

CLASSICAL DESCRIPTION OF THE POLARIZABILITY AND
DIELECTRIC CONSTANT OF MONATOMIC FLUIDS

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ABSTRACT

A simple classical description of the dependence of pair polarizability upon distance for the monatomics is developed through the extension of the authors' earlier theory of fluctuating polarizability. The result is shown to yield an analytically tractable theory for the dielectric constant of a fluid of such molecules.

I. INTRODUCTION

The dielectric constant ϵ of polarizable fluids is surprisingly well approximated by the simple Clausius-Mossotti relation. One may reasonably hope to account for the remaining small correction by writing

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3} \rho\alpha(1 + S) \quad (1)$$

and expanding S in either α or ρ , where α is the polarizability of an isolated particle and ρ is the number density of particles. For small densities one may write S in its "second virial-coefficient" approximation, i.e.

$$S = B_2^E \rho \quad (2)$$

with B_2^E density independent.

Direct computation shows that for model pair potentials appropriate to simple nonpolar molecules (e.g., the monatomics), B_2^E is positive in the classical DID (dipole-induced-dipole) model of a polarizable fluid, in which the polarizability of each particle is a fixed constant. The B_2^E in this model is given by

$$B_2^E = 2\alpha^2 \int e^{-\beta\phi(r)} r^{-6} (1 + \alpha r^{-3})^{-1} (1 - 2\alpha r^{-3})^{-1} dr \quad (3)$$

where $\phi(r)$ is the pair potential. Equation (3) essentially goes back to Silberstein.¹

It turns out that experiments on simple nonpolar molecules typically² give a B_2^E that is smaller than the one calculated according to (3). As an extreme case we have that of He, where B_2^E is negative.^{2,3} This disagreement between experiment and theory gives rise to a challenging situation: it seems that classical theory is unable to properly describe the dielectric behavior of polarizable fluids beyond the Clausius-Mossotti level.

In an effort to understand this failure, workers have turned to quantum mechanical computations, considering in particular two neighboring He atoms in a small external field and computing the polarization to see how it is affected by the relative distance between atoms.⁴ It is found that for short distances the resulting polarization is suppressed relative to that found in the DID model, where the polarization of an atom is unaffected by its neighbors.⁴ This effect is obviously caused by the perturbations arising from the overlap of the wave functions of the two He atoms. The resulting suppression of polarization makes it possible to understand the negative B_2^E for He; effectively the polarization will decrease sufficiently rapidly with increasing density to make B_2^E negative. This is because more and more atoms will be in close proximity of each other with increasing ρ . Thus there is effectively a density-dependent polarizability in the fluid. This concept of a varying polarizability has been hard to deal with on a first-principles basis in the language of classical theories.

Our goal here is to find a simple classical model that can account for a less positive S than found in the constant-polarizability model in a way that is consistent with the underlying quantum-mechanical genesis of the lowering of S . Although our final results will be based upon the use of α/R^3 rather than ρR^3 as a parameter of smallness, where R is particle diameter, we shall continue to find it convenient to use B_2^E rather than the full S as our guide in arriving at those results.

Our starting point is the model of fluctuating polarizability considered by Høye and Stell.⁵ In this model polarizable and polar fluids may be treated by the same methods. Use of the fluctuating model will give essentially the same ϵ as the non-fluctuating model, with the same B_2^E , when the dipole moment fluctuates in a harmonic potential (i.e., the average dipole moment or polarization of an atom is proportional to the local field). However, the fluctuating model is more general than the non-fluctuating one since the potential for fluctuations may be anharmonic. This anharmonicity will affect B_2^E . As an extreme case of anharmonicity we may consider fluctuations that are confined to a spherical surface of a certain radius in dipole-moment space. This extreme case of a polarizable fluid represents nothing but a polar fluid, since the magnitude of the dipole moment will be fixed. The B_2^E may be computed for a polar fluid. Accurate computation will give $B_2^E > 0$ (see ref. [6] and our Appendix).

Although anharmonicity in the inter-atomic potential that gives rise to fluctuations will indeed change B_2^E , we see that B_2^E stays positive even for extreme anharmonicity. Thus one must conclude that an anharmonic potential alone will not give rise to the observed negative B_2^E of He. So we seek other possible mechanisms. In the next section we locate the one we believe relevant in simple fluids.

II. A CLASSICAL DESCRIPTION OF THE POLARIZABILITY

In a previous study of polar fluids⁷ we have also considered the more general case where a piece $\phi_\Delta(r)\hat{s}_1\hat{s}_2$ is included in the interaction. In the mean-field limit (or equivalently, in lowest order in γ -ordering) one there finds the dielectric constant to be of the form⁷

$$\frac{\epsilon-1}{\epsilon+2} = \frac{y}{1+\theta y} = y - \theta y^2 + \dots \quad (4)$$

where

$$\frac{4\pi\theta m^2}{3} = \int \phi_\Delta(r) d\vec{r}, \quad (5)$$

with

$$y = \frac{4\pi}{3} \rho \alpha. \quad (6)$$

Thus we see that $\theta > 0$ can account for a negative B_2^E . The problem now will be to justify the added piece above in the two-particle interaction.

In our previously discussed model for fluctuating polarizability⁵ there is a potential energy connected to the polarization (i.e., positive and negative intra-atomic elements bound by some force such that they partake of thermal motion). If this potential is harmonic it becomes

$$\phi_0(s) = \frac{1}{2\alpha} s^2, \quad s = |\vec{s}|, \quad (7)$$

for one molecule that is free. Here the α is the "bare" polarizability while \vec{s} is the fluctuating dipole moment. For two molecules there will be a potential given by (7) for each of them. In addition, they also will interact with each other via the dipole-dipole interaction. This will give a potential energy of the form

$$\phi_{12}(\vec{s}_1, \vec{s}_2, \vec{r}) = \frac{1}{2\alpha} (s_1^2 + s_2^2) + \phi_D(r) D(12) s_1 s_2 \quad (8)$$

for such a pair. Here

$$D(12) = 3(\hat{r}\hat{s}_1)(\hat{r}\hat{s}_2) - \hat{s}_1\hat{s}_2 \quad \text{and} \quad \phi_D(r) = -r^{-3} \quad (9)$$

where the carets denote unit vectors.

If this molecular pair is placed in an electric field \vec{E} there will be an additional energy contribution

$$\phi_E = -(\vec{s}_1 + \vec{s}_2)\vec{E} \quad (10)$$

Since (8) is a harmonic potential the average polarization $\vec{p} = \langle \vec{s}_1 + \vec{s}_2 \rangle$ in the field \vec{E} is easily found by taking the minimum of $\phi_{12} + \phi_E$. One can then decompose \vec{E} into a component \vec{E}_{\parallel} along the relative distance \vec{r} and a component \vec{E}_{\perp} transverse to it, and it is easily found that

$$\vec{p}_{\parallel} = \alpha_{\parallel} \vec{E}_{\parallel} \quad \text{and} \quad \vec{p}_{\perp} = \alpha_{\perp} \vec{E}_{\perp} \quad (11)$$

where

$$\alpha_{\parallel} = \frac{2\alpha}{1 - 2\frac{\alpha}{r^3}} \quad \text{and} \quad \alpha_{\perp} = \frac{2\alpha}{1 + \frac{\alpha}{r^3}} \quad (12)$$

Equation (12) means that due to the dipolar interaction in (8) the two molecules for finite r will effectively have a polarizability that is different from that of the single molecules. Thus we see that the two-body interaction in (8) has the effect of an \vec{r} -dependent polarizability.

In quantum mechanical computations⁴ that consider a pair of He atoms in a weak external field, a polarizability much like (12) is found for large \vec{r} , as one might expect. However, for small \vec{r} , when the wave functions of the two atoms begin to overlap, Eq. (12) does not hold any longer, and α_{\parallel} and α_{\perp} both become smaller than the values suggested by this equation. This gives rise to an effective density dependence that has heretofore not been included in classical theories. Our purpose is to try to include this effect in such a way that it fits naturally into the theory of classical fluids without the introduction of density-dependent interactions, so that the density-dependence of the polarizability will only be an effective one, just as it is for real molecules.

A second goal is to do this in such a way that our classical formalism can be understood as resulting from the true quantum mechanical mechanism that underlies the phenomenon we are describing, so that the key parameters in the classical description can ultimately be computed quantum mechanically from first principles. To these ends we generalize Eq. (8) such that the average polarization of a pair of atoms is still proportional to the applied field, with the

ϕ_{12} unchanged by an equal rotation of \vec{s}_1 , \vec{s}_2 , and \vec{r} . Thus instead of (8) we write quite generally

$$\phi_{12}(\vec{s}_1, \vec{s}_2, \vec{r}) = \frac{1}{2} \left[\frac{1}{\alpha} + a(r) \right] (s_1^2 + s_2^2) + \phi_D(r)D(12)s_1s_2 + \phi_\Delta(r)\Delta(12)s_1s_2 \quad (13)$$

with

$$\Delta(12) = \hat{s}_1 \hat{s}_2 . \quad (14)$$

As we did to obtain (11) and (12) we can again apply an external field \vec{E} to the pair of atoms. Doing so, using (13) instead of (8), we now obtain instead of (12)

$$\alpha_{\parallel} = \frac{2\alpha}{1 + \alpha a(r) + \alpha \phi_1(r)} \quad \text{and} \quad \alpha_{\perp} = \frac{2\alpha}{1 + \alpha a(r) + \alpha \phi_2(r)} \quad (15)$$

with

$$\phi_1 = 2\phi_D + \phi_\Delta \quad \text{and} \quad \phi_2 = \phi_\Delta - \phi_D .$$

Thus we see that the coefficients of (13) can be related to the α_{\parallel} and α_{\perp} (that could come, e.g., from first-principle quantum mechanical computations). In (13) there are three \vec{r} -dependent coefficients, so they cannot be uniquely determined by (15) alone. But additional equations can be established by quantum computations if, e.g., the fields acting on the two atoms are not the same. If these two fields point in opposite directions we shall find, instead of (15), the polarizabilities

$$\alpha'_{\parallel} = \frac{2\alpha}{1 + \alpha a(r) - \alpha \phi_1(r)} \quad \text{and} \quad \alpha'_{\perp} = \frac{2\alpha}{1 + \alpha a(r) - \alpha \phi_2(r)} \quad (16)$$

Thus any computation or determination of α_{\parallel} , α_{\perp} , α'_{\parallel} , and α'_{\perp} as functions of r will give α , $a(r)$, $\phi_D(r)$, and $\phi_\Delta(r)$ to be used in (13).

It is easily seen that (13) may be split into three terms:

$$\phi_{12} = \phi_0(\vec{s}_1) + \phi_0(\vec{s}_2) + \phi(12) , \quad (17)$$

where ϕ_0 is given by (7) and $\phi(12)$ is the two-body interaction

$$\phi(12) = \frac{1}{2} a(r) (s_1^2 + s_2^2) + \left[\phi_D(r)D(12) + \phi_\Delta(r)\Delta(12) \right] s_1 s_2 . \quad (18)$$

From this we realize that the \vec{r} -dependent pair polarizability corresponds to nothing but the pair interaction (18) plus the one-body interaction (7) with fixed polarizability (7). From (18) we see that the interaction between fluctuating dipoles is not simply a pure dipole interaction. Instead it contains other pieces close to the repulsive cores, and $\phi_D(r)$ will also differ from (9) in this region. Besides (18), there will be \vec{s} -independent interactions modelled, typically, by a hard-sphere or Lennard-Jones interaction in the case of simple nonpolar fluids such as the noble-gas fluids.

We note that the last term of (18) is much like the exchange interaction used for magnetic systems, also due to overlap of the electron wavefunctions of neighboring atoms.

III. COMPUTATION OF THE DIELECTRIC CONSTANT

A. An integral-equation approach

We want to find ϵ for a system which has a pair interaction which consists of an \vec{s} -dependent piece (18) plus a piece that does not depend upon \vec{s} . This latter piece (which in our simplest model will be a hard-sphere core) we take as the reference piece of the potential with (18) considered the perturbation. To compute the equilibrium properties of our system we can again utilize the idea of Høye and Stell⁵ that different values of \vec{s} represent different species of a mixture, so that methods applicable to mixtures may be used. Our previous⁵ computations already included ϵ for a polarizable fluid with potential energy given by (8). The ϵ was found explicitly in the MSA (Mean Spherical Approximation), and approximations beyond the MSA were also considered. The same computations can be done based on the new interaction (18). In the spirit of the GMSA (Generalized Mean Spherical Approximation),⁸ the difference between (8) and (18) can be modelled by appropriate terms of Yukawa and Yukawa-like form. With such terms in $\phi_{\Delta}(r)$ and $\phi_D(r)$ the corresponding Ornstein-Zernike equation can again be solved explicitly,⁸ as the equations become that of the one-Yukawa problem.⁹ The MSA solution for ϵ will also depend upon the $a(r)$ term which decouples from the ϕ_{Δ} - and ϕ_D -terms upon solution of the Ornstein-Zernike equation. This dependence arises because the $a(r)$ will affect the magnitude of the fluctuating dipole moment or, more precisely, $\langle s^2 \rangle$. Upon solution the $a(r)$ will couple to the reference-system hard-core

potential, and through convolution an additional term with s -dependence $s_1^2 s_2^2$ will be induced. This will result in a three-component mixture problem (with common hard-core diameter). The solution of this latter problem can be obtained in the form of algebraic equations¹⁰ [for $a(r)$ of Yukawa form].

B. A perturbative approach

Although we hope to return to the above program in future work, we shall not pursue it here. Instead we shall follow a perturbative approach. The parameter α/R^3 , where R is an atomic diameter, is a small quantity, especially for He. Therefore only the lowest orders in α/R^3 beyond the Clausius-Mossotti result for ϵ will be of major interest to us. We aim to capture the lowest-order contribution to S in Eq. (1) that is already present in the harmonically fluctuating case given by (8), as well as in the constant-polarizability DID model. This is of second order in α/R^3 , as is well known. Deviations from this contribution as a result of the difference between (17) and (8) we shall consider only through first order in α/R^3 . To this end the potential (18) may be split into three pieces to obtain the following potential bonds for graphical expansions

$$v(12) = -\beta\phi(12) = v_a(12) + v_D(12) + v_{\delta}(12) \quad (19)$$

where

$$v_a(12) = -\frac{1}{2} \beta a(r) (s_1^2 + s_2^2); \quad v_D(12) = \beta \frac{s_1 s_2}{r^3} D(12);$$

$$v_\delta(12) = -\beta s_1 s_2 \left[\phi_\Delta(r) \Delta(12) + \left(\phi_D(r) + r^{-3} \right) D(12) \right] \quad (20)$$

This decomposition is made so that $v_D(12)$ represents the pure dipole interaction such that $v(12) = v_D(12)$ gives back (8), and we regard the v_a and v_δ as perturbations upon v_D . Therefore in our graphical analysis we shall treat v_D through second order while considering v_a and v_δ only to first order. This will insure our obtaining results to the desired orders of α/R^3 noted earlier in the paragraph.

Since our polarizable fluid with fluctuating polarizability may be considered as a polar fluid mixture we shall utilize the general result for ϵ for such mixtures.¹¹ It reads

$$\frac{\epsilon-1}{\epsilon+2} = \text{Tr}(z) \quad (21)$$

The z is a matrix

$$z = \sigma v \quad (22)$$

where

$$v_{ij} = \frac{4\pi}{9} \beta m_i m_j \quad (23)$$

and

$$\sigma = \int \Sigma(12) \Delta(12) \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} d\vec{r} \quad (24)$$

The m_i is the dipole moment of molecule i , which in the present case will be s . The $\Sigma(12)$ is the vertex (or "self energy") function such

that the pair correlation function $h_{ij}(12)$ is given by

$$\rho_i \delta_{ij} \delta(\vec{r}) + \rho_i \rho_j h_{ij}(12) = F_{ij}(12)$$

with

$$F(12) = \Sigma(12) + \iint \Sigma(13) v(34) F(42) \frac{d\Omega_3}{4\pi} \frac{d\Omega_4}{4\pi} d\vec{r}_3 d\vec{r}_4 \quad (25)$$

(Here $\int d\Omega$ means integration over orientations \hat{s} in the case of axial symmetry.) The $v_{ij}(12)$ is the dipole potential bond which in our case will be the $v_D(12)$ of Eq. (20), and which is to be cut inside some radius. We can choose to cut it sharply at the hard-sphere surface for simplicity but as in the one-component case⁷ it is also possible to include a piece $v_\Delta(r)\Delta(12)$ in $v(12)$ with a corresponding change in $\Sigma(12)$ as defined by (25), so that formula (21) is generalized to include the appearance of a θ -parameter.⁷

Expressed in terms of graphs the $\Sigma(12)$ has to be at least doubly connected with respect to the $v(12)$ bonds.¹²

We now expand the $\Sigma(12)$ to second order in v_D and first order in v_a and v_δ . With

$$\Sigma(12) = \rho \delta(12) + W(12)$$

$$[\rho \delta(12)]_{ij} = \rho_i \delta_{ij} \delta(\vec{r}) \quad (26)$$

we find

$$W(12) = \text{graph 1} + \text{graph 2} + \text{graph 3} + \text{graph 4} + \text{graph 5} + \text{graph 6} + \text{graph 7} + \text{graph 8} \quad (27)$$

The diagrammatic expansion of $W(12)$ consists of eight terms representing different graph topologies. The first term is a single bond between two vertices. The second term is a loop formed by two vertices connected by two bonds, labeled v_a . The third term is a loop formed by two vertices connected by two bonds, labeled v_δ . The fourth term is a loop formed by two vertices connected by two bonds, labeled v_D . The fifth term is a loop formed by two vertices connected by two bonds, labeled v_D , with an additional bond connecting the two vertices, labeled v_D . The sixth term is a loop formed by two vertices connected by two bonds, labeled v_D , with an additional bond connecting the two vertices, labeled v_D . The seventh term is a loop formed by two vertices connected by two bonds, labeled v_D , with an additional bond connecting the two vertices, labeled v_D . The eighth term is a loop formed by two vertices connected by two bonds, labeled v_D , with an additional bond connecting the two vertices, labeled v_D .

Here

$$\begin{aligned} \text{.....} &= h_0(r) = h_0(12) , & \triangle &= h_0(123) \\ \text{.....} &= \frac{1}{2} \int \frac{\delta^2 F_0(12)}{\delta \rho(5) \delta \rho(6)} F_0(35) F_0(46) d\vec{r}_5 d\vec{r}_6 , \end{aligned}$$

where $F_0(12) = \rho(1)\rho(2)h_0(12) + \rho(1)\delta(12)$

and $h_0(12)$ and $h_0(123)$ are the pair correlation and three-particle correlation functions respectively of the reference system. Equation (27) is to be used in (24), in which only four of the terms contribute.

We find $(\sigma_{ij} \rightarrow \sigma_{s_1 s_2})$

$$\sigma_{s_1 s_2} = \rho_{s_1} \delta_{s_1 s_2} + \frac{1}{3} [-L_1 + (L_2 + L_3)] \beta \rho_{s_1} \rho_{s_2} s_1 s_2 \quad (28)$$

where L_1 comes from the third and fifth graphs in (27), L_2 comes from the seventh, and L_3 from the eighth. Using (20) with $g_0(r) = h_0(r) + 1$, we have

$$\begin{aligned} L_1 &= \int \phi_\Delta(r) g_0(r) d\vec{r} \\ L_2 &= \frac{1}{3} \int \text{Tr}[T(13)T(32)] h_0(12) d\vec{r}_2 d\vec{r}_3 \\ L_3 &= \frac{1}{3} \int \text{Tr}[T(13)T(32)] h_0(123) d\vec{r}_2 d\vec{r}_3 \end{aligned} \quad (29a)$$

$$A = \frac{1}{3} \beta \rho \langle s^2 \rangle = \frac{1}{3} \beta \int \rho_s s^2 = \frac{1}{3} \beta \int \rho_s^+ s^2 d\vec{s} \quad (29b)$$

Here $\rho_s = \int \rho_s^+(d\Omega/4\pi)$ such that

$$\rho = \int \rho_s = \int \rho_s^+ d\vec{s} \quad (30)$$

The $T(12)$ is the dipole tensor ($i, j = 1, 2, 3$ here)

$$T_{ij}(12) = \frac{1}{r^3} (3\hat{r}_i \hat{r}_j - \delta_{ij}) \quad \text{for } r > R \quad (31)$$

where R will be taken to be the hard-core diameter. For smaller r T_{ij} can be chosen to be zero in keeping with our freedom to choose perturbing potentials inside a hard core for a prescribed full potential $v(12)$.

With Eq. (28) inserted in (22) we get

$$\begin{aligned} z_{s_1 s_2} &= \sum_{s_3} \sigma_{s_1 s_3} v_{s_3 s_2} = \frac{4\pi}{9} \beta \rho_{s_1} s_1 s_2 \\ &\times \{ \delta_{s_1 s_2} + \frac{1}{3} \beta \rho \langle s^2 \rangle [-L_1 + A(L_2 + L_3)] \} \end{aligned} \quad (32)$$

$$\text{Tr}(z) = \frac{4\pi}{9} \beta \rho \langle s^2 \rangle \{ 1 + A[-L_1 + A(L_2 + L_3)] \} \quad (33)$$

To obtain ϵ we need finally an expression for $\langle s^2 \rangle$, which we determine via the chemical potentials,^{5,13}

$$\mu_s^+ = \mu - \phi_0(s) . \quad (34)$$

The chemical potentials of the reference system will be (in our mixture picture, $\mu_s^+ = \mu_{0s^+}$)

$$\beta \mu_{0s^+} = \ln(\rho_s^+/\rho) + \beta g(\rho) \quad (35)$$

The first term of (35) is the ideal-mixture term and $g(\rho)$ is the chemical potential of the reference system of identical particles without the dummy index \vec{s} . Equating (35) to (34) one finds

$$\rho_s^+ = \rho e^{\beta(\mu-g)} e^{-\beta\phi_0(s)} \quad (36)$$

Normalization (30) will determine μ . However, we are more interested

in $\langle s^2 \rangle$. Inserting expression (7) for $\phi_0(s)$ one easily obtains

$$\langle s^2 \rangle = \frac{3\alpha}{\beta} . \quad (37a)$$

So from (29)

$$A = \alpha\rho . \quad (37b)$$

This lowest-order result for A is sufficient for use in (33), where A appears only as a coefficient of perturbing terms. The $\langle s^2 \rangle$ in the lowest-order term of (33) must be treated more accurately -- again to first order in v_a and v_δ and to second order in v_D . The excess chemical potential due to the perturbing interaction may be obtained via the Helmholtz free energy per unit volume F^{ex} . In terms of graphs this excess quantity becomes

$$I^{\text{ex}} = -\beta F^{\text{ex}} = \frac{1}{2} \left(\begin{array}{c} v_a \\ \bullet \text{---} \bullet \\ \bullet \text{---} \bullet \end{array} + \begin{array}{c} v_a \\ \bullet \text{---} \bullet \\ \bullet \text{---} \bullet \end{array} \right) + \frac{1}{4} \left(\begin{array}{c} v_D \\ \bullet \text{---} \bullet \\ \bullet \text{---} \bullet \\ \bullet \text{---} \bullet \end{array} + \begin{array}{c} v_D \\ \bullet \text{---} \bullet \\ \bullet \text{---} \bullet \\ \bullet \text{---} \bullet \end{array} \right) \quad (38)$$

The excess chemical potential μ_s^{ex} thus becomes

$$\beta\mu_s^{\text{ex}} = -\frac{\partial I^{\text{ex}}}{\partial \rho_s} = \frac{1}{2}\beta\rho[(s^2 + \langle s^2 \rangle)L_4 - s^2\alpha L_5] \quad (39)$$

where from (37), $\alpha = \frac{1}{3}\beta\langle s^2 \rangle$, and

$$L_4 = \int a(r)g_0(r)d\vec{r}$$

$$L_5 = \frac{1}{3} \int \text{Tr}[T(12)T(21)][h_0(12) + 1]d\vec{r}_2 \quad (40)$$

with T(12) given by (31).

The μ_s^{ex} is obtained by adding (39) to (35), i.e., $\mu_s^{\text{ex}} = \mu_{0s}^{\text{ex}} + \mu_s^{\text{ex}}$. Combining this instead of (35) with (34) we obtain, instead of (36),

$$\rho_s^{\text{ex}} = \rho \exp[\beta(\mu - g - \frac{1}{2}\rho\langle s^2 \rangle L_4)] \exp\{-\frac{\beta}{2}[\frac{1}{\alpha} + \rho(L_4 + \alpha L_5)]s^2\} \quad (41)$$

From this we easily obtain, instead of (37),

$$\langle s^2 \rangle = \frac{3\alpha}{\beta} \frac{1}{1 + \alpha\rho(L_4 + \alpha L_5)} \approx \frac{3\alpha}{\beta} [1 - \alpha\rho(L_4 + \alpha L_5)] \quad (42)$$

Inserting this into (33), along with A given by (37b) we find

$$\begin{aligned} \text{Tr}(z) &= \frac{4\pi}{3} \rho\alpha[1 - \alpha\rho(L_4 - \alpha L_5)][1 + \alpha\rho(-L_1 + \alpha\rho(L_2 + L_3))] \\ &= \frac{4\pi}{3} \rho\alpha[1 - \alpha\rho(L_1 + L_4) + \alpha^2\rho(L_2 + L_3 + L_5)] \\ &= \frac{4\pi}{3} \rho\alpha[1 - \alpha I_1 + \alpha^2(I_2 + I_3)] \end{aligned} \quad (43)$$

where [using (29), (31), and (40)]

$$\begin{aligned} I_1 &= \rho(L_1 + L_4) = \rho \int [a(r) + \phi_\Delta(r)]g_0(r)d\vec{r} \\ I_2 &= \frac{1}{3} \rho^2 \int \text{Tr}[T(13)T(32)]\hat{h}_0(12)d\vec{r}_2 d\vec{r}_3 \\ I_3 &= \frac{1}{3} \rho^2 \int \text{Tr}[T(13)T(32)]\hat{h}_0(123)d\vec{r}_2 d\vec{r}_3 \\ I_2 + I_3 &= \rho[L_5 + \rho(L_2 + L_3)] \end{aligned} \quad (44)$$

Here we have used

$$\begin{aligned} \rho\hat{h}_0(12) &= \rho h_0(12) + \delta(12) \\ \rho^2\hat{h}_0(123) &= \rho^2 h_0(123) + \rho[h_0(12)\delta(13) + h_0(13)\delta(12) \\ &\quad + h_0(23)\delta(12)] + \delta(12)\delta(13) \end{aligned} \quad (45)$$

with $\delta(12) = \delta(\vec{r}_{12})$. Note that condition (31) on $T(12)$ prevents some of the terms in (45) from contributing in (44). With (43) inserted into the right hand side of (21) we find the desired result for the dielectric constant ϵ for our model with interaction (13). The well known result of the constant polarizability (DID) model is recovered when I_1 is neglected in (43). To put the result in a more familiar form we may also write, instead of (44)

$$I_2 + I_3 = \frac{1}{3} \rho \int \text{Tr}[T(12)T(12)]g_0(12)d\vec{r}_2 + \frac{1}{3} \rho^2 \int \text{Tr}[T(13)T(32)][g_0(123) - g_0(13)g_0(32)]d\vec{r}_2d\vec{r}_3 \quad (46)$$

where we utilize the relations

$$g_0(12) = h_0(12) + 1$$

$$\rho^2 \hat{g}_0(123) = \rho^2 g_0(123) + \rho[g_0(12)\delta(13) + g_0(13)\delta(12) + g_0(23)\delta(12)] + \delta(12)\delta(13)$$

$$\hat{g}_0(123) = \hat{h}_0(123) + \hat{h}(12) + \hat{h}(13) + \hat{h}(23) + 1 \quad (47)$$

If we take the low-density limit we can find B_2^E of Eq. (2) for our model (to first order in v_a and v_δ and to second order in v_D). Equation (43) gives for $\rho \rightarrow 0$ [with $\phi_0(r)$ the reference-system pair potential]

$$B_2^E = -\alpha \int [a(r) + \phi_\Delta(r)]e^{-\beta\phi_0(r)}d\vec{r} + \frac{1}{3} \alpha^2 \int \text{Tr}[T(12)T(21)]e^{-\beta\phi_0(r)}d\vec{r}_2 \quad (48a)$$

For a hard-sphere reference system this simplifies to

$$B_2^E = -\alpha \int_{r>R} [a(r) + \phi_\Delta(r)]d\vec{r} + \frac{8\pi}{3} \frac{\alpha^2}{R^3} \quad (48b)$$

(with R the hard-core diameter). The first term of (48) can be negative. Thus our model of fluctuating polarization with s -dependent pair interaction (13) can accommodate a less positive B_2 than the DID result can, including the extreme case of the negative B_2 found in He.

Using the picture of a position-dependent pair polarizability, it is found⁴ that

$$B_2^E = \frac{1}{2\alpha} \int \alpha(r)e^{-\beta\phi_0(r)}d\vec{r} \quad (49a)$$

where

$$\alpha(r) = \frac{1}{3} [\alpha_{\parallel} + 2\alpha_{\perp}] - 2\alpha \quad (49b)$$

Expanding (15) we find that (49) agrees precisely with (48) to the order of $a(r)$, $\phi_\Delta(r)$ and $\phi_D(r)$ that we have considered. Thus, one can identify the difference, at least to this order, between the $\alpha(r)$ computed quantum-mechanically from first principles and the classical DID result [$\alpha(r) = 4\alpha^3 r^{-6}$ to this order] as our $-2\alpha^2[a(r) + \phi_\Delta(r)]$, despite the fact that $a(r)$ and $\phi_\Delta(r)$ cannot individually be extracted from a computation of only $\alpha_{\perp}(r)$ and $\alpha_{\parallel}(r)$, as noted in the discussion of Eq. (16).

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APPENDIX

The Second Virial Coefficients of a Polar Fluid

The pressure can be expanded in density,

$$\beta p = \rho + B_2 \rho^2 + \dots \quad (A1)$$

In a similar way the dielectric constant ϵ also can be expanded in density,

$$\frac{\epsilon-1}{\epsilon+2} = \gamma [1 + B_2^\epsilon \rho + \dots] ; \quad \gamma = \frac{4\pi}{9} m^3 \beta \rho . \quad (A2)$$

We want to compute B_2 and B_2^ϵ . B_2 has been computed previously for a Stockmayer potential,¹⁴ but B_2^ϵ apparently has not been considered before.¹⁵ Here we compute B_2 by means of a method alternative to that of [14]. Having found B_2 , we can give B_2^ϵ almost immediately by doing the corresponding calculations with some minor modifications. The orientational dependencies are integrated out explicitly, and we get a series which has to be integrated numerically with respect to the magnitude of the relative distance r except in simple cases (for instance, for dipolar hard spheres).

Let us consider molecules with spherically symmetric pair interaction except for the ideal dipole term,

$$\begin{aligned} \phi(\vec{r}, \hat{s}_1, \hat{s}_2) &= \psi(r) + \phi^{\text{ID}}(1,2) \\ \phi^{\text{ID}}(1,2) &= -\frac{m^2}{r^3} [3(\hat{r}\hat{s}_1)(\hat{r}\hat{s}_2) - \hat{s}_1\hat{s}_2] \end{aligned} \quad (A3)$$

(\hat{s}_1 and \hat{s}_2 are unit vectors giving the orientations of the two molecules, \vec{r} is the relative distance, \hat{r} the unit vector of \vec{r} , and m is the dipole moment.)

B_2 is then given by,

$$B_2 = -\frac{1}{2} \int (e^{-\beta\phi} - 1) \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} d\vec{r} \quad (A4)$$

Performing the integrations over \hat{s}_1 and \hat{s}_2 , one can write,

$$B_2 = -2\pi \int [e^{-\beta\psi(r)} I(r) - 1] r^2 dr \quad (A5)$$

[$I(r)$ will be independent of the direction of \vec{r} .] We want to find $I(r)$, which is given by,

$$I(r) = I = \int \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} \exp[2\alpha T_{ij} s_1^i s_2^j], \quad (A6)$$

where $2\alpha = \beta m^2 / r^3$, $T_{ij} = 3x_i x_j - \delta_{ij}$ (the x_i are components of the unit vector \hat{r}), and s_1^i and s_2^j are the i and j components of \hat{s}_1 and \hat{s}_2 , respectively. In (A6) and below, we use the Einstein summation convention for repeated indices.

If \hat{s}_1 and \hat{s}_2 were not restricted to the surface of the unit sphere, expression (A6) would be a "non-diagonalized" Gaussian integral. We now remove this restriction by introducing the δ -function and Laplace-transforming the integral

$$I = \int 2 \cdot \delta(s_1^i s_1^i - S_1) \cdot 2 \cdot \delta(s_2^i s_2^i - S_2) \exp[2\alpha T_{ij} s_1^i s_2^j] \frac{d\vec{s}_1}{4\pi} \frac{d\vec{s}_2}{4\pi} \quad (A7)$$

Expression (A7) equals expression (A6) for $S_1 = S_2 = 1$. Equation (A7)

we Laplace-transform with respect to S_1 and S_2 :

$$\begin{aligned} \tilde{I} &= \int_0^\infty \int_0^\infty I e^{-z_1 S_1} e^{-z_2 S_2} dS_1 dS_2 \\ &= \frac{1}{(2\pi)^2} \int \exp[-z_1 s_1^i s_1^i - z_2 s_2^i s_2^i + 2\alpha T_{ij} s_1^i s_2^j] d\vec{s}_1 d\vec{s}_2 \quad (A8) \end{aligned}$$

The exponent in the exponential we have to diagonalize to perform the integration. This can be done as follows. We introduce new variables

$$\begin{aligned} \vec{u}_1 &= \left(\frac{z_1}{z_2}\right)^{1/4} \vec{s}_1; & \vec{u}_2 &= \left(\frac{z_2}{z_1}\right)^{1/4} \vec{s}_2; \\ d\vec{u}_1 d\vec{u}_2 &= d\vec{s}_1 d\vec{s}_2; & z &= (z_1 z_2)^{1/2} \end{aligned} \quad (A9)$$

$$\tilde{I} = \frac{1}{(2\pi)^2} \int \exp[-z u_1^i u_1^i - z u_2^i u_2^i + 2\alpha T_{ij} u_1^i u_2^j] d\vec{u}_1 d\vec{u}_2 \quad (A10)$$

and then make the further transformation

$$\vec{u}_1 = \frac{1}{\sqrt{2}} (\vec{v}_1 - \vec{v}_2); \quad \vec{u}_2 = \frac{1}{\sqrt{2}} (\vec{v}_1 + \vec{v}_2); \quad d\vec{v}_1 d\vec{v}_2 = d\vec{u}_1 d\vec{u}_2 \quad (A11)$$

$$\begin{aligned} \tilde{I} &= \frac{1}{(2\pi)^2} \int \exp[-z v_1^i v_1^i + \alpha T_{ij} v_1^i v_1^j] d\vec{v}_1 \\ &\quad \times \int \exp[-z v_2^i v_2^i - \alpha T_{ij} v_2^i v_2^j] d\vec{v}_2 \end{aligned} \quad (A12)$$

Finally we have to diagonalize T_{ij} , but to find \tilde{I} we need only the eigenvalues of T_{ij} . The eigenvalues are independent of \hat{r} , so by choosing for instance $\hat{r} = \{1, 0, 0\}$ one easily finds the following eigenvalues,

$$\lambda = \begin{cases} 2 \\ -1 \\ -1 \end{cases} \quad (A13)$$

So by a suitable rotation $\vec{v}_1 \rightarrow \vec{w}_1$; $d\vec{v}_1 = d\vec{w}_1$, one gets,

$$-zv_1^i v_1^i + \alpha T_{ij} v_1^i v_1^j = -(z - 2\alpha)w_1^1 w_1^1 - (z + \alpha)(w_1^2 w_1^2 + w_1^3 w_1^3), \quad (\text{A14})$$

and similarly for a rotation $\vec{v}_2 \rightarrow \vec{w}_2$. Accordingly,

$$\begin{aligned} \tilde{I} &= \frac{1}{(2\pi)^2} \frac{\pi^{3/2}}{(z - 2\alpha)^{1/2} (z + \alpha)} \frac{\pi^{3/2}}{(z + 2\alpha)^{1/2} (z - \alpha)} \\ \tilde{I} &= \frac{\pi}{4(z^2 - 4\alpha^2)^{1/2} (z^2 - \alpha^2)} \\ &= \frac{\pi}{4z^3} \sum_{p=0}^{\infty} \frac{(2p)!}{(2^p p!)^2} (4x)^p \sum_{m=0}^{\infty} x^m, \quad x = (\alpha/2)^2. \quad (\text{A15}) \end{aligned}$$

Inversion of the transform for $S_1 = S_2 = 1$ yields the $I(r)$ given by (A6),

$$I = \frac{1}{(2\pi i)^2} \iint \tilde{I} e^{z_1} e^{z_2} dz_1 dz_2. \quad (\text{A16})$$

Using (A15) in (A16) we have $I = (\pi/4) \sum_{n=0}^{\infty} L_n$ where

$$\begin{aligned} L_n(r) &= \frac{1}{(2\pi i)^2} \iint \frac{1}{z^3} x^n e^{z_1} e^{z_2} dz_1 dz_2 \\ &= \left(\frac{1}{2\pi i} \int \frac{1}{z^{n+3/2}} e^z dz \right)^2 \alpha^{2n} \\ &= \frac{\alpha^{2n}}{[\Gamma(n + 3/2)]^2} = \frac{4}{\pi} \left\{ \frac{2^{n+1} (n+1)!}{[2(n+1)]!} \right\} (2\alpha)^{2n}, \end{aligned}$$

which yields

$$I(r) = \sum_{n=0}^{\infty} \left\{ \frac{2^{n+1} (n+1)!}{[2(n+1)]!} \right\}^2 (2\alpha)^{2n} \sum_{t=0}^n \frac{(2t)!}{(t!)^2}. \quad (\text{A17})$$

For dipolar spheres, use of (A17) in (A5) yields

$$B_2 = \frac{2\pi}{3} R^3 \left[1 - \sum_{n=1}^{\infty} \left\{ \frac{2^{n+1} (n+1)!}{[2(n+1)]!} \right\}^2 \frac{\mu^{*4n}}{2n-1} \sum_{t=0}^n \frac{(2t)!}{(t!)^2} \right], \quad (\text{A18})$$

where $(\mu^*)^2 = \beta m^2 / R^3$. Equation (A18) generalizes a result of Keesom,¹⁶ who did not obtain the general term in the expansion in μ^{*4} .

Next we want to compute B_2^E with the same interaction given by (A3). To compute B_2^E we need the "short-range" part $W(12)$ of the pair distribution function defined by Eqs. (25) and (26).¹² Fourier transforming at $\vec{k} = 0$, we work with

$$\tilde{W}(12) = \int W(12) d\vec{r}. \quad (\text{A19})$$

The $\tilde{W}(12)$, depending only on the relative orientation $\hat{s}_1 \hat{s}_2$, can be expanded in Legendre polynomials,

$$\tilde{W}(12) = 3\rho^2 B_2^E P_1(\hat{s}_1 \hat{s}_2) + \dots = 3\rho^2 B_2^E \hat{s}_1 \hat{s}_2. \quad (\text{A20})$$

B_2^E is then given by:

$$B_2^E = \int (\hat{s}_1 \hat{s}_2) \frac{\tilde{W}(12)}{\rho^2} \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} = \int (\hat{s}_1 \hat{s}_2) \frac{W(12)}{\rho^2} \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} d\vec{r} \quad (\text{A21})$$

To lowest order in density

$$W(12) = \rho^2 [e^{-\beta\phi} + \beta\phi^{ID} - 1]. \quad (\text{A22})$$

In analogy to (A5) and (A6) we now shall get,

$$B_2^E = 4\pi \int e^{-\beta\psi(r)} J(r) r^2 dr, \quad (\text{A23})$$

where $J(r)$ is given by

$$J(r) = J = \int \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} (\hat{s}_1 \hat{s}_2) \exp[2\alpha T_{ij} s_1^i s_2^j] \quad (A24)$$

since the last two terms of (A22) will not contribute.

Integral (A24) can be computed in the same way as integral (A6).

Taking the same steps this time we shall get an extra factor due to

$\hat{s}_1 \hat{s}_2$.

$$\hat{s}_1 \hat{s}_2 = \frac{1}{2} (v_1^i v_1^i - v_2^i v_2^i) = \frac{1}{2} (w_1^i w_1^i - w_2^i w_2^i), \quad (A25)$$

Accordingly

$$\tilde{J} = \frac{3\pi\alpha^3}{4(z^2 - 4\alpha)^{3/2} (z^2 - \alpha^2)^2} = \frac{3\pi\alpha^3}{4z^7} \sum_{n=1}^{\infty} x^{n-1} A_n, \quad (A26a)$$

where A_n can be expressed in various ways. For example,

$$A_n = \frac{1}{2} \sum_{t=1}^n \frac{(2t)!}{(t!)^2} t(n+1-t) \quad (A26b)$$

$$A_n = \sum_{t=0}^{n-1} \frac{(2t)!}{(t!)^2} (2t+1)(n-t), \quad (A26c)$$

which combined yields,

$$A_n = \frac{1}{3} \sum_{t=0}^n \frac{(2t)!}{(t!)^2} (3t-n). \quad (A26d)$$

Upon inversion, the general term of $J(r)$ can be evaluated,

$$\frac{1}{(2\pi i)^2} \iint \frac{\alpha^3}{z} x^{n-1} e^{z_1} e^{z_2} dz_1 dz_2 = \frac{2^5}{\pi} \left\{ \frac{2^n (n+1)!}{(2n+3)!} \right\}^2 (2\alpha)^{2n+1},$$

to yield

$$J(r) = 24 \sum_{n=1}^{\infty} \left\{ \frac{2^n (n+1)!}{(2n+3)!} \right\}^3 (2\alpha)^{2n+1} A_n. \quad (A27)$$

Putting this into (A23), we get for dipolar spheres

$$B_2^E = 4\pi\mu^* 2R^3 \sum_{n=1}^{\infty} \frac{4}{n} \left\{ \frac{2^n (n+1)!}{(2n+3)!} \right\}^2 A_n \mu^{*4n}. \quad (A28)$$

Since A_n is manifestly positive for all n [from, e.g., (A26a)], so is B_2^E . Equation (A26d) is the form of A_n used in the expression for B_2^E given in Ref. [6].

We emphasize that (A5) with (A17) and (A23) with (A27) are relevant to any spherically-symmetric reference-system potential $\psi(r)$ -- not just the hard-sphere potential.

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