution functions only by integrating over the positions of some of the particles. There are integral relations between the distribution functions, the so-called fluctuation theorems, but these relations are more complicated. We return to them in the next section.

For small density or small $z$, the distribution functions approach the Boltzmann factor

$$\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v) \to \frac{1}{v^s}$$

$$\times \exp\left[-\frac{1}{kT} \sum_{i<j}^{s} \varphi(|\mathbf{r}_i - \mathbf{r}_j|)\right], \quad (8)$$

and as we have already mentioned, the complete virial and fugacity expansions have been worked out (see reference 4).

After these preliminaries, let us return to our one-dimensional model. We prove that all the distribution functions can be expressed in terms of the eigenvalues $\lambda_n(s)$ and eigenfunctions $\psi_n(x, s)$ of the Kac integral equation (Part I, Eq. 10), and especially we will show that

$$l \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2(x; l) = \sum_{n=0} \langle 0, s \mid n, s + \sigma \rangle$$

$$\times \frac{\lambda_n(s + \sigma)}{\lambda_0(s) - \lambda_n(s + \sigma)} \langle n, s + \sigma \mid 0, s \rangle, \quad (9a)$$

$$l \iint_0^\infty dx\, dy\, e^{-\sigma x - \sigma' y} \bar{n}_3(x, y; l)$$

$$= \sum_{n=0}^\infty \sum_{n'=0}^\infty \langle 0, s \mid n, s + \sigma \rangle$$

$$\times \frac{\lambda_n(s + \sigma)}{\lambda_0(s) - \lambda_n(s + \sigma)} \langle n, s + \sigma \mid n', s + \sigma' \rangle$$

$$\times \frac{\lambda_{n'}(s + \sigma')}{\lambda_0(s) - \lambda_{n'}(s + \sigma')} \langle n', s + \sigma' \mid 0, s \rangle. \quad (9b)$$

Here, $s = p/kT$ and the symbol $\langle k, m \mid k', m' \rangle = \langle k', m' \mid k, m \rangle$, stands for the matrix element

$$\langle k, m \mid k', m' \rangle = \int_{-\infty}^{+\infty} dx\, \psi_k(x, m) \psi_{k'}(x, m'). \quad (10)$$

The distribution functions are expressed in relative coordinates, so that

$$\bar{n}_2(x; l) = \bar{n}_2(t_2 - t_1; l) \qquad t_2 \geq t_1, \quad (11)$$

$$\bar{n}_3(x, y; l) = \bar{n}_3(t_2 - t_1, t_3 - t_2; l) \quad t_3 \geq t_2 \geq t_1,$$

where $t_1, t_2, t_3$ are the coordinates of the particles. We have not derived in detail, the expression for the Laplace transform of the $s$-particle distribution function, but the structure of the Eqs. (9a) and (9b) is so transparent, that the generalization to the higher distribution functions seems obvious.

### Proof of Eq. (9a)

As an artifice, we introduce an additional exponential attraction between all pairs of molecules and start from the new partition function

$$\bar{Z}(L, N) = \frac{1}{\Lambda^N N!} \int_0^L \cdots \int_0^L dt_1 \cdots dt_N \prod_{i<j} S(|t_i - t_j|)$$

$$\times \exp\left[\nu \sum_{i<j} e^{-\gamma|t_i-t_j|} + \epsilon \sum_{i<j} e^{-\sigma|t_i-t_j|}\right], \quad (12)$$

using the same notation as Part I, Eq. (2). It is then easy to show, that

$$\left(\frac{\partial \ln \bar{Z}}{\partial \epsilon}\right)_{\epsilon=0} = \frac{1}{2} \iint_0^L dt_1\, dt_2\, e^{-\sigma|t_1-t_2|} n_2(t_1, t_2; N, L),$$

from which follows the analogous expression

$$\left(\frac{\partial \ln \tilde{G}}{\partial \epsilon}\right)_{\epsilon=0} = \frac{1}{2} \iint_0^L dt_1\, dt_2\, e^{-\sigma|t_1-t_2|} \rho_2(t_1, t_2; L, z)$$

$$(13)$$

in terms of the grand-canonical quantities. Since in the thermodynamic limit, $\ln \tilde{G} \to L\tilde{\chi}(z, \epsilon)$, one obtains from (13) in this limit,

$$\left(\frac{\partial \tilde{\chi}(z, \epsilon)}{\partial \epsilon}\right)_{\epsilon=0} = \int_0^\infty dx\, e^{-\sigma x} \bar{\rho}_2(x; z), \quad (14)$$

where $x = t_2 - t_1$.

Exactly in the same way as in Part I, Sec. II, one can associate with the partition function (12) the integral equation

$$\iint_{-\infty}^{+\infty} dy\, dy'\, \tilde{K}_s(x, x'; y, y') \Psi(y, y') = \Lambda \Psi(x, x'), \quad (15)$$

with

$$\tilde{K}_s(x, x'; y, y') = \left[\frac{W(x)W(x')}{W(y)W(y')}\right]^{\frac{1}{2}}$$

$$\times \exp\left[\frac{1}{2}\nu^{\frac{1}{2}}(x + y) + \frac{1}{2}\epsilon^{\frac{1}{2}}(x' + y')\right]$$

$$\times \int_\delta^\infty d\tau\, e^{-s\tau} P_\gamma(x \mid y, \tau) P_\sigma(x' \mid y', \tau). \quad (16)$$

We omit the proof, since it will be obvious to the reader. The notation is again the same as in Part I except that in the $P$ functions, the different ranges of the exponential attractions are indicated. The function $\tilde{\chi}(z, \epsilon)$ is related to the maximum eigenvalue $\Lambda_0(s, \epsilon)$ of Eq. (15) by the equation [similar to Part I, Eq. (18)]

$$\Lambda_0(s, \epsilon) = (1/z) \exp\left[\frac{1}{2}(\nu + \epsilon)\right], \quad (17)$$

where $s = \bar{p}/kT = \tilde{\chi}(z, \epsilon)$. To calculate the left-hand side of Eq. (14), one must make therefore a perturbation calculation for $\Lambda_0$ up to first order in $\epsilon$.

It is easy to see that for $\epsilon = 0$, Eq. (15) is separable and that then the eigenfunctions are given by

$$\Psi_{n,n'}^{(0)}(x, x', s) = \psi_n(x, s + n'\sigma) N_{n'} D_{n'}(x'), \quad (18)$$

corresponding to the eigenvalues

$$\Lambda_{nn'}^{(0)}(s) = \lambda_n(s + n'\sigma), \quad (19)$$

where $\psi_n(x, s)$, $\lambda_n(s)$ are the eigenfunctions and eigenvalues of the Kac equation, Part I, (10), $D_n(x)$ are the Weber functions, and $N_n$ are the normalization constants $(2\pi)^{-\frac{1}{4}}(n!)^{-\frac{1}{2}}$. Setting

$$\Lambda(s, \epsilon) = \Lambda^{(0)}(s) + \epsilon\Lambda^{(1)}(s) + \cdots,$$

$$\Psi(x, x', s, \epsilon) = \Psi^{(0)}(x, x', s) + \epsilon^{\frac{1}{2}}\Psi^{(1)}(x, x', s) + \cdots,$$

one finds by a straightforward perturbation calculation for the maximum eigenvalue and the corresponding eigenfunction

$$\Psi_{00}^{(1)}(x, x', s) = \frac{1}{2} \sum_{n=0}^\infty \frac{\lambda_0(s) + \lambda_n(s + \sigma)}{\lambda_0(s) - \lambda_n(s + \sigma)}$$

$$\times \langle 0, s \mid n, s + \sigma\rangle \Psi_{n_1}^{(0)}(x, x', s),$$

$$\Lambda_{00}^{(1)}(s) = \lambda_0(s)$$

$$\times \left[\frac{1}{2} + \sum_{n=0}^\infty \frac{\lambda_n(s + \sigma)}{\lambda_0(s) - \lambda_n(s + \sigma)} \langle 0, s \mid n, s + \sigma\rangle^2\right], \quad (20)$$

where the completeness relation

$$\sum_n \langle 0, s \mid n, s + \sigma\rangle^2 = 1 \quad (21)$$

has been used.

Now return to Eq. (17). We have found the maximum eigenvalue of (15):

$$\Lambda_0(s, \epsilon) = \lambda_0(s) + \epsilon\Lambda_{00}^{(1)}(s) + \cdots.$$

Introduce here:

$$s = \tilde{\chi}(z, \epsilon) = \bar{\chi}(z) + \epsilon\chi_1(z) + \cdots,$$

where $\bar{\chi}(z) = p/kT$ follows from Part I, Eq. (18). One then obtains from (17), by equating the terms proportional to $\epsilon$,

$$\bar{\chi}_1(z) = \left(\frac{\partial \tilde{\chi}(z, \epsilon)}{\partial \epsilon}\right)_{\epsilon=0} = \frac{1}{l}\left[\frac{\Lambda_{00}^{(1)}(\bar{\chi})}{\lambda_0(\bar{\chi})} - \frac{1}{2}\right], \quad (22)$$

using Eq. (20) from Part I. Substituting in (14) one obtains Eq. (9a), from (20), since in the thermodynamic limit $\bar{\rho}_2(x, z) = \bar{n}_2(x, l)$ with $1/l = z\bar{\chi}'(z)$.

### Proof of Eq. (9b)

To generalize the trick used for the two-point distribution function, one is inclined to introduce three additional exponential potentials corresponding to the three distances between the three particles. However to ensure the triangular relation between the three distances it then becomes necessary to

associate with each molecule, an additional "internal coordinate" $\mu_i$, which can be $\pm 1$, and to average over-all sets of values of the $\mu_i$. We start therefore from the new partition function

$$\tilde{Z}(L, N, \epsilon_1, \epsilon_2, \epsilon_3) = \frac{1}{2^N \Lambda^N N!}$$

$$\times \sum_{\{\mu_i\}} \int_0^L \cdots \int_0^L dt_1 \cdots dt_N \prod_{i<j} S(|t_i - t_j|)$$

$$\times \exp\left[ \nu \sum_{i<j} e^{-\gamma|t_i-t_j|} + \sum_{\alpha=1}^3 \epsilon_\alpha \sum_{i<j} \mu_i \mu_j e^{-\sigma_\alpha|t_i-t_j|} \right].$$

(23)

By differentiating after the $\epsilon_\alpha$ and then setting them equal to zero, and by summing over the $\mu_i$, it is found, using also the fact that $\rho_3(t_1, t_2, t_3; L, z)$ is symmetric in $t_1, t_2, t_3$:

$$\left( \frac{\partial^3 \ln \tilde{G}}{\partial \epsilon_1 \, \partial \epsilon_2 \, \partial \epsilon_3} \right)_{\epsilon_\alpha=0}$$

$$= \iiint_{0 \le t_1 \le t_2 \le t_3 \le L} dt_1 \, dt_2 \, dt_3 \, \rho_3(t_1, t_2, t_3; L, z)$$

$$\times \sum_{P_i} \exp\left[-\sigma_{P_1}|t_1-t_2|-\sigma_{P_2}|t_2-t_3|-\sigma_{P_3}|t_3-t_1|\right],$$

where the sum goes over the six permutations of the indices 1, 2 and 3. This result is similar to Eq. (13). By going to the thermodynamic limit, setting $\ln \tilde{G} = L\tilde{\chi}(z, \epsilon_1, \epsilon_2, \epsilon_3)$ and $t_2 - t_1 = x$, $t_3 - t_2 = y$, one obtains

$$\left( \frac{\partial^3 \tilde{\chi}}{\partial \epsilon_1 \, \partial \epsilon_2 \, \partial \epsilon_3} \right)_{\epsilon_\alpha=0} = \iint_0^\infty dx \, dy \, \bar{\rho}_3(x, y; z)$$

$$\times \sum_{P_i} \exp\left[-\sigma_{P_1}x - \sigma_{P_2}y - \sigma_{P_3}(x + y)\right], \quad (24)$$

which is similar to Eq. (14).

One now associates again with the partition function (23), the corresponding integral equation, which is

$$\iiiint_{-\infty}^{+\infty} dy \, dy_1 \, dy_2 \, dy_3 \, K_0(\mathbf{x}, \mathbf{y})$$

$$\times \left[ \cosh\left( \sum_{\alpha=1}^3 x_\alpha \epsilon_\alpha^{\frac{1}{2}} \right) \cosh\left( \sum_{\alpha=1}^3 y_\alpha \epsilon_\alpha^{\frac{1}{2}} \right) \right]$$

$$\times \Psi(\mathbf{y}) = \Lambda \Psi(\mathbf{x}), \quad (25)$$

with $\mathbf{x} = (x, x_1, x_2, x_3)$, $\mathbf{y} = (y, y_1, y_2, y_3)$ and

$$K_0(\mathbf{x}, \mathbf{y}) = \left[ \frac{W(x)W(x_1)W(x_2)W(x_3)}{W(y)W(y_1)W(y_2)W(y_3)} \right]^{\frac{1}{2}}$$

$$\times \exp\left[\tfrac{1}{2}\nu^{\frac{1}{2}}(x + y)\right]$$

$$\times \int_{\delta}^\infty d\tau \, e^{-\tau}P_\gamma(x \mid y, \tau) \prod_{\alpha=1}^3 P_{\sigma_\alpha}(x_\alpha \mid y_\alpha, \tau), \quad (26)$$

which is similar to Eqs. (15) and (16). The appearance of the cosh functions instead of exponential functions is due to the summation over the $\mu_i$. The maximum eigenvalue $\Lambda_0(s, \epsilon_1, \epsilon_2, \epsilon_3)$ of Eq. (25) is again related to the function $\tilde{\chi}(z, \epsilon_1, \epsilon_2, \epsilon_3)$ by

$$\Lambda_0(s, \epsilon_1, \epsilon_2, \epsilon_3) = (1/z) \exp\left[\tfrac{1}{2}(\nu + \epsilon_1 + \epsilon_2 + \epsilon_3)\right], \quad (27)$$

with $s = \tilde{p}/kT = \tilde{\chi}(z, \epsilon_1, \epsilon_2, \epsilon_3)$, and to determine the left-hand side of Eq. (24) one must perform a perturbation calculation for $\Lambda_0$ up to first order in $\epsilon_1$, $\epsilon_2$ and $\epsilon_3$. This is now much more involved, and we refer to Appendix A for some of the details and the completion of the proof.

By introducing the *resolvent* $R_s(x, y; \rho)$ of the Kac integral equation, [Part I, Eq. (10)], the expressions (9a) and (9b) for the distribution functions can be transformed into

$$l \int_0^\infty dx \, e^{-\sigma x} \bar{n}_2(x; l) = \frac{1}{\lambda_0(s)} \iint_{-\infty}^{+\infty} dx \, dy \, \psi_0(x, s)$$

$$\times R_{s+\sigma}\left(x, y; \frac{1}{\lambda_0(s)}\right) \psi_0(y, s) \quad (28a)$$

$$l \iint_0^\infty dx \, dy \, e^{-\sigma x - \sigma' y} \bar{n}_3(x, y; l)$$

$$= \frac{1}{\lambda_0^2(s)} \iiint_{-\infty}^{+\infty} dx_1 \, dx_2 \, dx_3$$

$$\times \psi_0(x_1, s) R_{s+\sigma}\left(x_1, x_2; \frac{1}{\lambda_0(s)}\right)$$

$$\times R_{s+\sigma'}\left(x_2, x_3; \frac{1}{\lambda_0(s)}\right) \psi_0(x_3, s). \quad (28b)$$

The proof is simple. The resolvent is defined in terms of the iterated kernels by

$$R_s(x, y; \rho) = K_s(x, y) + \rho K_s^{(1)}(x, y)$$
$$+ \rho^2 K_s^{(2)}(x, y) + \cdots, \quad (29)$$

where

$$K_s^{(l)}(x, y) = \int_{-\infty}^{+\infty} dz \, K_s^{(l-1)}(x, z) K_s(z, y),$$

with $K_s^{(0)}(x, y) \equiv K_s(x, y)$. Since in terms of the eigenfunctions,

$$K_s^{(l)}(x, y) = \sum_{n=0}^\infty \lambda_n^{l+1}(s) \psi_n(x, s) \psi_n(y, s), \quad (30)$$

then Eq. (28a) and (28b) follow from (9a) and (9b)

by expanding the fractions in the latter equations in powers of $\lambda_n(s + \sigma)/\lambda_0(s)$, and performing the summations over $n$.

We conclude this section with some simple checks of the general formulas (9a) and (9b).

(a) For $\nu = 0$, i.e. for a gas of hard rods, the $\psi_n$ are independent of $s$, so that $\langle 0, s \mid n, s + \sigma \rangle = \delta_{n0}$, and $\lambda_0(s) = e^{-s\delta}/s$. Therefore Eq. (9a) gives

$$l \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2^{\text{h.c.}}(x; l) = \frac{1}{[1 + \sigma(l - \delta)]e^{\delta\sigma} - 1} , \quad (31)$$

using $s = p/kT = 1/(l - \delta)$. This is equivalent to a well-known result first derived by Zernike and Prins.[8]

(b) For $\nu = 0$, one obtains from Eq. (9b)

$$l \iint_0^\infty dx\, dy\, e^{-\sigma x - \sigma' y} \bar{n}_3^{\text{h.c.}}(x, y; l)$$

$$= l \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2^{\text{h.c.}}(x; l)$$

$$\cdot\, l \int_0^\infty dy\, e^{-\sigma' y} \bar{n}_2^{\text{h.c.}}(y; l), \quad (31a)$$

which is expected, since it is known[9] that Kirkwood's superposition principle is valid for one-dimensional systems with nearest-neighbor interaction.

(c) For large $x$, $\bar{n}_2(x; l) \to 1/l^2$, since

$$\lim_{x \to \infty} \bar{n}_2(x, l) = \lim_{\sigma \to 0} \sigma \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2(x, l)$$

$$= -\frac{1}{l} \frac{\lambda_0(s)}{\lambda_0'(s)} = \frac{1}{l^2} ,$$

using the fact that $\langle 0, s \mid n, s \rangle = \delta_{n0}$. In a similar way one proves that for large $y$

$$\lim_{y \to \infty} \int_0^\infty dx\, e^{-\sigma x} \bar{n}_3(x, y; l) = \frac{1}{l} \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2(x, l).$$

We have thus verified the product property for $\bar{n}_2$ and $\bar{n}_3$. It can also be shown that for large $l$, $\bar{n}_2$ and $\bar{n}_3$ approach the corresponding Boltzmann factor [see Eq. (8)], but we will leave the proof to the reader.

[8] The result of Zernike and Prins [Z. Physik. 41, 184 (1927)] can be written

$$n_2^{\text{h.c.}}(x; l) = \frac{1}{l} \sum_{k=1}^{\infty} S(x - k\delta) \frac{(x - k\delta)^{k-1}}{(l - \delta)^k (k - 1)!}$$

$$\times \exp\left[-\frac{x - k\delta}{l - \delta}\right],$$

where $S(y)$ is again the stepfunction. By taking the Laplace transform one obtains (31).

[9] Z. W. Salsburg, R. W. Zwanzig, and J. G. Kirkwood, J. Chem. Phys. 21, 1098 (1953). Compare also the discussion of one-dimensional systems by A. Munster (*Statistische Thermodynamik*, Sec. 8.8).

## III. THE FLUCTUATION AND VIRIAL THEOREMS

From the product property of the distribution functions $\bar{n}_s$ and $\bar{p}_s$, it follows that the corresponding *cluster functions*, defined by

$$\chi_1(\mathbf{r}_1; z) = \bar{p}_1(\mathbf{r}_1; z)$$

$$\chi_2(\mathbf{r}_1, \mathbf{r}_2; z) = \bar{p}_2(\mathbf{r}_1, \mathbf{r}_2; z) - \bar{p}_1(\mathbf{r}_1; z)\bar{p}_1(\mathbf{r}_2; z)$$

$$\chi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; z) = \bar{p}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; z) - \bar{p}_2(\mathbf{r}_1, \mathbf{r}_2; z)\bar{p}_1(\mathbf{r}_3; z)$$

$$- \bar{p}_2(\mathbf{r}_2, \mathbf{r}_3; z)\bar{p}_1(\mathbf{r}_1; z)$$

$$- \bar{p}_2(\mathbf{r}_3, \mathbf{r}_1; z)\bar{p}_1(\mathbf{r}_2; z)$$

$$+ 2\bar{p}_1(\mathbf{r}_1; z)\bar{p}_1(\mathbf{r}_2; z)\bar{p}_1(\mathbf{r}_3; z), \quad (32)$$

etc.,[10] have the *cluster property*, which means that for any configuration where the $s$ particles are divided in two or more noninteracting groups the $\chi_s(\mathbf{r}_1 \cdots \mathbf{r}_s; z)$ vanishes. As a consequence the integrals

$$\lim_{V \to \infty} \frac{1}{V} \int_V \cdots \int_V \chi_s(\mathbf{r}_1 \cdots \mathbf{r}_s; z)\, d\mathbf{r}_1 \cdots d\mathbf{r}_s \quad (33)$$

must have a thermodynamic meaning, and the results are the so-called fluctuation theorems. From the definitions of the $\bar{p}_s$ one easily finds[11]

[10] The general rule is as follows: Divide the $s$ particles in a number of groups and form the product of the functions $\bar{p}_l$ which depend on the particles in each group. Then $\chi_s$ will be the sum of products for all possible ways of division of the $s$ particles with the coefficient $(-1)^{k-1}(k - 1)!$, where $k$ is the number of groups into which the $s$ particles were divided. Similar formulas hold for the functions $\bar{n}_s$; one obtains the same functions $\chi_s$ except that $z$ must be expressed in $v$.

[11] There is the following difficulty: Eqs. (34 a & b) are derived, starting from the normalization condition

$$\int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_s\, \rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s; V, z) = \left\langle \frac{N!}{(N - s)!} \right\rangle_{\text{av}}$$

which follows from the definition of $\rho_s$. The average of $N!/(N - s)!$ over the grand canonical ensemble can be expressed in terms of $\bar{N}$ and its derivatives after the chemical potential $\mu$ and this then leads to the Eqs. (34 a & b). Now if one uses the *same* argument for the canonical distribution function $n_s(\mathbf{r}_1 \cdots \mathbf{r}_s; N, V)$, which is normalized according to

$$\int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_s\, n_s(\mathbf{r}_1 \cdots \mathbf{r}_s; N, V) = \frac{N!}{(N - s)!},$$

then one obtains a different answer because it is the averaging over $N$ which brings in the derivatives of the specific volume after the pressure. On the other hand, for a single-fluid phase, the limit functions $\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v)$ and $\bar{p}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; z)$ are identical and therefore also the cluster functions formed from them should be the same if one expresses $v$ in $z$ or vice versa. This paradox has often been discussed in the literature [see for instance J. C. Mayer, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1958) Vol. XII, p. 156)]. The mathematical reason for the apparent discrepancy must lie in the interchange of the two limiting processes which are required to derive Eqs. (34 a & b). Apparently this interchange is *not* allowed for the canonical distribution functions, although the exact reason is not clear to us.

$$\lim_{V \to \infty} \frac{1}{V} \iint_V d\mathbf{r}_1 \, d\mathbf{r}_2 \, \chi_2 = \frac{kT}{v} \frac{\partial}{\partial p}\left(\frac{1}{v}\right) - \frac{1}{v}, \quad (34a)$$

$$\lim_{V \to \infty} \frac{1}{V} \iiint_V d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 \, \chi_3 = \frac{k^2 T^2}{v} \frac{\partial}{\partial p}\left[\frac{1}{v} \frac{\partial}{\partial p}\left(\frac{1}{v}\right)\right]$$

$$- \frac{3kT}{v} \frac{\partial}{\partial p}\left(\frac{1}{v}\right) + \frac{2}{v}, \quad (34b)$$

etc.

These results can also be derived directly from the expressions (9a), and (9b) for the distribution functions. For instance from (9a), it follows that

$$\int_0^\infty dx \, e^{-\sigma x}\left[\bar{n}_2(x, l) - \frac{1}{l^2}\right] = -\frac{1}{\sigma l^2} - \frac{1}{l}$$

$$+ \frac{1}{l} \sum_{n=0}^\infty \frac{\lambda_0(s)}{\lambda_0(s) - \lambda_n(s + \sigma)} \langle 0, s \mid n, s + \sigma \rangle^2, \quad (35)$$

using the completeness relation (21). Now for $\sigma \to 0$, $\langle 0, s \mid n, s + \sigma \rangle \to 0$ for $n \neq 0$, and $\langle 0, s \mid 0, s + \sigma \rangle \to 1 + O(\sigma^2)$, which follows from the normalization condition. Therefore for $\sigma \to 0$ the right-hand side of (35) becomes

$$-\frac{1}{\sigma l^2} - \frac{1}{l} + \frac{\lambda_0(s)(1 + O(\sigma^2))}{-\sigma \lambda_0'(s) - \frac{1}{2}\sigma^2 \lambda_0''(s) - \cdots}$$

$$= -\frac{1}{l} - \frac{1}{2l^2} \frac{\lambda_0''(s)}{\lambda_0'(s)} = -\frac{1}{2l} - \frac{kT}{2l^3} \frac{\partial l}{\partial p},$$

using $l = -\lambda_0'/\lambda_0$, $s = p/kT$. Therefore

$$\lim_{L \to \infty} \frac{1}{L} \iint_L dt_1 \, dt_2 \, \chi_2$$

$$= 2 \int_0^\infty dx \left[\bar{n}_2(x; l) - \frac{1}{l^2}\right] = -\frac{1}{l} - \frac{kT}{l^3} \frac{\partial l}{\partial p}, \quad (36)$$

which is Eq. (34a). In a similar way one can verify Eq. (34b).

A second group of "thermodynamical" relations for the distribution functions follow from the fact that the Helmholtz free energy $\Psi = -kT \ln Z(V, T, N)$. This has as a consequence that the internal energy is given by

$$E = \Psi - T \frac{\partial \Psi}{\partial T} = \frac{3NkT}{2}$$

$$+ \frac{1}{2} \iint_V d\mathbf{r}_1 \, d\mathbf{r}_2 \, \varphi(|\mathbf{r}_1 - \mathbf{r}_2|) n_2(\mathbf{r}_1, \mathbf{r}_2; V, N), \quad (37)$$

and the pressure by[12]

[12] Following H. S. Green [Proc. Roy. Soc. (London) 189, 103 (1947)], the simplest way of deriving Eq. (38) is by assuming a cubical vessel of volume $V = L^3$. By setting $\mathbf{r}_i^* = \mathbf{r}_i/L$, the limits of integral in $\Psi$ then become independent of $L$ and one can carry out the differentiation after $V$ or $L$ under the integral signs.

$$p = -\frac{\partial \Psi}{\partial V} = \frac{NkT}{V}$$

$$- \frac{1}{6V} \iint_V d\mathbf{r}_1 \, d\mathbf{r}_2 \left(r_{12} \frac{d\varphi}{dr_{12}}\right) n_2(\mathbf{r}_1, \mathbf{r}_2; V, N), \quad (38)$$

which becomes, in the thermodynamic limit,

$$p = \frac{kT}{v} - \frac{1}{6} \int d\mathbf{r} \, r \frac{d\varphi}{dr} \, \bar{n}_2(r; v). \quad (39)$$

This is called the virial theorem, since it can also be derived directly from the virial theorem of Clausius. If the intermolecular potential $\varphi(r)$ contains a hard-sphere repulsion, then at $r = d = $ diameter of the sphere, $d\varphi/dr$ is not defined and (39) must be replaced by

$$p = \frac{kT}{v} + bkT\bar{n}_2(d^+; v)$$

$$- \frac{2}{3}\pi \int_d^\infty dr \, r^3 \frac{d\varphi_{\text{attr}}}{dr} \, \bar{n}_2(r; v), \quad (40)$$

where $b = \frac{2}{3}\pi d^3$ and $\bar{n}_2(d^+; v) = \lim_{r \to d} n_2(r; v)$. Note that the one-dimensional version of Eq. (40) is

$$p = \frac{kT}{l} + \delta kT n_2(\delta^+; l)$$

$$- \int_\delta^\infty dx \, x \frac{d\varphi_{\text{attr}}}{dx} \, \bar{n}_2(x; l), \quad (40a)$$

where $\delta$ is again the length of the hard rod.

By further differentiation after $T$ and $V$, one obtains from (37) and (38), thermodynamic relations involving the higher distribution functions. For instance, from (37) one gets for the specific heat per particle at constant volume, the general expression

$$c_v = \frac{3k}{2} + \frac{v}{2kT^2} \int d\mathbf{r} \, \varphi(r)\bigg\{\varphi(r)\bar{n}_2(r; v)$$

$$+ \int d\mathbf{r}_3 \, [\varphi(r_{13}) + \varphi(r_{23})]\bar{n}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; v)$$

$$+ \frac{1}{2} \iint d\mathbf{r}_3 \, d\mathbf{r}_4 \, [\bar{n}_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4; v)$$

$$- \bar{n}_2(\mathbf{r}_1, \mathbf{r}_2; v)\bar{n}_2(\mathbf{r}_3, \mathbf{r}_4; v)]\bigg\}.$$

The question arises as to the verification of these relations directly from the expressions (9) or (28) for the distribution functions, and here one encounters the following apparent difficulty. Since $\varphi_{\text{attr}} = -\alpha e^{-\gamma x}$, the integrals in (37) and (40a) involving $\bar{n}_2(x; l)$, are similar to the Laplace transform of $\bar{n}_2(x; l)$, if $\sigma$ is made equal to $\gamma$. However, according to (9a), the Laplace transform of $\bar{n}_2(x; l)$

depends on *all* the eigenvalues and eigenfunctions of the Kac equation, while according to (37) [which for our model becomes ($\epsilon = E/N$)],

$$\epsilon = \frac{kT}{2} - \alpha l \int_\delta^\infty dx \, e^{-\gamma x} \bar{n}_2(x; l); \qquad (41)$$

the Laplace transform for $\sigma = \gamma$ has thermodynamic meaning and therefore can depend only on the maximum eigenvalue $\lambda_0$. The reason for the remarkable simplification occurring when $\sigma = \gamma$ becomes clear if we go back to the derivation of Eq. (9a). Clearly, if $\sigma = \gamma$, the device of adding the exponential attraction $\epsilon e^{-\sigma x}$ amounts to increasing the strength of the real attractive potential from $\nu$ to $\nu + \epsilon$. Equations (14) and (17) are still valid, but the associated integral equation is now almost exactly like the Kac equation, except that $\nu$ is replaced by $\nu + \epsilon$. The kernel, developed in powers of $\epsilon$ is therefore

$$K_s(x, y, \epsilon) = K_s(x, y)[1 + (\epsilon/4\nu^{\frac{1}{2}})(x + y) + \cdots],$$

and performing the perturbation calculation one now finds

$$\Lambda_0(s, \epsilon) = \lambda_0(s) + \epsilon\lambda_0^{(1)}(s) + \cdots ,$$

with

$$\lambda_0^{(1)}(s) = \frac{\lambda_0(s)}{2\nu^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx \, x\psi_0^2(x).$$

From the analog of (22) one therefore obtains instead of (9a), the equation

$$l \int_0^\infty dx \, e^{-\gamma x} \bar{n}_2(x; l) = \frac{1}{2\nu^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx \, x\psi_0^2(x) - \frac{1}{2}. \quad (42)$$

It is easy to verify that this equation is equivalent to (41). In fact, since in terms of the chemical potential,

$$\epsilon = \mu - T(\partial\mu/\partial T) - p(\partial\mu/\partial p),$$

and since [see Part I, Eqs. (18), (19)]

$$\mu = kT \ln (\Lambda z),$$

$$\ln \lambda_0(s, \nu) = \tfrac{1}{2}\nu - \ln z,$$

one finds

$$\epsilon/kT = \tfrac{1}{2}\nu - (\nu/\lambda_0)(\partial\lambda_0/\partial\nu)_s + \tfrac{1}{2},$$

which, together with

$$\frac{\partial\lambda_0}{\partial\nu} = \iint_{-\infty}^{+\infty} dx \, dy \, \frac{\partial K_s(x, y)}{\partial\nu} \, \psi_0(x)\psi_0(y)$$

$$= \frac{\lambda_0}{2\nu^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx \, x\psi_0^2(x),$$

reduces (41) to (42).

The virial theorem (39a) can be verified in a similar manner. We omit the details, because in a way these verifications are simply a rearrangement of the general thermodynamic argument. The question remains how to derive the basic identities like Eq. (42), which can also be written in the form

$$\frac{\lambda_0(s)}{2\nu^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx \, x\psi_0^2(x, s) - \frac{\lambda_0(s)}{2}$$

$$= \iint_{-\infty}^{+\infty} dx \, dy \, \psi_0(x, s)\psi_0(y, s)R_{s+\gamma}\left(x, y; \frac{1}{\lambda_0(s)}\right),$$

directly from the Kac integral equation. Such a derivation is given in Appendix B.

## IV. THE VAN DER WAALS LIMIT OF THE TWO-POINT DISTRIBUTION FUNCTION; THE SHORT-RANGE BEHAVIOR

To investigate in the range $x$ of order $\delta$, the behavior of $\bar{n}_2(x; l)$ in the van der Waals limit, i.e. for $\gamma \to 0$ after setting $\nu = \nu_0\gamma$, it is simplest to start from Eq. (28a). The first step is to "tame" the kernel $K_{s+\sigma}(x, y)$ as in Part I, Sec. III, by the substitution

$$x = x' + \eta(2/\gamma)^{\frac{1}{2}}, \qquad y = y' + \eta(2/\gamma)^{\frac{1}{2}},$$

where $\eta(s)$ is determined by Eq. (29) in Part I. The contribution of the first term of the resolvent series (29), to Eq. (28a) then becomes

$$\frac{1}{\lambda_0(s)} \iint dx' \, dy' \, h(x')h(y')\left[\frac{W(x')}{W(y')}\right]^{\frac{1}{2}} \cdot \int_\delta^\infty d\tau \, e^{-(s+\sigma)\tau}$$

$$\times P_\gamma(x' \mid y', \tau) \exp \{\tfrac{1}{2}(\nu_0\gamma)^{\frac{1}{2}}(x' + y' + 2\eta[2/\gamma]^{\frac{1}{2}})$$

$$- [\eta^2/\gamma + \eta(x' + y')/(2\gamma)^{\frac{1}{2}}] \tanh (\tfrac{1}{2}\gamma\tau)\},$$

where $h(x')$ is defined by Eq. (34) in Part I. One must now substitute the expansions (36) in Part I, for $h(x')$ and $\lambda_0(s)$, and expand everything in powers of $\gamma$. Because of the taming, the zeroth approximation is very simple, since for $\gamma \to 0$, $P_\gamma(x' \mid y', \tau \to \delta(x' - y')$, and since $h^{(0)}(x')$ is normalized to unity, one obtains for $\gamma \to 0$,

$$\frac{e^{\eta(2\nu_0)^{\frac{1}{2}}}}{\omega(s)} \int_\delta^\infty d\tau \, \exp [-(s + \sigma)\tau - \tfrac{1}{2}\eta^2\tau]$$

$$= \frac{\exp [\eta(2\nu_0)^{\frac{1}{2}} - (s + \sigma + \tfrac{1}{2}\eta^2)\delta]}{\omega(s)(s + \sigma + \tfrac{1}{2}\eta^2)} \equiv \frac{A}{\omega(s)}, \quad (43)$$

or one can say that for $\gamma \to 0$, $K_{s+\sigma}(x, y)$ can be replaced by $A\delta(x' - y') = A\delta(x - y)$ where $A$ is defined by (43). Hence $K_{s+\sigma}^{(2)}(x, y) \to A^2\delta(x - y)$, etc., and one obtains

$$l \int_0^\infty dx \, e^{-\sigma x} \bar{n}_2(x; l)$$

$$= \frac{A}{\omega} + \frac{A^2}{\omega^2} + \frac{A^3}{\omega^3} + \cdots = \frac{1}{[1 + \sigma(l - \delta)]e^{\sigma\delta} - 1},$$

using $s + (\frac{1}{2}\eta^2) = 1/(l - \delta)$ which follows from I, Eqs. (30) and (31).

In zeroth approximation, one obtains therefore, exactly the same result as for a gas of hard rods [see Eq. (31)]. This would of course be expected, since for small $\gamma$, the attractive force at distances of order $\delta$ is very weak and, in zeroth approximation, will not affect the arrangement of the molecules, which arrangement will be determined only by the repulsive core.

In the first approximation, the attractive force will have an influence even at distances of order $\delta$. To calculate this effect, one must collect all terms of order $\gamma$ in the resolvent series. One then finds

$$l \int_0^\infty dx \, e^{-\sigma x} \bar{n}_2(x, l) = \frac{1}{[1 + \sigma(l - \delta)]e^{\sigma\delta} - 1}$$

$$+ \frac{\gamma v_0 (l - \delta)^4}{lB} \frac{\sigma^2 e^{2\sigma\delta}}{\{[1 + \sigma(l - \delta)]e^{\sigma\delta} - 1\}^3} + \cdots. \quad (44)$$

See Appendix C for some of the details of the lengthy calculation. The results derived in Part I, Sec. III must be used.

As mentioned previously in the introduction, it is interesting to check these results with the virial theorem in the form of Eq. (40a). To do this, one must find $\bar{n}_2(\delta^+; l)$ from Eq. (44). Multiply both sides of (44) by $\sigma e^{\sigma\delta}$ and then go to the limit $\sigma \to \infty$. The left-hand side, (with $x' = x - \delta$) becomes

$$\lim_{\sigma \to \infty} \sigma \int_0^\infty dx' \, e^{-\sigma x'} \bar{n}_2(x' + \delta; l)$$

$$\cong \bar{n}_2(\delta^+; l)\sigma \int_0^\infty dx' \, e^{-\sigma x'} = \bar{n}_2(\delta^+; l),$$

and by calculating the limit of the right-hand side, one obtains

$$\bar{n}_2(\delta^+; l) = 1/l(l - \delta) + \gamma v_0(l - \delta)/l^2 B + \cdots. \quad (45)$$

Consider first the zeroth approximation, and substitute in (40a). One obtains

$$\frac{p}{kT} = \frac{1}{l - \delta} - v_0 \gamma^2 \int_\delta^\infty dx \, x \, e^{-\gamma x} \bar{n}_2(x, l),$$

If we introduce $\gamma x = x'$ into the integral, then since in the limit $\gamma \to 0$, $\bar{n}_2(x'/\gamma; l) = 1/l^2$, the integral becomes

$$-\frac{v_0}{l^2} \int_0^\infty dx' \, x' e^{-x'} = -\frac{v_0}{l^2},$$

so that the van der Waals equation is obtained once more. The second term in (45) leads to a part of the correction to the van der Waals equation of order $\gamma$ mentioned at the end of Part I, Sec. IV. For the complete correction, one must know also the $\gamma$ correction to the long-range behavior of $n_2(x; l)$, and this is also needed to resolve the difficulty of the apparent *nonagreement* of the fluctuation theorem [Eq. (36)] and the first term of (44) with van der Waals' equation. In fact, from the first term of (44) one finds

$$\int_0^\infty dx \left[ \bar{n}_2(x; l) - \frac{1}{l^2} \right] = -\frac{1}{2l} + \frac{(l - \delta)^2}{2l^3}, \quad (46)$$

which agrees with (36) if $p/kT = 1/(l - \delta)$. We shall see that the long-range behavior of $\bar{n}_2(x; l)$, which is of order $\gamma$, gives in the fluctuation integral, a zeroth-order contribution, which brings Eq. (36) into agreement with the van der Waals equation.

## V. THE VAN DER WAALS LIMIT OF THE TWO-POINT DISTRIBUTION FUNCTION; THE LONG-RANGE BEHAVIOR

To determine the behavior of $\bar{n}_2(x; l)$ for $x$ of order $1/\gamma$, we use Eq. (9a) for $\bar{n}_2(x; l)$. Replace $\sigma$ by $\sigma\gamma$ and then expand the right-hand side in powers of $\gamma$. First consider the matrix element

$$\langle 0, s \mid n, s + \sigma\gamma \rangle$$

$$= \int_{-\infty}^{+\infty} dx \, \psi_0(x, s, \gamma)\psi_n(x, s + \sigma\gamma, \gamma). \quad (47)$$

With $x = x' + \eta(s)(2/\gamma)^{\frac{1}{2}}$, we know that

$$\psi(x, s, \gamma) \equiv h(x', s, \gamma)$$

$$= h^{(0)}(x', s) + \gamma^{\frac{1}{2}} h^{(1)}(x', s) + \cdots,$$

where the $h^{(k)}(x', s)$ are determined in Part I, Sec. III. Therefore,

$$\psi_n(x, s + \sigma\gamma, \gamma)$$

$$= h_n(x - \eta(s + \sigma\gamma)(2/\gamma)^{\frac{1}{2}}, s + \sigma\gamma, \gamma)$$

$$= h_n^{(0)}(x', s) + \gamma^{\frac{1}{2}}$$

$$\times \left[ h_n^{(1)}(x', s) - 2^{\frac{1}{2}}\sigma \frac{d\eta}{ds} \frac{\partial h_n^{(0)}(x', s)}{\partial x'} \right] + O(\gamma).$$

Since $h_n^{(1)}$ is orthogonal to $h_0^{(0)}$ for $n > 0$, then for $n > 0$ [using Eqs. (38) and (39) in Part I], one finds

$$\langle 0, s \mid n, s + \sigma\gamma \rangle = -\sigma \left( \frac{\gamma B}{2l} \right)^{\frac{1}{2}} \frac{d\eta}{ds} \delta_{n1} + O(\gamma). \quad (48)$$

For $n = 0$, one obtains

$$\langle 0, s \mid 0, s + \sigma\gamma \rangle = 1 - \sigma^2 \frac{\gamma B}{4l} \left( \frac{d\eta}{ds} \right)^2 + O(\gamma^{\frac{3}{2}}). \quad (49)$$

Note that (48) and (49) are consistent up to order $\gamma$ with the completeness requirement

$$\sum_{n=0}^{\infty} \langle 0, s \mid n, s + \sigma\gamma \rangle^2 = 1.$$

Next we consider the eigenvalues. We know that

$$\lambda_n(s, \gamma) = \omega(s)[1 + \gamma\mu_n^{(1)}(s) + O(\gamma^2)], \qquad (50)$$

where $\mu_n^{(1)}$ is given by Eq. (39) in Part I. Therefore,

$$\lambda_n(s + \sigma\gamma, \gamma) = \omega(s)$$
$$\times \left\{ 1 + \gamma\left[ \sigma\frac{\omega'(s)}{\omega(s)} + \mu_n^{(1)}(s) \right] + O(\gamma^2) \right\}. \quad (51)$$

Using all this one obtains from Eq. (9a),

$$l\int_0^\infty dx\, e^{-\sigma\gamma x}\bar{n}_2(x; l) = -\frac{\omega}{\gamma\sigma\omega'} - 1$$
$$+ \frac{\omega}{\sigma\omega'}\left[ \frac{\sigma}{2}\frac{\omega''}{\omega'} + \frac{\omega}{\omega'}\frac{d\mu_0^{(1)}}{ds} \right] + \frac{\sigma^2 B}{2l}\left(\frac{d\eta}{ds}\right)^2$$
$$\times \left[ \frac{\omega}{\sigma\omega'} + \frac{1}{-\sigma(\omega'/\omega) + \mu_0^{(1)} - \mu_1^{(1)}} \right] + \cdots . \quad (52)$$

Now there is the following complication: One would be inclined to replace $\omega'(s)/\omega(s)$ by $(-l)$ according to Part I, Eq. (31), but this is *not* correct. The expansion of the eigenfunctions and eigenvalues was done at constant $s$, while the Laplace transform of $\bar{n}_2(x; l)$ is taken for a fixed value of $l = -\lambda_0'(s)/\lambda_0(s)$. Since $\lambda_0(s)$ and $\omega(s)$ differ by a quantity of order $\gamma$ [see Eq. (50)], one has

$$-l = \frac{\lambda_0'(s)}{\lambda_0(s)} = \frac{\omega'}{\omega}\left[ 1 + \gamma\frac{\omega}{\omega'}\frac{d\mu_0^{(1)}}{ds} + \cdots \right],$$

and so up to order $\gamma$,

$$\frac{\omega'}{\omega} = -l\left[ 1 + \frac{\gamma}{l}\frac{d\mu_0^{(1)}}{ds} \right]. \qquad (53)$$

This $\gamma$ correction must be taken into account in the first term in Eq. (52), but can of course be neglected in the other terms. Since in zeroth order

$$\frac{\omega''}{\omega'} = -l + \frac{1}{l}\frac{\partial l}{\partial s} = -l - \frac{l(l - \delta)^2}{B^2}$$

$$\eta(s) = \frac{(2\nu_0)^{\frac{1}{2}}}{l}; \qquad \left(\frac{d\eta}{ds}\right)^2 = \frac{2\nu_0(l - \delta)^4}{B^4}$$

$$\mu_0^{(1)} - \mu_1^{(1)} = B; \qquad l^2 - B^2 = \frac{2\nu_0(l - \delta)^2}{l},$$

one can simplify (52) to

$$\int_0^\infty dx\, e^{-\sigma\gamma x}\bar{n}_2(x; l) = \frac{1}{\gamma\sigma l^2} - \frac{1}{2l}$$
$$+ \frac{(l - \delta)^2}{2l^3} + \frac{\nu_0(l - \delta)^4}{l^4 B}\cdot\frac{1}{B + \sigma l}.$$

Since for a gas of hard rods one finds [see Eq. (46)], up to zeroth order in $\gamma$,

$$\int_0^\infty dx\, e^{-\sigma\gamma x}\bar{n}_2^{\text{h.c.}}(x; l) = \frac{1}{\gamma\sigma l} - \frac{1}{2l} + \frac{(l - \delta)^2}{2l^3},$$

one obtains

$$\int_0^\infty dx\, e^{-\sigma\gamma x}[\bar{n}_2(x; l) - \bar{n}_2^{\text{h.c.}}(x; l)]$$
$$= \frac{\nu_0(l - \delta)^4}{l^4 B}\cdot\frac{1}{B + \sigma l}.$$

Hence by inverting the Laplace transform one concludes

$$\bar{n}_2(x; l) = \bar{n}_2^{\text{h.c.}}(x; l)$$
$$+ \gamma\frac{\nu_0(l - \delta)^4}{l^5 B}\exp\left[-(B/l)\gamma x\right]. \qquad (54)$$

This holds for $x$ of order $1/\gamma$, so that $\bar{n}_2^{\text{h.r.}}(x; l)$ should be replaced by $1/l^2$. However in the form (54), it can be seen that our result connects with the short-range expression (44) derived in the previous section, since from (44) follows that for $\sigma \to 0$,

$$\int_0^\infty dx\, e^{-\sigma x}\bar{n}_2(x, l) = \frac{1}{\sigma}\left[ \frac{1}{l^2} + \frac{\gamma\nu_0(l - \delta)^4}{l^5 B} \right] + \cdots ,$$

so that for $x \to \infty$, we obtain

$$\bar{n}_2(x; l) = \frac{1}{l^2} + \frac{\gamma\nu_0(l - \delta)^4}{l^5 B},$$

and the second term is just the amplitude of the long-range exponential decay in (54). Note also that if one substitutes (54) into the fluctuation theorem (36), one obtains [using (46)]

$$\int_0^\infty dx\left[ \bar{n}_2(x, l) - \frac{1}{l^2} \right] = -\frac{1}{2l} + \frac{(l - \delta)^2}{2l^3}$$
$$+ \frac{\nu_0(l - \delta)^4}{l^4 B^2} = -\frac{1}{2l} + \frac{(l - \delta)^2}{2lB^2},$$

as is expected since according to the van der Waals equation

$$-\frac{kT}{2l^3}\frac{\partial l}{\partial p} = -\frac{1}{2l^3}\frac{\partial l}{\partial s} = \frac{(l - \delta)^2}{2lB^2}.$$

It is also easy to verify that, (54) together with (45) substituted into the virial theorem (40a), gives the complete $\gamma$ correction to the van der Waals equation.

We have also calculated the terms of order $\gamma^2$ in the long-range behavior of $\bar{n}_2(x; l)$. Because the calculation is straightforward although very lengthy, we will record only the result since it is needed in Part III of this series. Call the inverse Laplace transform of the right-hand side of Eq. (44) $\bar{n}_2(x; l)_{\text{short range}}$, which consists therefore of $\bar{n}_2^{\text{h.r.}}(x; l)$ plus the first correction due to the attractive force. Then we find

$$\bar{n}_2(x; l) = \bar{n}_2(x; l)_{\text{short range}} + \frac{\gamma v_0 (l - \delta)^4}{l^5 B} (e^{-B\gamma x/l} - 1)$$

$$+ \frac{v_0^3 (l - \delta)^8}{l^8 B^5} \left[ -\delta(2l - 3\delta) + \frac{2}{3} \frac{v_0 (l - \delta)^2}{l} \right] \gamma^3 \, x e^{-B\gamma x/l} - \frac{2v_0^2 (l - \delta)^6}{l^4 B^6}$$

$$\times \left[ \delta(2l - 3) - \frac{v_0 (l - \delta)^2 (4l^2 + 18l\delta - 27\delta^2)}{6l^3} + \frac{v_0^2 (l - \delta)^4 (11l^2 - 12l\delta + 18\delta^2)}{9l^6} \right] \gamma^2 e^{-B\gamma x/l}$$

$$+ \frac{v_0^2 (l - \delta)^6 (l - 3\delta)^2}{2l^4 B^6} \left\{ 1 - \frac{8v_0 (l - \delta)^2}{3l^2} \right\}^2 \gamma^2 e^{-2B\gamma x/l}. \qquad (55)$$

As a check, one can place this expression in the fluctuation integral, and obtain the expected result with $\partial l / \partial p$ computed from the van der Waals equation, plus the correction of order $\gamma$. The most interesting feature of (55) is the appearance of the exponential with half the range of the exponential occurring in first approximation.[13]

## VI. THE DISTRIBUTION FUNCTIONS IN THE TWO-PHASE REGION

Since at the condensation value $\bar{z}$ of the fugacity $z$, the specific volume $v$ is a discontinuous function of $z$, all the grand canonical distribution functions $\bar{\rho}_s(\mathbf{r}_1 \cdots \mathbf{r}_s, z)$ are discontinuously changing from $\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v_1)$ to $\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v_2)$, where $v_1$ and $v_2$ are the specific volumes of the saturated vapor and liquid. In the condensation region, the functions $\bar{\rho}_s$ therefore lose their meaning, but we can still ask for the meaning of the canonical distribution functions $\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v)$. Following Mayer, we assert that for any finite $s$, one should expect

$$\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v) = (1/v)[\xi_1 v_1 \bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v_1)$$
$$+ \xi_2 v_2 \bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v_2)], \qquad (56)$$

where $\xi_1$ and $\xi_2$ are the mole fractions of the vapor and the liquid phase, so that $v = \xi_1 v_1 + \xi_2 v_2$. The reason is that Eq. (56) expresses the geometrical

separation of the two phases because of the following argument: Physically, since there is no outside force field, one must expect that in the equilibrium state the condensed phase is in the form of a large sphere surrounded by the vapor phase and that the position of the sphere is purely random. Of course, since we are discussing the thermodynamic limit exclusive of surface phenomena, this cannot be proved in detail, but one might expect that all results are in harmony with this picture. This is the case if the $\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v)$ fulfill Eq. (56). The first factor $(1/v)$ in (56) is the probability per unit volume of finding one particle say at $\mathbf{r}_1$; it is independent of whether the particle is in the liquid or vapor phase because the position of the large liquid sphere is random. However *if* the first particle is in the liquid or vapor phase, then all remaining $(s - 1)$ particles will be in the same phase, because the chance that some of them are in the other phase will be proportional to the ratio of surface to volume of the liquid sphere and is therefore negligible in the thermodynamic limit. Since $v_1 \bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v_1)$ and $v_2 \bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v_2)$ are the conditional probabilities to find $(s - 1)$ particles in phase 1 and 2 if the first particle is in the same phase, and since $\xi_1$ and $\xi_2$ are the *a priori* probabilities to find the first particle in phase 1 or 2, this accounts for the second factor in Eq. (56).

Several points should be noted:

(a) The $\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v)$ are still spatially homogeneous, although there are two phases. This is clearly again due to the fact that the position of the liquid sphere is random.

(b) The $\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v)$ do *not* have the product property. The presence of the two phases produce correlations even when the particles are far apart. In particular,

$$\bar{n}_2(\mathbf{r}_1, \mathbf{r}_2; v) \rightarrow \frac{1}{v} \left( \frac{\xi_1}{v_1} + \frac{\xi_2}{v_2} \right)$$

if the two particles are far apart, and since

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[13] We have also calculated from Eq. (28b), the long-range behavior of the three-particle distribution function. Up to order $\gamma$ one finds

$$\bar{n}_3(x, y; l) = \bar{n}_3^{\text{h.c.}}(x, y; l)$$

$$+ \frac{\gamma v (l - \delta)^4}{l^5 B} \left\{ \exp\left[ -\frac{B}{l} \gamma(x + y) \right] \right.$$

$$\left. + \exp\left[ -\frac{B}{l} \gamma x \right] + \exp\left[ -\frac{B}{l} \gamma y \right] \right\}.$$

In the far range we have therefore up to $O(\gamma)$ the superposition principle

$$\bar{n}_3(t_1, t_2, t_3; l) = l^3 \bar{n}_2(t_1, t_2; l) \bar{n}_2(t_1, t_3; l) \bar{n}_2(t_2, t_3; l),$$

which should be contrasted with the form of the superposition principle for the hard core given by Eq. (31a).

$$\frac{1}{v}\left(\frac{\xi_1}{v_1} + \frac{\xi_2}{v_2}\right) - \frac{1}{v^2} = \frac{\xi_1\xi_2(v_2 - v_1)^2}{v^2 v_1 v_2} > 0,$$

the fluctuation integral will go to infinity, which is in accord with the constant vapor pressure.

(c) If one substitutes (56) for $s = 2$ into the virial theorem [Eq. (39)], then since

$$\frac{1}{6}\int d\mathbf{r}\, r\, \frac{d\varphi}{dr}\, \bar{n}_2(r; v)$$

$$= \frac{1}{6v}\int d\mathbf{r}\, r\, \frac{d\varphi}{dr}\, [\xi_1 v_1 \bar{n}_2(r; v_1) + \xi_2 v_2 \bar{n}_2(r; v_2)]$$

$$= \frac{\xi_1 v_1}{v}\left(\frac{kT}{v_1} - p_s\right) + \frac{\xi_2 v_2}{v}\left(\frac{kT}{v_2} - p_s\right)$$

$$= \frac{kT}{v} - p_s,$$

using the virial theorem for each of the two phases separately, one obtains that the pressure $p$ is really constant and equal to $p_s$.

Thus far, all these general statements are of course not really proved. It is therefore of great interest that for our one-dimensional model, the relations (56) follow strictly in the van der Waals limit. This can easily be seen from Eqs. (28a) and (28b). We know from Part I, Sec. IV, that in the two-phase region, the maximum eigenvalue in the van der Waals limit is doubly degenerate and that the two eigenfunctions for small $\gamma\delta$ do not overlap. Since we also showed that corresponding to a given $l = \xi_1 l_1 + \xi_2 l_2$, the eigenfunction is given by

$$\psi_0(x; l) = \xi_1^{\frac{1}{2}}\psi_0(x; l_1) + \xi_2^{\frac{1}{2}}\psi_0(x; l_2),$$

one immediately sees from (28a) and (28b) that $\bar{n}_2(x; l)$ and $\bar{n}_3(x, y; l)$ fulfill the one-dimensional form of Eq. (56) for $s = 2$ and $s = 3$. Equations (28a) and (28b) are so obviously generalizable that there is little doubt that Eq. (56) also holds for arbitrary $s$.

## VII. THE RELATION TO THE ORNSTEIN–ZERNIKE THEORY

To show the connection between our results and the Ornstein–Zernike theory, we will first present the one-dimensional version of this theory. We start with an integral equation connecting the correlation function $g(t_1, t_2)$ defined by

$$g(t_1, t_2) \equiv g(x) = l[\bar{n}_2(x; l) - 1/l^2], \qquad (57)$$

with the so-called direct correlation function $c(t_1, t_2) \equiv c(x)$. Both functions depend only on the absolute value of the distance $x = t_2 - t_1$ between the two particles at $t_1$ and $t_2$, and in the one phase

region they both go to zero for $x \to \infty$. The equation is:

$$g(t_1, t_2) = c(t_1, t_2) + \int_{-\infty}^{+\infty} dt_3\, g(t_1, t_3)c(t_3, t_2), \qquad (58)$$

and to make it plausible one can argue as follows: The correlation in position of two particles is in the first instance caused by the direct interaction between the two molecules and this is expressed by the term $c(t_1, t_2)$. In addition, there is an indirect effect through the action of a third particle in the neighborhood of the two particles, and this is described by the second term in (58). We do not try to give a formal derivation of (58).[14] From the way in which Eq. (58) is used, it seems clear that it is valid only in some asymptotic sense and for long-range attractive forces. Note that one can write (58) in the form:

$$g(x) = c(x) + \int_{-\infty}^{+\infty} dy\, g(x - y)c(y), \qquad (58a)$$

which implies that for the Fourier transforms, one has the simple relation

$$\tilde{g}(k) = \tilde{c}(k) + \tilde{g}(k)\tilde{c}(k). \qquad (59)$$

We now observe that near the critical point the range of $g(x)$ is magnified because of the small compressibility of the gas. This follows from the fluctuation theorem, which gives

$$\int_{-\infty}^{+\infty} dx\, g(x) = \tilde{g}(0) = -1 - \frac{kT}{l^2}\left(\frac{\partial l}{\partial p}\right)_T. \qquad (60)$$

However the range of the direct correlation function $c(x)$ should *not* increase near the critical point since it is determined by the attractive force. This is confirmed by the relation

$$\int_{-\infty}^{+\infty} c(x)\, dx = \tilde{c}(0) = \frac{\tilde{g}(0)}{1 + \tilde{g}(0)}$$

$$= 1 + \frac{l^2}{kT}\left(\frac{\partial p}{\partial l}\right)_T, \qquad (61)$$

which follows from (59) and (60).

In the critical region, therefore, Ornstein and Zernike develop in Eq. (58a), $g(x - y)$ in powers of $y$ up to $y^2$. Since in the range we are concerned with $g(x) \gg c(x)$, one can neglect $c(x)$, and using the fact that $c(x) = c(-x)$, one obtains the differential equation

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[14] In a second paper, ("Statistical Thermodynamics of Non-Uniform Fluids" (Preprint) (to be published), J. L. Lebowitz and J. K. Percus have given a formal derivation of the Ornstein–Zernike equation (58) which they claim to be exact. However, at present it is not yet clear whether this leads to a successive approximation method which would start with Eq. (69) as first approximation.

$$d^2g/dx^2 - \kappa^2 g = 0, \qquad (62)$$

with

$$\kappa^2 = \frac{2\left[1 - \int_{-\infty}^{+\infty} dy\, c(y)\right]}{\int_{-\infty}^{+\infty} dy\, y^2 c(y)} = \frac{-\left(\frac{2l^2}{kT}\right)\left(\frac{\partial p}{\partial l}\right)_T}{\int_{-\infty}^{+\infty} dy\, y^2 c(y)}, \qquad (63)$$

which has the solution [using (60)]

$$g(x) = \kappa\left(-\frac{kT}{2l^2}\frac{\partial l}{\partial p}\right) e^{-\kappa x}. \qquad (64)$$

This can now be compared with the long-range behavior of $\bar{n}_2(x; l)$ discussed in Sec. VI. Clearly, the first approximation (54), agrees with (64) both in form and in the dependence on the compressibility $\partial p/\partial l$. Since $\kappa$ depends on the unknown function $c(x)$, we cannot proceed further. However, as Lebowitz and Percus (see reference 7) have pointed out, one can analyze the Ornstein–Zernike equation (58a) in more detail by using the basic ideas of the theory of van der Waals. In the first place, it is clear that for large $x$, $c(x)$ should be proportional to the potential of the attractive force $\varphi(x)$, and that only for $x$ close to zero will $c(x)$ deviate from $\varphi(x)$ due to the hard core. Then, since according to van der Waals the equation of state has the form

$$p = p^{\text{b.c.}} - \alpha_0/l^2 \qquad (65)$$

with

$$\alpha_0 = -\int_0^\infty dx\, \varphi(x) = -\tfrac{1}{2}\tilde{\varphi}(0),$$

and since $\tilde{c}(0)$ has to fulfill Eq. (61), a very plausible ansatz for $\tilde{c}(k)$ is

$$\tilde{c}(k) = \tilde{c}^{\text{b.c.}}(0) - \tilde{\varphi}(k)/lkT, \qquad (66)$$

with

$$\tilde{c}^{\text{b.c.}}(0) = 1 + (l^2/kT)(\partial p^{\text{b.c.}}/\partial l). \qquad (67)$$

From Eq. (66), we obtain $\tilde{g}(k)$ by (59), and if we now define the long-range behavior of $\tilde{g}(k)$ by

$$\tilde{g}^{\text{l.r.}}(k) = \tilde{g}(k) - \tilde{g}^{\text{b.c.}}(0), \qquad (68)$$

where

$$\tilde{g}^{\text{b.c.}}(0) = \tilde{c}^{\text{b.c.}}(0)/[1 - \tilde{c}^{\text{b.c.}}(0)],$$

one finds

$$\tilde{g}^{\text{l.r.}}(k) = \frac{lkT}{\tilde{\varphi}(0) + l^3(\partial p/\partial l)}$$
$$\times \frac{\tilde{\varphi}(k)}{\tilde{\varphi}(k) - \tilde{\varphi}(0) - l^3(\partial p/\partial l)}, \qquad (69)$$

which is the result of Lebowitz and Percus. It is easy to verify that for our model, where

$$\varphi(x) = -\alpha_0 e^{-\gamma|x|}; \qquad \tilde{\varphi}(k) = -2\alpha_0\gamma/(\gamma^2 + k^2),$$

one obtains from (69) *exactly* the first approximation to the long-range behavior of $\bar{n}_2(x, l)$ derived in Sec. V. *For low density*, $l^3(\partial p/\partial l) \cong -lkT$ is very large, and Eq. (69) therefore becomes

$$\tilde{g}^{\text{l.r.}}(k) \cong -\tilde{\varphi}(k)/lkT,$$

which is in agreement with the expected result

$$\bar{n}_2(x, l) \cong \frac{1}{l^2} e^{-\varphi(x)/kT} \cong \frac{1}{l^2}\left[1 - \frac{\varphi(x)}{kT}\right]. \qquad (70)$$

*Near the critical point* $\partial p/\partial l$ is very small, and Eq. (69) can then be approximated for small $k$ by

$$\tilde{g}^{\text{l.r.}}(k) \cong lkT/[\tfrac{1}{2}\tilde{\varphi}''(0)k^2 - l^3(\partial p/\partial l)]$$

which gives

$$\tilde{g}^{\text{l.r.}}(x) \cong \frac{lkT}{2R}\left(-2\alpha_0 l^3 \frac{\partial p}{\partial l}\right)^{-\frac{1}{2}}$$
$$\times \exp\left[-\frac{x}{R}\left(-\frac{l^3}{2\alpha_0}\frac{\partial p}{\partial l}\right)^{\frac{1}{2}}\right], \qquad (71)$$

where $R$ is defined by

$$R^2 = \frac{\tfrac{1}{2}\int_{-\infty}^{+\infty} x^2\varphi(x)\, dx}{\int_{-\infty}^{+\infty} dx\, \varphi(x)} = \frac{\tilde{\varphi}''(0)}{4\alpha_0}. \qquad (72)$$

This has precisely the same form as the Ornstein–Zernike result (64) except that now the range $1/\kappa$ is expressed in the intermolecular potential. In fact (64) becomes (71) by setting

$$\kappa = \frac{1}{R}\left(-\frac{l^3}{2\alpha_0}\frac{\partial p}{\partial l}\right)^{\frac{1}{2}}. \qquad (73)$$

We believe that Eq. (69) is an exact result in the sense that it gives the long-range behavior of the correlation function in first approximation for *any* long-range potential, and for the whole range of density from the ideal gas to the critical region. We are able to confirm this belief by generalizing the discussion in Sec. V to the case that the attractive potential is the sum of exponentials as in Part I, Eq. (52). We found again that Eq. (69) is fulfilled exactly. Since the calculations follow the same lines as for one exponential, we will present only an outline of the proof. For a potential

$$\varphi_{\text{attr}}/kT = -\gamma \sum_{i=1}^m \nu_i \exp(-\sigma_i\gamma x),$$

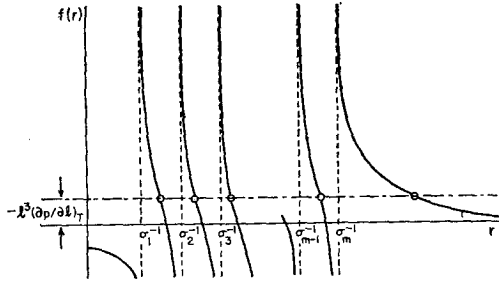where $\nu_i = \alpha_i/kT$, the Kac integral equation is in

FIG. 1. Graphical determination of the ranges from Eq. (84).

$m$ variables, and the kernel is given by

$$K_s(x_1 \cdots x_m, y_1 \cdots y_m)$$

$$= \int_0^\infty d\tau\, e^{-s\tau} \prod_{i=1}^m \left[ \frac{W(x_i)}{W(y_i)} \right]^{\frac{1}{2}} \exp\left[ \frac{\nu_i^{\frac{1}{2}}}{2}(x_i + y_i) \right]$$

$$\times P_{\sigma_i\gamma}(x_i \mid y_i, \tau).$$

To investigate the approach to the limit $\gamma \to 0$, one has to "tame" the integral equation by the substitutions

$$x_i = x_i' + \eta_i(2/\gamma\sigma_i)^{\frac{1}{2}}, \qquad y = y_i' + \eta_i(2/\gamma\sigma_i)^{\frac{1}{2}},$$

where

$$\eta_i = \frac{\eta(\nu_i/\sigma_i)^{\frac{1}{2}}}{[\sum_i (\nu_i/\sigma_i)]^{\frac{1}{2}}},$$

with $\eta$ defined as in Part I, Eq. (33). In zeroth approximation one then obtains, instead of Eq. (37) in Part I, the differential equation

$$\sum_i \frac{\partial^2 H^{(0)}}{\partial z_i^2} + \left[ \sum_i \frac{\sigma_i}{l} - \frac{\mu^{(1)}}{l} - \frac{1}{4} \sum_{i,j} M_{ij} z_i z_j \right]$$

$$\times H^{(0)}(z_1 \cdots z_m) = 0, \quad (74)$$

where $z_i = x_i'(\sigma_i)^{-\frac{1}{2}}$, and the matrix $M$ is given by

$$M_{ij} = \sigma_i^2 \delta_{ij} - \sigma_i\sigma_j(c_i c_j)^{\frac{1}{2}}, \qquad (75)$$

with

$$c_i = 2\nu_i(l - \delta)^2/\sigma_i l^3. \qquad (76)$$

Since by an orthogonal transformation $z_i = \sum_k a_{ik} y_k$, one can diagonalize the matrix $M$, so that

$$\sum_{i,j} M_{ij} z_i z_j = \sum_k A_k y_k^2; \qquad (77)$$

one finds in this approximation,

$$H^{(0)}_{n_1 \cdots n_m} = \prod_{i=1}^m N_{n_i} D_{n_i}(y_i A_i^{\frac{1}{2}}), \qquad (78)$$

$$\lambda_{n_1 \cdots n_m} = \omega(s)\left\{ 1 + \gamma l\left[ \sum_i \frac{\sigma_i}{2} \right.\right.$$

$$\left.\left. - \sum_i (n_i + \tfrac{1}{2})A_i^{\frac{1}{2}} \right] + \cdots \right\},$$

with $N_{n_i} = (n_i!)^{-\frac{1}{2}}(2\pi\sigma_i)^{-\frac{1}{4}}$. Since the maximum eigenvalue is still $\omega(s)$, one again obtains the van der Waals equation of state as already noted in

Part I. The van der Waals constant $\alpha_0$ is given by [see Part I, Eq. (53)]

$$\nu_0 \equiv \frac{\alpha_0}{kT} = -\frac{1}{kT} \int_0^\infty dx\, \varphi_{\text{attr.}}(x) = \sum_i \frac{\nu_i}{\sigma_i}, \quad (79)$$

so that

$$\sum_i c_i = 1 - (B/l)^2, \qquad (80)$$

where $B$ is given by Eq. (38) in Part I.

With these results, the generalization of the calculation of the long-range behavior of $\bar{n}_2(x; l)$ is straightforward and we find

$$\bar{n}_2(x; l) = \bar{n}_2^{\text{h.o.}}(x; l) + \frac{\gamma l(l - \delta)^2}{2B^4}$$

$$\times \sum_{k=1}^m s_k^2 A_k^{3/2} \exp[-A_k^{1/2}\gamma x], \quad (81)$$

where

$$s_k = \sum_{i=1}^m a_{ik}(c_i^{1/2}/\sigma_i). \qquad (82)$$

In the derivation one must use the identity

$$\sum_{k=1}^m A_k s_k^2 = \frac{B^2(l^2 - B^2)}{l^4}, \qquad (83)$$

which follows immediately from (77) by setting $y_k = c_k^{\frac{1}{2}}/\sigma_k$. For the discussion of Eq. (81), the $A_k$ are needed. It is now easy to show that the secular determinant of the matrix $M$ can be written in the form

$$||M_{ij} - A\delta_{ij}|| = \prod_{i=1}^m (\sigma_i^2 - A)\left( 1 - \sum_{i=1}^m \frac{c_i\sigma_i^2}{\sigma_i^2 - A} \right).$$

Hence the $A_k$ are the $m$ real roots of the equation

$$\sum_{i=1}^m \frac{c_i\sigma_i^2}{\sigma_i^2 - A} = 1.$$

By putting in the expression for $c_i$, and by using Eq. (79) and the expression for $B$, one can write this as

$$f(r) \equiv \sum_{i=1}^m \frac{(2\alpha_i/\sigma_i)}{(r\sigma_i)^2 - 1} = -l^3\left( \frac{\partial p}{\partial l} \right)_T, \quad (84)$$

where $r = A^{-\frac{1}{2}}$. From (81) it can be seen that the $m$ roots $r_i$ of this equation are the ranges of the exponentials in $\bar{n}_2(x; l)$. The function $f(r)$ is plotted in Fig. 1. For low densities $-l^3\partial p/\partial l \cong lkT$, and thus it becomes very large. Then $r_i \to 1/\sigma_i$ and since $c_i \to 0$, one sees from (75) that the orthogonal matrix $a_{ij} \to \delta_{ij}$, and from (82) it follows that the amplitudes $s_k^2 A_k^{\frac{1}{2}}$ of the exponentials in (81) become $2\nu_k/l$, so that $\bar{n}_2(x; l)$ approaches the expected form (70). Near the critical point, $-l^3\partial p/\partial l$ is very small, and from Fig. 1 we see that $r_m$ becomes very large, while all the other ranges remain finite. From (84) we find that in this limit, $r_m$ is determined by

$$\frac{1}{r_m^2} \sum_i \frac{2\alpha_i}{\sigma_i^3} = -l^3 \frac{\partial p}{\partial l} ,$$

which can be rewritten as

$$\frac{1}{r_m} = A_m^{1/2} = \frac{1}{\gamma R} \left( -\frac{l^3}{2\alpha_0} \frac{\partial p}{\partial l} \right)^{\frac{1}{2}} , \quad (85)$$

where $R$ is defined by (72). The range of the $m$th exponential becomes therefore the Ornstein–Zernike range (73). To show that also the amplitude checks with Eq. (71), notice that since according to (80), near the critical point $\sum_i c_i \to 1$, the eigenvector $a_{im}$ must approach the value

$$a_{im}^{(0)} = \frac{c_i^{1/2}/\sigma_i}{\left( \sum_i (c_i/\sigma_i^2) \right)^{\frac{1}{2}}} ,$$

because this will give the eigenvalue zero to which $A_m$ approaches. From (82) then follows

$$s_m^2 \to \sum_i \frac{c_i}{\sigma_i^2} = \frac{2\nu_0(l-\delta)^2}{l^3} \gamma^2 R^2, \quad (86)$$

which leads to the amplitude of Eq. (71). Finally, we can show that not only the ranges, but also the amplitudes of the remaining $(m-1)$ exponentials, remain finite near the critical point. This follows from the identity (83), since it allows us to conclude that

$$\sum_{k=1}^{m-1} A_k s_k^2 = \frac{B^2}{l^2} - \frac{B^4}{l^4} - A_m s_m^2 = O(B^4),$$

using (85) and (86), and noting that near the critical point $(-l^3/2\alpha_0)(\partial p/\partial l) \cong B^2/l^2$. Hence, since all the $A_k$ are positive, all the $s_k^2$ must go to zero at least as $B^4$, and from (81) it then follows that all amplitudes except the $m$th remain finite at the critical point.

We have seen therefore that Eq. (81) behaves in the same way as the Lebowitz–Percus result (69) in the ideal gas and in the critical region. To show that the Fourier transform of (81) fulfills (69) exactly, requires the proof of the identity

$$\sum_{j=1}^{m} \frac{A_j^2 s_j^2}{k^2 + A_j} = \left( 1 - \sum_{i=1}^{m} c_i \right)^2 \frac{\Phi(k)}{1 - \Phi(k)} , \quad (87)$$

where

$$\Phi(k) = \sum_{i=1}^{m} \frac{c_i \sigma_i^2}{\sigma_i^2 + k^2} ,$$

which is given in Appendix D.

## VIII. CONCLUDING REMARKS

Although we have restricted ourselves mainly to the one-dimensional case, it is clear that several aspects of the discussion can be generalized to three dimensions.

1. The connection between the virial theorem and the van der Waals equation discussed in Sec. IV can be discussed in the same way for the three-dimensional case. For a weak but long-range attractive force, the virial theorem in the form of Eq. (40) shows that one can separate, in zeroth approximation, the effect of the hard core from the effect of the attractive force. The $\bar{n}_2(d^+; v)$ will be determined by the hard-sphere repulsion, while in the last term in Eq. (40), the $\bar{n}_2(r; v)$ can be replaced by the asymptotic value $1/v^2$; this leads to

$$p = p^{\text{h.c.}} - a/v^2 \quad (88)$$

with

$$a = \tfrac{2}{3}\pi \int_0^\infty dr \, r^3 \frac{d\varphi_{\text{attr}}}{dr} = -\tfrac{1}{2} \int d\mathbf{r} \, \varphi_{\text{attr}}(r),$$

which agrees with the value $C/2$ derived in Part I, Sec. V. Of course, $\bar{n}_2(d^+; v)$ for a gas of hard spheres is *not* known, so that as in Part I, Sec. V one can only conclude that the equation of state is van der Waals-like. One should note also that this derivation is completely equivalent to the original considerations by van der Waals and Lorentz.

2. The Ornstein–Zernike theory and especially Eq. (69) are clearly valid in any number of dimensions. The first approximation of the long-range behavior of $\bar{n}_2(r; v)$, which this theory gives, agrees with the van der Waals-like equation (88) through the fluctuation theorem, and it gives a correction to the inner pressure $(-a/v^2)$ through the virial theorem. If one could still find a physical (and therefore generalizable) argument for (a) the next approximation to the short-range behavior of $\bar{n}_2(r, v)$, corresponding to the last term in Eq. (44), and (b) the higher approximations to the long-range behavior of $\bar{n}_2(r; v)$, corresponding to Eq. (55), then it would be possible, through the fluctuation and virial theorem, to develop a successive approximation method for the equation of state which would start from (88) as the zeroth approximation.

3. We believe that the linear relations (56) for the distribution functions in the two-phase region are also valid in any number of dimensions. We have shown in Sec. VI that through the virial theorem, these relations lead to the constant vapor pressure in the two-phase region. Of course this does not prove that there *are* two phases. The linear functional equation (like the Kac equation), whose maximum eigenvalue is doubly degenerate in the condensation region with nonoverlapping eigenfunctions, is lacking in the three-dimensional

theory. Whether it will be possible to construct such a functional equation from the set of distribution functions as Mayer has tried to do, and whether the degeneracy of the maximum eigenvalue and the relations (56) can then be shown rigorously, remains to be seen.

### APPENDIX A—COMPLETION OF THE PROOF OF EQ. (9b)

We must solve the integral equation (25) by a perturbation calculation with the parameters $\epsilon_i^{\frac{1}{2}}$. Setting

$$\Psi = \Psi^{(000)} + \sum_{klm} \epsilon_1^{k/2} \epsilon_2^{l/2} \epsilon_3^{m/2} \Psi^{(klm)},$$
$$\Lambda = \Lambda^{(000)} + \sum_{klm} \epsilon_1^{k/2} \epsilon_2^{l/2} \epsilon_3^{m/2} \Lambda^{(klm)}, \tag{A1}$$

one finds immediately that in zeroth order the eigenfunctions and eigenvalues are given by

$$\Psi_{\mathbf{n}}^{(000)}(\mathbf{x}) = \psi_n(x; s + n_1\sigma_1 + n_2\sigma_2 + n_3\sigma_3)$$
$$\times \prod_{i=1}^{3} N_{n_i} D_{n_i}(x_i),$$

$$\Lambda_{\mathbf{n}}^{(000)} = \lambda_n(s + n_1\sigma_1 + n_2\sigma_2 + n_3\sigma_3),$$

where $\mathbf{n} = (n, n_1, n_2, n_3)$. The $\Lambda_{0000}^{(klm)}$ and especially $\Lambda_{0000}^{(222)}$, are needed. Since the calculation is lengthy, we will only list the intermediate results which are required for the final result. One easily sees that $\Psi^{(100)} = \Psi^{(010)} = \Psi^{(001)} = 0$ and that in $\Lambda$, only the integral powers of $\epsilon_i$ contribute. One finds

$$\Psi_{0000}^{(110)}(\mathbf{x}) = \sum_{n=0}^{\infty} a_n^{(110)} \Psi_{n110}^{(000)}(\mathbf{x}),$$

with

$$a_n^{(110)} = \frac{1}{2} \frac{\lambda_0(s) + \lambda_n(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_n(s + \sigma_1 + \sigma_2)}$$
$$\times \langle 0, s \mid n, s + \sigma_1 + \sigma_2 \rangle,$$

and similar expressions for $\Psi_{0000}^{(101)}$ and $\Psi_{0000}^{(011)}$. In the order $\epsilon_1$, one obtains

$$\Lambda_{0000}^{(200)} = \tfrac{1}{2}\Lambda_{0000}^{(000)} = \tfrac{1}{2}\lambda_0(s), \tag{A2}$$

$$\Psi_{0000}^{(200)}(\mathbf{x}) = \sum_{n=0}^{\infty} a_n^{(200)} \Psi_{n200}^{(000)}(\mathbf{x}),$$

with

$$a_n^{(200)} = \frac{1}{4} \frac{\lambda_0(s) + \lambda_n(s + 2\sigma_1)}{\lambda_0(s) - \lambda_n(s + 2\sigma_1)} \langle 0, s \mid n, s + 2\sigma_1 \rangle,$$

and similar formula for the terms of order $\epsilon_2$ and $\epsilon_3$.

Then in the order $\epsilon_1\epsilon_2$ one finds

$$\Lambda_{0000}^{(220)} = \lambda_0(s)\left[ \frac{1}{4} + \sum_{n=0}^{\infty} \frac{\lambda_n(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_n(s + \sigma_1 + \sigma_2)} \right.$$
$$\left. \times \langle 0, s \mid n, s + \sigma_1 + \sigma_2 \rangle^2 \right]. \tag{A3}$$

The only thing we need know about the eigenfunction $\Psi_{0000}^{(220)}(x)$ is the fact that the integral

$$\int d\mathbf{x} \, \Psi_{0000}^{(220)} \Psi_{\mathbf{n}}^{(000)}$$

is proportional to $\delta_{n,0}$.

In the order $\epsilon_1(\epsilon_2\epsilon_3)^{\frac{1}{2}}$, one obtains for the development coefficients, $a_n^{(211)}$ of $\Psi_{0000}^{(211)}$ in $\Psi_{n011}^{(000)}$, that is, for the integral

$$a_n^{(211)} = \int d\mathbf{x} \, \Psi_{0000}^{(211)} \Psi_{n011}^{(000)},$$

the expression

$$a_n^{(211)} = -\tfrac{1}{4} \langle 0, s \mid n, s + \sigma_2 + \sigma_3 \rangle$$
$$+ \frac{1}{2} \frac{\lambda_0(s) + \lambda_n(s + \sigma_2 + \sigma_3)}{\lambda_0(s) - \lambda_n(s + \sigma_2 + \sigma_3)}$$
$$\times \sum_{m=0}^{\infty} \left[ \langle n, s + \sigma_2 + \sigma_3 \mid m, s + \sigma_1 + \sigma_2 \rangle \right.$$
$$\times \frac{\lambda_m(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_m(s + \sigma_1 + \sigma_2)} \langle m, s + \sigma_1 + \sigma_2 \mid 0, s \rangle$$
$$+ \langle n, s + \sigma_2 + \sigma_3 \mid m, s + \sigma_1 + \sigma_3 \rangle$$
$$\left. \times \frac{\lambda_m(s + \sigma_1 + \sigma_3)}{\lambda_0(s) - \lambda_m(s + \sigma_1 + \sigma_3)} \langle m, s + \sigma_1 + \sigma_3 \mid 0, s \rangle \right].$$

No other development coefficients are needed. This leads finally in the order $\epsilon_1\epsilon_2\epsilon_3$, to

$$\frac{\Lambda_{0000}^{(222)}}{\lambda_0(s)} = \frac{1}{8} + \frac{1}{2} \sum_{n=0}^{\infty} \left[ \frac{\lambda_n(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_n(s + \sigma_1 + \sigma_2)} \langle 0, s \mid n, s + \sigma_1 + \sigma_2 \rangle^2 \right.$$

$$+ \frac{\lambda_n(s + \sigma_1 + \sigma_3)}{\lambda_0(s) - \lambda_n(s + \sigma_1 + \sigma_3)} \langle 0, s \mid n, s + \sigma_1 + \sigma_3 \rangle^2 + \frac{\lambda_n(s + \sigma_2 + \sigma_3)}{\lambda_0(s) - \lambda_n(s + \sigma_2 + \sigma_3)}$$

$$\left. \times \langle 0, s \mid n, s + \sigma_2 + \sigma_3 \rangle^2 \right] + 2 \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \left[ \langle 0, s \mid n, s + \sigma_2 + \sigma_3 \rangle \right.$$

$$\times \frac{\lambda_n(s + \sigma_2 + \sigma_3)}{\lambda_0(s) - \lambda_n(s + \sigma_2 + \sigma_3)} \langle n, s + \sigma_2 + \sigma_3 \mid m, s + \sigma_1 + \sigma_2 \rangle \frac{\lambda_m(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_m(s + \sigma_1 + \sigma_2)}$$

$$\times \langle m, s + \sigma_1 + \sigma_2 \mid 0, s \rangle + 2 \text{ similar terms with } (\sigma_2, \sigma_3), (\sigma_1, \sigma_2), \text{ replaced by } (\sigma_1, \sigma_3),$$

$$(\sigma_1, \sigma_2), \text{ and by } (\sigma_1, \sigma_3), (\sigma_2, \sigma_3)]. \tag{A4}$$

To calculate the left-hand side of Eq. (24), one must still expand Eq. (27) by substituting for $s$ in the expansion for $\Lambda_{0000}(s)$,

$$s = \bar{p}/kT = \tilde{\chi}(z, \epsilon_1, \epsilon_2, \epsilon_3)$$

$$= \bar{\chi}(z) + \sum_{k,l,m} \epsilon_1^{k/2}\epsilon_2^{l/2}\epsilon_3^{m/2} \tilde{\chi}^{(klm)}.$$

By equating in (27), equal powers of the $\epsilon_i$, one can then express the $\bar{\chi}^{(klm)}$ in terms of the $\Lambda_{0000}^{(klm)}(s)$, where now $s = p/kT = \bar{\chi}(z)$. One finds

$$\bar{\chi}^{(200)} = \bar{\chi}^{(020)} = \bar{\chi}^{(002)} = 0,$$

$$l\bar{\chi}^{(220)} = \frac{1}{\lambda_0(s)} \Lambda_{0000}^{(220)}(s) - \tfrac{1}{4},$$

and finally

$$l\bar{\chi}^{(222)} = \frac{1}{4} + \frac{1}{\lambda_0(s)}$$
$$\times \{\Lambda_{0000}^{(222)} - \tfrac{1}{2}[\Lambda_{0000}^{(220)} + \Lambda_{0000}^{(202)} + \Lambda_{0000}^{(022)}]\}. \quad (A5)$$

Substituting in this equation the results (A3) and (A4), one finds that $l\bar{\chi}^{(222)}$ is exactly equal to the double sum in Eq. (A4). Since this double sum is symmetric in $\sigma_1$, $\sigma_2$, $\sigma_3$, all the six terms on the right-hand side of (24) are equal to each other, so that one can write Eq. (24) in the form

$$6l \iint_0^\infty dx\, dy\, \bar{p}_3(x, y; z)e^{-\sigma_1 x - \sigma_2 y - \sigma_3(x+y)} = l\bar{\chi}^{(222)}. \quad (A6)$$

Since the Laplace transform is over the two relative distances $x$ and $y$, we need only two $\sigma$ variables. Setting

$$\sigma_2 = \sigma_3 = \tfrac{1}{2}\sigma', \qquad \sigma_1 = \sigma - \tfrac{1}{2}\sigma',$$

one easily verifies that the three terms under the double sum in (A4) become equal to each other and hence that (A6) reduces to Eq. (9b).

### APPENDIX B—PROOF OF THE IDENTITY (42)

From Eqs. (8) and (9) in Part I of this series, one can easily verify that the kernel $K_s(x, y)$ of the Kac integral equation fulfills the identity

$$\partial K_{s+\gamma}/\partial y + \partial K_s/\partial x$$
$$= (\tfrac{1}{2}\nu^{1/2})(K_{s+\gamma} + K_s) + \tfrac{1}{2}yK_{s+\gamma} - \tfrac{1}{2}xK_s.$$

Multiply this equation with $\psi_k(y; s)\psi_n(x; s+\gamma)$, and integrate over $x$ and $y$. In each term, one of the integrations can be performed. After a partial integration of the second term, the result can be written in the form

$$\frac{1}{2}\frac{\lambda_k(s) + \lambda_n(s+\gamma)}{\lambda_k(s) - \lambda_n(s+\gamma)} \int_{-\infty}^{+\infty} dx\, \psi_n(x; s+\gamma)\psi_k(x; s)$$

$$= \frac{1}{2\nu^{1/2}} \int_{-\infty}^{+\infty} dx\, x\psi_n(x; s+\gamma)\psi_k(x; s)$$

$$+ \frac{1}{\nu^{1/2}} \int_{-\infty}^{+\infty} dx\, \psi_n(x; s+\gamma) \frac{\partial}{\partial x} \psi_k(x; s).$$

Multiply this equation with

$$\int_{-\infty}^{+\infty} dy\, \psi_n(y; s+\gamma)\psi_k(y; s),$$

and sum over all $n$. On the right-hand side, use the completeness relation

$$\sum_{n=0}^\infty \psi_n(x; s+\gamma)\psi_n(y; s+\gamma) = \delta(x-y).$$

The term with $\partial/\partial x$ then vanishes and one is left with

$$\frac{1}{2} \sum_{n=0}^\infty \frac{\lambda_k(s) + \lambda_n(s+\gamma)}{\lambda_k(s) - \lambda_n(s+\gamma)}$$
$$\times \left[ \int_{-\infty}^{+\infty} dx\, \psi_k(x; s)\psi_n(x; s+\gamma) \right]^2$$
$$= \frac{1}{2\nu^{1/2}} \int_{-\infty}^{+\infty} dx\, x\psi_k^2(x; s).$$

This holds for all $k$. By letting $k = 0$ and by using (9a), Eq. (42) follows. We leave it to the reader to prove, in a similar way, the identity implied by the virial theorem (40a).

### APPENDIX C—PROOF OF EQ. (44)

After the "taming" substitution and after expanding up to $O(\gamma)$, the contribution of the $n$th term of the resolvent series (29) to Eq. (28a), can be written in the form

$$\frac{\exp[n\eta(2\nu_0)^{1/2}]}{\lambda_0^n(s)} \iint_{-\infty}^{+\infty} dx'\, dy'\, h(x')h(y')$$

$$\times \left[ \frac{W(x')}{W(y')} \right]^{1/2} \int_{-\infty}^{+\infty} \cdots \int dz_1' \cdots dz_{n-1}'$$

$$\times \int_0^\infty \cdots \int dt_1' \cdots dt_n' \prod_{i=1}^n e^{-\alpha' t_i}[1 + \gamma^{1/2} a_i(z_{i-1}' + z_i')$$

$$+ \tfrac{1}{2}\gamma a_i^2(z_{i-1}' + z_i')^2]P_\gamma(z_{i-1}' \mid z_i', t_i),$$

where

$$\alpha = s + \sigma + \tfrac{1}{2}\eta^2; \qquad a_i = \tfrac{1}{2}\eta(\tfrac{1}{2}\gamma)^{1/2}(l - t_i);$$

$$z_0' \equiv x', \qquad z_n' \equiv y',$$

and where for $\lambda_0(s)$, $h(x')$ and $h(y')$, one should still substitute the expansions (36) of Part I. We have already seen that in zeroth order, one obtains $(A/\omega)^n$

with

$$A = (1/\alpha) \exp\left[-\alpha\delta + \eta(2\nu_0)^{\frac{1}{2}}\right].$$

There are six sources of terms proportional to $\gamma$.

1. In zeroth order, $s + \frac{1}{2}\eta^2 = 1/(l - \delta)$. Since one develops at constant $l$, one obtains up to first order,

$$s + \frac{1}{2}\eta^2 = 1/(l + \Delta l - \delta),$$

with $\Delta l = \gamma \, d\mu_0^{(1)}/ds$, where $\mu_0^{(1)}(s)$ is given by Eq. (39) in Part I. From the zeroth approximation one therefore obtains the contribution

$$-P^n n\sigma \Delta l/[1 + \sigma(l - \delta)],$$

where

$$P = e^{-\sigma\delta}/[1 + (l - \delta)].$$

2. From the $\lambda_0^n(s)$, one clearly obtains the contribution

$$-P^n n\gamma \mu_0^{(1)} = -\tfrac{1}{2}n\gamma(l - B)P^n.$$

3. From the $\gamma$ terms in the square brackets one obtains

$$nP^n \frac{\gamma\nu_0 l}{2B}\left\{1 - \frac{2}{l}\left(\delta + \frac{1}{\alpha}\right) + \frac{1}{l^2}\left(\delta^2 + \frac{2\delta}{\alpha} + \frac{2}{\alpha^2}\right)\right\}.$$

4. From the $\gamma^{\frac{1}{2}}$ terms in the square brackets combined with the correction of $O(\gamma^{\frac{1}{2}})$ in the eigenfunctions $h(x')$ and $h(y')$, one obtains

$$nP^n \frac{2\nu_0\gamma}{l^2}\left(l - \delta - \frac{1}{\alpha}\right)\frac{(l - \delta)^2}{B}$$

$$\times\left[1 - \frac{l}{2B} + \frac{\nu_0 l}{2B^2}\left(1 - 4\frac{\delta}{l} + 3\frac{\delta^2}{l^2}\right)\right].$$

5. From the product of two $\gamma^{\frac{1}{2}}$ terms in the square brackets, one obtains

$$\tfrac{1}{2}n(n - 1)P^n \frac{\nu_0\gamma}{lB}(l - \delta - 1/\alpha)^2.$$

6. In all these contributions, the function $P_\gamma(z'_{i-1} \mid z'_i, t_i)$ was replaced by the zeroth approximation, which is $\delta(z'_i - z'_{i-1})$. One must therefore still calculate the contribution due to the deviation of $P_\gamma$ from the $\delta$ function. All other factors can now be replaced by the zeroth approximation. From the Markoff property of $P_\gamma$ all the $z'_i$ integrals can be performed immediately. One then carries out the $y'$ integral using the result that up to $O(\gamma)$,

$$\int_{-\infty}^{+\infty} dy' \, F(y')P_\gamma(x' \mid y', t)$$

$$= F(x') - \gamma x' t F'(x') + \gamma t F''(x').$$

The $x'$ integral can be performed and one finally obtains

$$nP^n \frac{\gamma}{2}\left(\delta + \frac{1}{\alpha}\right)\left[1 - \frac{l}{B} + \frac{\nu_0(l - \delta)^2}{l^2 B}\right].$$

Combining all these results, and summing over $n$ then leads to Eq. (44). Here, as in many of the other calculations, a principle of maximum simplification seemed to be operative. If the final answer was not simple, we invariably found that we had made some algebraic errors!

### APPENDIX D—PROOF OF THE IDENTITY (87)

For the proof we are indebted to Dr. J. H. Halton of the Brookhaven National Laboratory. The first step is to develop the left-hand side of (87) in inverse powers of $k^2$. Using the fact that

$$\sum_{i,j} (M^{r+2})_{ij} z_i z_j = \sum_j A_j^{r+2} y_j^2,$$

from which follows by putting $z_i = c_i^{\frac{1}{2}}/\sigma_i$,

$$\sum_{i,j} (M^{r+2})_{ij} \frac{(c_i c_j)^{1/2}}{\sigma_i \sigma_j} = \sum_j A_j^{r+2} s_j^2;$$

one obtains for the left-hand side

$$\frac{1}{k^2}\sum_{r=0}^{\infty} \frac{(-1)^r}{k^{2r}} \sum_{i,j} (M^{r+2})_{ij}\frac{(c_i c_j)^{1/2}}{\sigma_i \sigma_j}. \qquad (A7)$$

It is now slightly more convenient to introduce instead of the matrix $M$ [given by (75)], the matrix

$$L_{ik} = \frac{1}{\sigma_i \sigma_k}\left(\frac{c_k}{c_i}\right)^{1/2} M_{ik} = \delta_{ik} - c_k.$$

In this way, (A7) can be written

$$\frac{1}{k^2}\sum_{r=0}^{\infty} \frac{(-1)^r}{k^{2r}} \sum_{i,i_1\cdots i_{r+1},j} c_i L_{ii_1} L_{i_1 i_2}\cdots L_{i_{r+1}j}$$
$$\times \sigma_{i_1}^2 \sigma_{i_2}^2 \cdots \sigma_{i_{r+1}}^2.$$

The summation over $i$ and $j$ can be performed immediately and give the factor

$$c_{i_1}\left(1 - \sum_j c_j\right)^2.$$

Call $\rho_i = -\sigma_i^2/k^2$, and for convenience of writing, set $c_i = -d_i$. It is then easily seen that the identity (87) can be written in the form

$$\sum_{r=1}^{\infty} \sum_{i_1, i_2\cdots i_r} d_{i_1} L_{i_1 i_2} L_{i_2 i_3}\cdots L_{i_{r-1} i_r}$$
$$\times \rho_{i_1}\rho_{i_2}\cdots\rho_{i_r} = \frac{\Phi}{1 - \Phi}, \qquad (A8)$$

where now

$$\Phi = \sum_i d_i \frac{\rho_i}{1 - \rho_i}, \qquad L_{ij} = \delta_{ij} + d_j.$$

By substituting $L$ and by working out the product, one can verify that the sum over the $i_1, i_2 \cdots i_r$ can be written as

$$\sum_{s=1}^{r} \sum_{i_1 i_2 \cdots i_s} \sum_{r_1, r_2 \cdots r_s}' \prod_{k=1}^{s} d_{i_k} \rho_{i_k}^{r_k},$$

where the summation over the integers $r_k$ go from 1 to $(r-1)$, and are restricted by the condition (denoted by the prime)

$$r_1 + r_2 \cdots + r_s = r.$$

Interchanging in (A8) the summations over $r$ and $s$, the left-hand side of (A8) becomes

$$\sum_{s=1}^{\infty} \sum_{i_1 \cdots i_s} \sum_{r_1 \cdots r_s} \prod_{k=1}^{s} d_{i_k} \rho_{i_k}^{r_k},$$

where the summation over the $r_k$ are now unrestricted and go from one to infinity. One therefore obtains

$$\sum_{s=1}^{\infty} \sum_{i_1 \cdots i_s} \prod_{k=1}^{s} \frac{d_{i_k} \rho_{i_k}}{1 - \rho_{i_k}}$$

$$= \sum_{s=1}^{\infty} \left( \sum_i \frac{d_i \rho_i}{1 - \rho_i} \right)^s = \frac{\Phi}{1 - \Phi},$$

which verifies Eq. (A8).