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Existence of the dielectric constant in rigid-dipole fluids: The functional-derivative approach*

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In a previous article [J. Chem. Phys. 57, 2684 (1972)] sufficient conditions were established for the existence of the dielectric constant ϵ in rigid-dipole fluids. One of these conditions was an unrealistic restriction on the angular dependence of the direct correlation function $c(12)$ at short range. Here it is shown that this restriction can be removed without altering the previous conclusions. Consequently, ϵ rigorously exists if $c(12)$ depends only upon relative positions and orientations of molecules 1 and 2, and becomes asymptotic to $-\phi_d(12)/kT$ at long range, where $\phi_d(12)$ is the dipole-dipole potential. The development is based upon the functional-derivative interpretation of $c(12)$ in terms of the response of the single-molecule distribution function to a single-molecule external field. The consequences of formally separating $c(12)$ and the total correlation function $h(12)$ into short- and long-range parts are briefly explored. A relation between the angular moments of the short-range parts of $c(12)$ and $h(12)$ is derived in an appendix.

I. INTRODUCTION AND SUMMARY

This article is the third in a series dealing with dielectric behavior and two-molecule correlations in rigid-dipole fluids. Here, as in the previous articles^{1,2} (hereafter referred to as I and II, respectively), the term "rigid-dipole fluid" refers to a hypothetical fluid composed of axially symmetric unpolarizable polar molecules. The primary concern of this series of articles is with the question of whether the dielectric constant ϵ exists (i. e., is well-defined), and with the relation of this question to the nature of the long-range intermolecular correlations in zero applied field. For many years it was customary, in both macroscopic and molecular contexts, to simply assume without proof that ϵ exists. A number of recent articles have been concerned with the molecular justification for this assumption in both polar and nonpolar fluids.¹⁻⁶ Considerable work has also been done in the area of long-range correlations in polar fluids,⁷⁻¹⁷ although most of this work does not bear directly on the existence of ϵ .

In I the question of whether ϵ exists was precisely formulated, and the basic foundation was laid for a molecular investigation of this question in rigid-dipole fluids. By means of a density expansion, the existence of ϵ to second order in the density was established. In II it was shown that the direct correlation function $c(12)$ is of fundamental importance to dielectric behavior, and that sufficient conditions for the existence of ϵ can be simply expressed in terms of it. A set of two conditions on $c(12)$, called conditions (a) and (b), was found which are rigorously sufficient to ensure the existence of ϵ . Condition (a) is a condition on the asymptotic behavior of $c(12)$ at long range, namely,

$$c(12) \sim -\beta\phi_d(12) \quad \text{for large } |\mathbf{r}_{12}|, \quad (1)$$

where $\beta = (kT)^{-1}$, $\phi_d(12)$ is the dipole-dipole intermolecular potential, and $|\mathbf{r}_{12}|$ is the intermolecular separation. The term "large" in Eq. (1) refers to a molecular length scale; it is understood that $c(12)$ approaches its asymptotic value very closely while $|\mathbf{r}_{12}|$ is still small in a macroscopic sense. The validity of condition (a) is indicated by a number of independent treat-

ments^{4,10,13,14,17-21} and may therefore be regarded as reasonably well established. Condition (b), on the other hand, involves an unrealistic restriction on the angular dependence of $c(12)$ at short range. This restriction is given by Eq. (36) of II. Condition (b) is satisfied for certain artificial models^{11,17} but, as was emphasized in II, cannot be expected to be satisfied in general.

A new expression for ϵ in terms of $c(12)$ was also obtained in II as a byproduct of the development. This expression is

$$\frac{\epsilon - 1}{\epsilon + 2} = y \left[1 - (\rho/16\pi^2) \int d\mathbf{r}_2 d\omega_1 d\omega_2 c(12) \mathbf{e}_1 \cdot \mathbf{e}_2 \right]^{-1}, \quad (2)$$

where $y = (4\pi/9)\mu_0^2\beta\rho$, μ_0 is the magnitude of the molecular dipole moment, ρ is the number density, \mathbf{r}_k and ω_k are the position and orientation of molecule k , and \mathbf{e}_k is the unit vector with orientation ω_k . [Throughout this article we use the conventional shorthand notation of representing (\mathbf{r}_k, ω_k) simply by (k) ; e. g., $c(12) = c(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2)$.] Høye and Stell¹³ subsequently derived Eq. (2) without assuming condition (b), but not within a context which permits a definite conclusion as to the existence of ϵ .

Equation (2) has been criticized^{13,22} on the basis that its original derivation in II was limited by the obviously unrealistic condition (b). This criticism is certainly valid, but its focus is too narrow. The essential point is that condition (b) was not adopted merely to derive a new expression for ϵ , but rather in order to investigate the existence of ϵ . The result of this investigation was that conditions (a) and (b) constitute a set of rigorous sufficient conditions for the existence of ϵ in rigid-dipole fluids. Prior to this demonstration no such sufficient conditions were known, and conditions (a) and (b) have remained the only proven set of such conditions up to the present time. Thus not only Eq. (2), but the very concept of a dielectric constant, has been limited by condition (b). A desire to alleviate rigorously this stringent restriction was the impetus for the present work.

The preceding remarks are at variance with the views

expressed in a recent review article by Adelman and Deutch²³ (AD). This article implies that Nienhuis and Deutch⁴ (ND) and also Wertheim¹² have established the existence of ϵ under less restrictive conditions than those of II. However, an examination of the work in question shows that this implication is incorrect. The development of ND is limited by the approximation made in replacing their Eq. (3.28) by their Eq. (3.29). [Although AD do not say so, precisely the same type of approximation is made in replacing their Eq. (1.21) by their Eq. (1.22).] ND do not identify any well-defined conditions under which this approximation becomes exact, and hence do not obtain sufficient conditions (restrictive or otherwise) for the existence of ϵ . In discussing Wertheim's work, AD state that Wertheim has established the existence of ϵ for fluids composed of polarizable polar molecules. However, this aspect of his work is presented only as a conjecture and not as a proven result. Wertheim does claim (in agreement with the present article) that the rigid-dipole results of II can be derived without using condition (b), but he does not give a proof.

With the above background, we are now in a position to describe the contribution of the present article. We originally suspected that conditions (a) and (b) are necessary as well as sufficient for the existence of ϵ . As has already been indicated, this suspicion was incorrect. We show here that the results of II are unchanged if condition (b) is replaced by the much weaker condition that the short-range part of $c(12)$ depends only upon relative positions and orientations of molecules 1 and 2. We thereby establish a new and far less restrictive set of sufficient conditions for the existence of ϵ in rigid-dipole fluids. These conditions may be summarized by the following statement: If $c(12)$ satisfies Eq. (1) [condition (a)] and if it depends only upon relative positions and orientations of molecules 1 and 2 at short range, then ϵ rigorously exists and is given by Eq. (2).

The derivation of this result is given in Sec. II. The development exploits the functional-derivative interpretation of $c(12)$ as the inverse kernel associated with the response of the single-molecule distribution function to a single-molecule external field. This interpretation is rigorous and allows one to avoid condition (b), as well as approximations of the Nienhuis-Deutch type, by focusing attention on the single-molecule distribution function itself, rather than on the angular moment of it which determines the polarization $\mathbf{P}(\mathbf{r})$. Ultimately $\mathbf{P}(\mathbf{r})$ emerges naturally at a later point in the derivation.

In Sec. III we briefly consider the implications of formally separating $c(12)$ and the total correlation function $h(12)$ into short- and long-range parts in the spirit of Lebowitz, Stell, and Baer.¹⁹ It is shown that Eq. (2) can be directly converted into an expression for ϵ in terms of the short-range part of $h(12)$. The conversion is performed by using a simple relation between the first angular moments of the short-range parts of $c(12)$ and $h(12)$. This relation is a special case of a general angular moment relation derived in the Appendix.

II. THE MAIN DEVELOPMENT

As usual, we consider a finite volume V of arbitrary shape containing N rigid polar molecules. The number density N/V is denoted by ρ . We begin by summarizing some of the basic results from the functional-derivative approach to the theory of fluids. An excellent review of these results is given by Rushbrooke.²⁴ Although Rushbrooke is concerned with spherical molecules interacting via short-range forces, most of his relations are of more general validity. It is easy to verify that the relations we will use continue to hold for a finite sample composed of molecules having angular degrees of freedom and interacting via long-range forces. It is merely necessary to interpret the shorthand notation $\langle k \rangle$ in the generalized sense (\mathbf{r}_k, ω_k) and to replace Rushbrooke's ρ by ρ/Ω , where $\Omega = \int d\omega_k$. For the axially symmetric molecules of interest here, $\Omega = 4\pi$.

Suppose that the sample under consideration is subjected to a single-molecule external field $\phi(1)$, by which it is meant that the field adds a term

$$\sum_{k=1}^N \phi(k)$$

to the total potential energy of the system. The single-molecule generic distribution function $n(1)$ will then differ from its zero-field value of ρ/Ω . To first order in $\phi(1)$ this deviation is given by

$$\delta n(1) = n(1) - \rho/\Omega = \int d(2) \gamma(2) \delta n(1)/\delta \gamma(2), \quad (3)$$

where $\gamma(1) = -\beta\phi(1)$. The functional derivative $\delta n(1)/\delta \gamma(2)$, which is understood to be evaluated in zero applied field, is given by

$$\delta n(1)/\delta \gamma(2) = (\rho/\Omega) [(\rho/\Omega) h(12) + \delta(12)], \quad (4)$$

where $h(12)$ is the total correlation function, defined in the usual way, and $\delta(12)$ is the Dirac delta function. Equation (3) can be formally inverted to give

$$\gamma(1) = \int d(2) \delta n(2) \delta \gamma(1)/\delta n(2). \quad (5)$$

The kernel $\delta \gamma(1)/\delta n(2)$, which is the inverse of the kernel $\delta n(1)/\delta \gamma(2)$, is related to the direct correlation function by

$$\delta \gamma(1)/\delta n(2) = -c(12) + (\Omega/\rho) \delta(12), \quad (6)$$

where $c(12)$ is defined in terms of $h(12)$ by the Ornstein-Zernike equation,

$$h(12) = c(12) + (\rho/\Omega) \int d(3) c(13) h(32). \quad (7)$$

Combining Eqs. (5) and (6), we obtain

$$-\beta\phi(1) = (\Omega/\rho) \delta n(1) - \int d(2) \delta n(2) c(12). \quad (8)$$

Historically, the definition of $c(12)$ by Eq. (7) was intuitively motivated. However, the above consequences of this definition are perfectly rigorous. In fact it may be said that the fundamental significance of $c(12)$ as a defined quantity is that embodied in Eq. (6). This equation is closely analogous to the fluctuation-dissipation theorems, as it provides a relation between zero-field

correlations and the response of the system to an external field. This aspect of $c(12)$ has received little emphasis in previous work, where the external field has usually been regarded as a purely formal device rather than a physical perturbation.

We now proceed to apply these results to the problem of dielectric polarization. The external field $\phi(1)$ is given by

$$\phi(1) = -\mu_0 \mathbf{e}_1 \cdot \mathbf{E}_0(\mathbf{r}_1), \quad (9)$$

where $\mathbf{E}_0(\mathbf{r})$ is the externally applied electric field. The polarization $\mathbf{P}(\mathbf{r})$ is given by

$$\mathbf{P}(\mathbf{r}_1) = \mu_0 \int d\omega_1 \mathbf{e}_1 \delta n(1). \quad (10)$$

To begin with, we substitute Eq. (9) into Eq. (8), multiply the resulting equation by $\rho\mu_0 \mathbf{e}_1$, and integrate over ω_1 . The result is

$$3y\mathbf{E}_0(\mathbf{r}_1) = 4\pi\mathbf{P}(\mathbf{r}_1) - \rho\mu_0 \int d(2) d\omega_1 \delta n(2) c(12) \mathbf{e}_1. \quad (11)$$

Next we assume that $c(12)$ satisfies the condition given in Eq. (1); i. e., that

$$c(12) = c_s(12) + \beta\mu_0^2 \mathbf{e}_1 \cdot \mathbf{T}_0(\mathbf{r}_{12}) \cdot \mathbf{e}_2, \quad (12)$$

where $c_s(12)$ is a short-ranged function of (12), $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{T}_0(\mathbf{r}) = H(|\mathbf{r}| - \delta) \nabla \nabla |\mathbf{r}|^{-1}$, and $H(x)$ is unity if $x \geq 0$ and zero otherwise. It is understood that the limit $\delta \rightarrow 0$ is to be taken after the performance of any spatial integral in which $\mathbf{T}_0(\mathbf{r})$ appears. Substitution of Eq. (12) into Eq. (11) yields

$$3y\mathbf{E}_L(\mathbf{r}_1) = 4\pi\mathbf{P}(\mathbf{r}_1) - \rho\mu_0 \int d(2) d\omega_1 \delta n(2) c_s(12) \mathbf{e}_1, \quad (13)$$

where the Lorentz electric field $\mathbf{E}_L(\mathbf{r})$ is defined by

$$\mathbf{E}_L(\mathbf{r}_1) = \mathbf{E}_0(\mathbf{r}_1) + \int d\mathbf{r}_2 \mathbf{T}_0(\mathbf{r}_{12}) \cdot \mathbf{P}(\mathbf{r}_2). \quad (14)$$

Since $c_s(12)$ is short-ranged, the integral over \mathbf{r}_2 in Eq. (13) can be extended over all space instead of just over the volume V .

The external electric field $\mathbf{E}_0(\mathbf{r})$ is assumed to vary slowly with \mathbf{r} , in the sense that variations in $\mathbf{E}_0(\mathbf{r})$ over distances of molecular magnitude are negligible. Because the system is a fluid, $\delta n(1)$ and $\mathbf{P}(\mathbf{r})$ will also be slowly varying functions of position. Therefore, since $c_s(12)$ is short-ranged, we can simplify the integral in Eq. (13) by evaluating the slowly varying function $\delta n(2) = \delta n(\mathbf{r}_2, \omega_2)$ at the point $\mathbf{r}_2 = \mathbf{r}_1$ and taking it outside the integral over \mathbf{r}_2 . Equation (13) then becomes

$$3y\mathbf{E}_L(\mathbf{r}_1) = 4\pi\mathbf{P}(\mathbf{r}_1) - \rho\mu_0 \int d\omega_2 \delta n(\mathbf{r}_1, \omega_2) \int d\mathbf{r}_2 d\omega_1 c_s(12) \mathbf{e}_1. \quad (15)$$

We next assume that $c_s(12)$ depends only upon relative positions and orientations of molecules 1 and 2. Then it is clear from the symmetry of the problem that

$$\int d\mathbf{r}_2 d\omega_1 c_s(12) \mathbf{e}_1 = \alpha \mathbf{e}_2, \quad (16)$$

where α is a constant, independent of \mathbf{r}_1 and ω_2 . The value of α is determined by taking the dot product of \mathbf{e}_2

with Eq. (16). (We also integrate over ω_2 to make the result look more symmetrical.) One obtains

$$\alpha = (4\pi)^{-1} \int d\mathbf{r}_2 d\omega_1 d\omega_2 c_s(12) \mathbf{e}_1 \cdot \mathbf{e}_2. \quad (17)$$

Since $\mathbf{e}_1 \cdot \mathbf{e}_2$ is orientationally orthogonal to $\phi_d(12)$,^{1,2} Eq. (17) can be rewritten as

$$\alpha = (4\pi)^{-1} \int d\mathbf{r}_2 d\omega_1 d\omega_2 c(12) \mathbf{e}_1 \cdot \mathbf{e}_2. \quad (18)$$

Combining Eqs. (15) and (16), we obtain

$$3y\mathbf{E}_L(\mathbf{r}_1) = (4\pi - \rho\alpha) \mathbf{P}(\mathbf{r}_1). \quad (19)$$

According to the discussion given in II, Eq. (19) implies that the dielectric constant exists and is given by

$$\frac{3}{4\pi} \left(\frac{\epsilon - 1}{\epsilon + 2} \right) = \frac{3y}{4\pi - \rho\alpha}, \quad (20)$$

which combines with Eq. (18) to give Eq. (2). This completes the proof that if $c(12)$ has the form given in Eq. (12), where $c_s(12)$ is a short-ranged function which depends only upon the relative positions and orientations of molecules 1 and 2, then ϵ exists and is given by Eq. (2).

It is instructive to contrast the present approach to that previously followed in I and II. In the previous approach, Eq. (3) was multiplied by $\mu_0 \mathbf{e}_1$ and then integrated over ω_1 to yield

$$\mathbf{P}(\mathbf{r}_1) = \int d\mathbf{r}_2 \mathbf{K}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{E}_0(\mathbf{r}_2), \quad (21)$$

where the dyadic kernel \mathbf{K} is given by

$$\mathbf{K}(\mathbf{r}_1, \mathbf{r}_2) = (3y/4\pi) \left[\delta(\mathbf{r}_{12}) \mathbf{U} + (3\rho/16\pi^2) \int d\omega_1 d\omega_2 h(12) \mathbf{e}_1 \mathbf{e}_2 \right], \quad (22)$$

and \mathbf{U} is the unit dyadic. The development of II then proceeded by inverting Eq. (21) to obtain

$$\mathbf{E}_0(\mathbf{r}_1) = \int d\mathbf{r}_2 \mathbf{L}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{P}(\mathbf{r}_2), \quad (23)$$

where the inverse kernel \mathbf{L} is defined by

$$\int d\mathbf{r}_3 \mathbf{K}(\mathbf{r}_1, \mathbf{r}_3) \cdot \mathbf{L}(\mathbf{r}_3, \mathbf{r}_2) = \mathbf{U} \delta(\mathbf{r}_{12}). \quad (24)$$

However, when this approach was pursued it was found necessary to adopt condition (b) in order to demonstrate the existence of ϵ . In the present approach this difficulty is avoided by inverting the equation that expresses the response of the fluid to the external field *before* performing the integration over ω_1 . In this way one obtains, instead of Eq. (23), the more useful Eq. (11), which involves $c(12)$ directly and from which $\mathbf{P}(\mathbf{r})$ emerges naturally in due course.

Although the inverse kernel \mathbf{L} does not play a central role in the present approach, an expression for it can readily be derived. To do so, we introduce the tensor $\mathbf{C}(\mathbf{r}, \mathbf{r}')$ utilized in II:

$$\mathbf{C}(\mathbf{r}_1, \mathbf{r}_2) = (4\pi)^{-2} \int d\omega_1 d\omega_2 c(12) \mathbf{e}_1 \mathbf{e}_2. \quad (25)$$

By combining Eqs. (25) and (12) and making use of the

assumed behavior of $c_s(12)$, one can show that

$$\int d\mathbf{r}_2 \mathbf{C}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{P}(\mathbf{r}_2) = (\alpha/12\pi) \mathbf{P}(\mathbf{r}_1) + (\mu_0^2 \beta / 9) \int d\mathbf{r}_2 \mathbf{T}_\delta(\mathbf{r}_{12}) \cdot \mathbf{P}(\mathbf{r}_2). \quad (26)$$

Combining Eqs. (26), (19), and (14), we obtain

$$\mathbf{E}_0(\mathbf{r}_1) = (4\pi/3y) \int d\mathbf{r}_2 [\mathbf{U} \delta(\mathbf{r}_{12}) - 3\rho \mathbf{C}(\mathbf{r}_1, \mathbf{r}_2)] \cdot \mathbf{P}(\mathbf{r}_2). \quad (27)$$

A comparison of Eqs. (27) and (23) leads to the identification

$$\mathbf{L}(\mathbf{r}_1, \mathbf{r}_2) = (4\pi/3y) [\mathbf{U} \delta(\mathbf{r}_{12}) - 3\rho \mathbf{C}(\mathbf{r}_1, \mathbf{r}_2)], \quad (28)$$

which is just the result obtained in II by assuming condition (b). The fact that condition (b) is not necessary for this result was first stated, without proof, by Wertheim.¹² This fact must be qualified, however, by the statement that \mathbf{L} as given by Eq. (28) is the inverse of \mathbf{K} only in a coarse-grained or macroscopic sense (that is, when used in conjunction with slowly varying test functions), and not in a molecular or microscopic sense. If one were to substitute Eqs. (28) and (22) into the left member of Eq. (24), one would obtain not $\mathbf{U} \delta(\mathbf{r}_{12})$, but rather a short-ranged dyadic function of \mathbf{r}_{12} whose spatial integral is \mathbf{U} . Fortunately this is all that is needed in the present context, a fact that the present development implicitly takes into account but one that was not fully exploited in II.

III. SUBSIDIARY DEVELOPMENTS

In this section we consider some of the consequences of separating $c(12)$ and $h(12)$ into short-range and long-range parts in the manner of Lebowitz, Stell, and Baer.¹⁹ The separation is performed as follows. One first writes

$$c(12) = c_0(12) + c_1(12), \quad (29)$$

where $c_0(12)$ is a short-ranged function of (12); i. e., $|\mathbf{r}_{12}|^3 c_0(12) \rightarrow 0$ as $|\mathbf{r}_{12}| \rightarrow \infty$. One then defines $h_0(12)$ in terms of $c_0(12)$ by the Ornstein-Zernike equation:

$$h_0(12) = c_0(12) + (\rho/4\pi) \int d(3) c_0(13) h_0(32). \quad (30)$$

Clearly $h_0(12)$ is also short-ranged. Finally, $h_1(12)$ is defined by requiring that

$$h(12) = h_0(12) + h_1(12). \quad (31)$$

The above separation is clearly not unique because $c_0(12)$ is arbitrary except for the constraint that it be short-ranged.

In the case of present interest $c(12)$ is given by Eq. (12). Thus we can write

$$c_0(12) = c_s(12) - s(12), \quad (32)$$

$$c_1(12) = s(12) + \beta \mu_0^2 \mathbf{e}_1 \cdot \mathbf{T}_\delta(\mathbf{r}_{12}) \cdot \mathbf{e}_2, \quad (33)$$

where $s(12)$ is a short-ranged function which is assumed to depend only on the relative positions and orientations of the pair (12) but is otherwise left arbitrary. Combining Eqs. (32) and (17), we obtain

$$\alpha = (4\pi)^{-1} \int d\mathbf{r}_2 d\omega_1 d\omega_2 c_0(12) \mathbf{e}_1 \cdot \mathbf{e}_2 + 4\pi\sigma, \quad (34)$$

where

$$\sigma = (4\pi)^{-2} \int d\mathbf{r}_2 d\omega_1 d\omega_2 s(12) \mathbf{e}_1 \cdot \mathbf{e}_2. \quad (35)$$

We now wish to eliminate $c_0(12)$ in favor of $h_0(12)$. This can be done by setting $k=1$ in Eq. (A5) of the Appendix and using the result to eliminate the integral in Eq. (34). One then obtains

$$\alpha = 4\pi[(1 + \rho\eta)^{-1} \eta + \sigma], \quad (36)$$

where

$$\eta = (4\pi)^{-2} \int d\mathbf{r}_2 d\omega_1 d\omega_2 h_0(12) \mathbf{e}_1 \cdot \mathbf{e}_2. \quad (37)$$

Combining Eqs. (36) and (20), we find

$$\frac{3}{4\pi} \left(\frac{\epsilon - 1}{\epsilon + 2} \right) = \frac{3y}{4\pi} \left(\frac{1}{1 + \rho\eta} - \rho\sigma \right)^{-1}, \quad (38)$$

which, together with Eq. (37), expresses ϵ in terms of $h_0(12)$ instead of $c(12)$.

Two special cases of Eq. (38) are of interest. The first case is defined by taking $s(12)=0$, which seems the simplest and most natural choice. Then $\sigma=0$ and Eq. (38) becomes

$$(\epsilon - 1)/(\epsilon + 2) = y \left[1 + (\rho/16\pi^2) \int d\mathbf{r}_2 d\omega_1 d\omega_2 h_0(12) \mathbf{e}_1 \cdot \mathbf{e}_2 \right]. \quad (39)$$

Equation (39) bears a striking similarity to the usual expression for ϵ derived by considering a spherical sample and assuming the existence of ϵ .²⁵ This expression may be written in the form

$$(\epsilon - 1)/(\epsilon + 2) = y \left[1 + (\rho/16\pi^2 V) \int d(1)d(2) h(12) \mathbf{e}_1 \cdot \mathbf{e}_2 \right], \quad (40)$$

where the spatial integrals are of course extended over the spherical sample volume. A comparison of Eqs. (39) and (40) shows that for the case of a spherical sample and the choice $s(12)=0$, $h_1(12)$ does not contribute to the integral in Eq. (40).

The second special case we shall consider is defined by

$$s(12) = - (3y/\rho) \delta(\mathbf{r}_{12}) \mathbf{e}_1 \cdot \mathbf{e}_2. \quad (41)$$

This case does not appear to be of intrinsic interest, but it deserves mention here as the choice implicitly made by Nienhuis and Deutch⁴ (ND). Although the ND theory was not originally formulated with $c(12)$ in mind, Adelman and Deutch²³ subsequently showed that Eq. (3.28) of ND is rigorously equivalent to the much simpler statement:

$$c_1(12) = \beta \mu_0^2 \mathbf{e}_1 \cdot \mathbf{T}_{\text{ND}}(\mathbf{r}_{12}) \cdot \mathbf{e}_2. \quad (42)$$

However, the tensor $\mathbf{T}_{\text{ND}}(\mathbf{r}_{12})$ used by ND implicitly contains a delta function at the origin; in our notation, this tensor is given by

$$\mathbf{T}_{\text{ND}}(\mathbf{r}_{12}) = \mathbf{T}_\delta(\mathbf{r}_{12}) - (4\pi/3) \mathbf{U} \delta(\mathbf{r}_{12}). \quad (43)$$

Equations (42) and (43) combine with Eq. (33) to give Eq. (41). Thus Eq. (41), together with Eq. (33), is

rigorously equivalent to Eq. (3.28) of ND.

By combining Eqs. (41) and (35) we find that $\rho\sigma = -y$. Equation (38) then reduces, after a little algebra, to

$$\epsilon - 1 = 3y \left[1 + (\rho/16\pi^2) \int d\mathbf{r}_2 d\omega_1 d\omega_2 h_0(12) \mathbf{e}_1 \cdot \mathbf{e}_2 \right], \quad (44)$$

which is the formula for ϵ obtained by ND as a consequence of their approximate Eq. (3.29). Thus we directly confirm that this approximation did not lead to an error in ϵ , a conclusion reached earlier by Høye and Stell.¹³

Although the separation of $c(12)$ and $h(12)$ into short- and long-range parts is often formally advantageous and enlightening, one must keep in mind that the separation is not unique; thus formulas which depend, for example, on $h_0(12)$ but not on $h_1(12)$ must be applied with caution. We have introduced the arbitrary short-ranged function $s(12)$ partly for convenience but also partly to emphasize this nonuniqueness. It is of interest to note that in the dipolar case the nonuniqueness appears to be related to the dependence of improper integrals involving the singular tensor $\nabla\nabla|\mathbf{r}|^{-1}$ upon the shape of the cavity excluded at the singularity.¹⁷ That is, one can effectively vary the cavity shape by varying $s(12)$. From this point of view, the ND choice of $s(12)$ corresponds to the use of a needle-shaped cavity, instead of the spherical cavity which is built into $\mathbf{T}_6(\mathbf{r}_{12})$.

It is also well to emphasize the important fact that, although we may loosely speak of $h_0(12)$ and $h_1(12)$ as the "short- and long-range parts" of $h(12)$, this does not mean that $h(12) \cong h_0(12)$ at short range. The function $h_1(12)$ is in general neither zero nor negligible at short range, and must be included in evaluating $h(12)$ at short range as well as at long range.

APPENDIX: ANGULAR MOMENT RELATIONS BETWEEN SHORT-RANGE DIRECT AND TOTAL CORRELATION FUNCTIONS

Consider the case in which both $c(12)$ and $h(12)$ are short-ranged and depend only upon relative positions and orientations of molecules 1 and 2. The spatial integral in the Ornstein-Zernike equation,

$$h(12) = c(12) + (\rho/4\pi) \int d(3)c(13)h(32), \quad (A1)$$

can then be extended over all space even for a finite system, provided that neither \mathbf{r}_1 nor \mathbf{r}_2 is in a region of negligible volume near the walls. Now it is clear that

$$\int d\mathbf{r}_2 h(12) \quad \text{and} \quad \int d\mathbf{r}_2 c(12)$$

can depend only on the orientation of molecule 1 relative to molecule 2; i. e., on $\mathbf{e}_1 \cdot \mathbf{e}_2$. The functional dependences of these quantities on $\mathbf{e}_1 \cdot \mathbf{e}_2$ can be expanded in terms of Legendre polynomials:

$$\int d\mathbf{r}_2 h(12) = \sum_k h_k P_k(\mathbf{e}_1 \cdot \mathbf{e}_2), \quad (A2)$$

$$\int d\mathbf{r}_2 c(12) = \sum_k c_k P_k(\mathbf{e}_1 \cdot \mathbf{e}_2). \quad (A3)$$

The Legendre polynomials satisfy the following angular convolution relation:

$$\int d\omega_3 P_k(\mathbf{e}_1 \cdot \mathbf{e}_3) P_j(\mathbf{e}_3 \cdot \mathbf{e}_2) = 4\pi(2k+1)^{-1} \delta_{kj} P_k(\mathbf{e}_1 \cdot \mathbf{e}_2), \quad (A4)$$

where δ_{kj} is the Kronecker delta. Equation (A4) is easily verified by means of the addition theorem for spherical harmonics.²⁶ From Eqs. (A1)–(A4) it follows immediately that

$$h_k = c_k + (2k+1)^{-1} \rho c_k h_k, \quad (A5)$$

which can readily be solved for either c_k or h_k as desired. The coefficients c_k and h_k are essentially angular moments of the quantities $\int d\mathbf{r}_2 c(12)$ and $\int d\mathbf{r}_2 h(12)$:

$$h_k = (4\pi)^{-2}(2k+1) \int d\mathbf{r}_2 d\omega_1 d\omega_2 h(12) P_k(\mathbf{e}_1 \cdot \mathbf{e}_2), \quad (A6)$$

$$c_k = (4\pi)^{-2}(2k+1) \int d\mathbf{r}_2 d\omega_1 d\omega_2 c(12) P_k(\mathbf{e}_1 \cdot \mathbf{e}_2). \quad (A7)$$

Equations (A6) and (A7) follow directly from Eqs. (A2)–(A4), with the special choice of $\mathbf{e}_2 = \mathbf{e}_1$ in Eq. (A4). Equations (A5)–(A7) generalize a well-known relation between the spatial integrals of c and h in a simple fluid.²⁴ Equation (A5) can be written in the alternative form

$$\left(1 + \frac{\rho}{2k+1} h_k\right) \left(1 - \frac{\rho}{2k+1} c_k\right) = 1. \quad (A8)$$

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¹J. D. Ramshaw, *J. Chem. Phys.* **55**, 1763 (1971). Referred to as I in the text.

²J. D. Ramshaw, *J. Chem. Phys.* **57**, 2684 (1972). Referred to as II in the text.

³A. N. Kaufman and K. M. Watson, *Phys. Fluids* **4**, 931 (1961).

⁴G. Nienhuis and J. M. Deutch, *J. Chem. Phys.* **55**, 4213 (1971).

⁵J. D. Ramshaw, *Physica* **62**, 1 (1972).

⁶M. S. Wertheim, *Mol. Phys.* **25**, 211 (1973).

⁷D. W. Jepsen and H. L. Friedman, *J. Chem. Phys.* **38**, 846 (1963).

⁸D. W. Jepsen, *J. Chem. Phys.* **44**, 774 (1966).

⁹D. W. Jepsen, *J. Chem. Phys.* **45**, 709 (1966).

¹⁰F. M. Kuni, *Phys. Lett. A* **26**, 305 (1968).

¹¹M. S. Wertheim, *J. Chem. Phys.* **55**, 4291 (1971).

¹²M. S. Wertheim, *Mol. Phys.* **26**, 1425 (1973).

¹³J. S. Høye and G. Stell, *J. Chem. Phys.* **61**, 562 (1974).

¹⁴J. S. Høye, J. L. Lebowitz, and G. Stell, *J. Chem. Phys.* **61**, 3253 (1974).

¹⁵J. S. Høye and G. Stell, *J. Chem. Phys.* **63**, 5342 (1975).

¹⁶J. S. Høye and G. Stell, *J. Chem. Phys.* **64**, 1952 (1976).

¹⁷J. D. Ramshaw, *J. Chem. Phys.* **64**, 3666 (1976).

¹⁸J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 248 (1963).

¹⁹J. L. Lebowitz, G. Stell, and S. Baer, *J. Math. Phys.* **6**, 1282 (1965).

²⁰D. J. Gates, *Physica* **81A**, 47 (1975).

²¹G. Stell, in *Modern Theoretical Chemistry*, Vol. IV, edited by B. J. Berne (Plenum, New York, 1976).

²²J. M. Deutch, *Ann. Rev. Phys. Chem.* **24**, 301 (1973).

²³S. A. Adelman and J. M. Deutch, *Adv. Chem. Phys.* **31**, 103 (1975).

²⁴G. S. Rushbrooke, in *Physics of Simple Liquids*, edited by H. N. V. Temperley *et al.* (Wiley-Interscience, New York, 1968), p. 25.

²⁵J. G. Kirkwood, *J. Chem. Phys.* **7**, 911 (1939).

²⁶A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, NJ, 1960).