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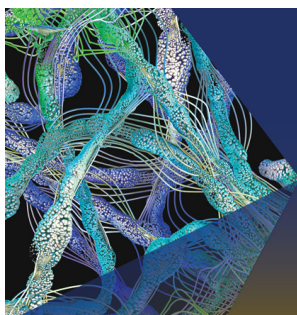
Dynamics and ensemble averages for the polarization models of molecular interactions

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Dynamics and ensemble averages for the polarization models of molecular interactions

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A family of "polarization models" has been generated for description of polarizable and deformable molecules in condensed phases. Within these models the intermolecular forces are not pairwise additive, but have a many-body component that generalizes the polarization interactions present in conventional electrostatics. It is shown that the classical dynamical equations have a rather compact form, in spite of the many-body interactions. Novel molecular distribution functions are introduced in terms of which the usual formulas of statistical thermodynamics can be expressed. Finally, the static dielectric constant is discussed for the polarization models, and it is related to fluctuating local moments in the system.

I. INTRODUCTION

In the interests of conceptual and computational simplicity, it has often been advantageous to treat liquids composed of polyatomic substances as though the constituent molecules were rigid bodies engaging in pairwise interactions. Water provides an important example of this strategy.¹ It is generally accepted that these simplifications still permit local intermolecular structure and thermodynamic properties to be reasonably well described for water. Likewise, its kinetic behavior is predicted with acceptable accuracy. In addition, the phase transitions likely are not grossly affected by the rigid molecule and pairwise additivity assumptions. Other substances (e.g., HF, CCl₄, benzene, Br₂) can probably be similarly treated with similar success.

Nevertheless, there are important phenomena with which such simplified statistical models cannot adequately cope. Obviously, vibrational spectroscopy (infrared and Raman) remains essentially unexplained, though it certainly probes condensed-phase interactions. Furthermore, dielectric behavior of the liquid medium cannot properly be described since electronic polarization (a manifestly many-molecule effect) is absent. The distortion of solvent molecules in contact with dissolved ions is also an important phenomenon that must be overlooked. Finally, discussion of dissociation in polar media to produce solvated protons, and of proton transfer kinetics and reactions in those media, is ruled out.

In order to rectify some of these shortcomings, a class of "polarization models" has recently been introduced. Specific applications both to water² and to hydrofluoride³ have been examined. The early indications are sufficiently favorable that we can look forward to further applications as well, at least encompassing solutions of monatomic ions in several polar solvents.

Presence of many-body polarization interactions in the polarization models fundamentally alters the formats both of the classical equations of motion necessary to describe molecular dynamics, and of the statistical mechanics necessary to characterize ensemble behavior. It is the purpose of this paper to provide both. In particular, we expect that results obtained here will be useful for molecular dynamics simulation studies, by computer, of gas-phase cluster reactions and of condensed-phase phenomena.

In the following (Sec. II), we define the general polarization model and derive the form of its classical dynamical equations. This is followed in Sec. III by consideration of the virial theorem. Section IV introduces novel particle distribution functions necessary to relate thermodynamic properties to local order, and shows explicit formulas that should be used for that purpose. Dielectric properties are discussed in Sec. V. Section VI provides concluding remarks.

II. CLASSICAL DYNAMICS

The polarization model specifies the ground state potential energy Φ for a collection of atoms $1 \cdots N$ at arbitrary positions $\mathbf{r}_1 \cdots \mathbf{r}_N$. These atoms may be of several species; each species exhibits a characteristic charge (oxidation state) q_i and a scalar polarizability α_i .

The function $\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)$ consists of two parts:

$$\Phi = \Phi_I + \Phi_{II} \quad (2.1)$$

The first part is a sum of radial atom-pair potentials

$$\Phi_I = \sum_{i < j=1}^N \phi_{ij}(r_{ij}), \quad (2.2)$$

where each species pair possesses its own characteristic ϕ that includes the Coulombic charge-charge interaction. The second part is a many-body "polarization" interaction

$$\Phi_{II} = \frac{1}{2} \sum_{i, l=1}^N \frac{(\mu_l \cdot \mathbf{r}_{il}) q_i}{r_{il}^3} [1 - L_i(r_{il})] \quad (2.3)$$

that depends upon the dipole moments μ_l which have been induced in atoms indexed by l . The factor $1 - L_i$ accounts for the spatial extension of the electron cloud surrounding atom i ; were it not for this factor, Φ_{II} would be a standard electrostatic interaction for point charges and induced point dipoles.

The induced atomic moments μ_l are determined by the charges and moments on the other atoms through linear relations of the form

$$\mathbf{R}_l(\mu_1 \cdots \mu_N) = 0, \quad (2.4)$$

where

$$\begin{aligned} \mathbf{R}_i &= \mu_i + \alpha_i \sum_{j(\neq i)} \frac{\mathbf{r}_{ij} q_j}{r_{ij}^3} [1 - K_i(r_{ij})] \\ &+ \alpha_i \sum_{m(\neq i)} \frac{\mathbf{T}_{im} \cdot \mu_m}{r_{im}^3} [1 - K_i(r_{im})], \\ \mathbf{T}_{im} &= 1 - \frac{3\mathbf{r}_{im}\mathbf{r}_{im}}{r_{im}^2}. \end{aligned} \quad (2.5)$$

The factors $1 - K_i$ once again are included to account for the spatial extension of the electron cloud surrounding atom 1, and in their absence Eq. (2.5) would have exactly the form specified by classical electrostatics.

On general grounds, we expect each of the modification factors $1 - K_i$ and $1 - L_i$ to vanish at least cubically with distance at the origin.² By convention, Φ and each of its components will vanish when all atoms recede from one another to infinity.

Equations (2.4) demand that each of the linear functions \mathbf{R}_i of the moments $\mu_1 \cdots \mu_N$ vanishes when those moments have their proper "physical" values. Consequently, the potential energy Φ will be unchanged if we add to it an arbitrary linear combination of the components of the \mathbf{R}_i . Therefore, we introduce a set of vectors ν_i ($i = 1 \cdots N$) and consider the quantity

$$\Psi = \Phi + \frac{1}{2} \sum_{i=1}^N \alpha_i^{-1} \nu_i \cdot \mathbf{R}_i. \quad (2.6)$$

From what has just been said, Ψ reduces to Φ when the physical values of $\mu_1 \cdots \mu_N$ are inserted into Eq. (2.6).

It is now possible to require that the first variations of Ψ with respect to the μ_i vanish for the physical set $\mu_1 \cdots \mu_N$:

$$\frac{\delta \Psi}{\delta \mu_i} = 0 \quad (i = 1 \cdots N). \quad (2.7)$$

This requirement leads to the following set of vector equations:

$$\mathbf{S}_i (\nu_1 \cdots \nu_N) = 0 \quad (i = 1 \cdots N), \quad (2.8)$$

where

$$\begin{aligned} \mathbf{S}_i &= \nu_i + \alpha_i \sum_{j(\neq i)} \frac{\mathbf{r}_{ij} q_j}{r_{ij}^3} [1 - L_i(r_{ij})] \\ &+ \alpha_i \sum_{m(\neq i)} \frac{\mathbf{T}_{im} \cdot \nu_m}{r_{im}^3} [1 - K_m(r_{im})]. \end{aligned} \quad (2.9)$$

The comparison between these last two equations for the ν_i , and prior Eqs. (2.4) and (2.5) for the μ_i , reveals an obvious similarity. Indeed, they are distinguishable only by virtue of the way that they incorporate the electron cloud factors.

We can now proceed to calculate the force \mathbf{F}_i acting on particle i for use in the Newtonian dynamical equations

$$\mathbf{F}_i = m_i (d^2 \mathbf{r}_i / dt^2). \quad (2.10)$$

We have

$$\mathbf{F}_i = -\nabla_i \Phi = -\nabla_i \Psi, \quad (2.11)$$

so that

$$\mathbf{F}_i = -\frac{\partial \Psi}{\partial \mathbf{r}_i} - \sum_k \frac{\partial \Psi}{\partial \mu_k} \cdot \frac{\partial \mu_k}{\partial \mathbf{r}_i}. \quad (2.12)$$

The variational constraints ensure that the second set of terms in this last expression will vanish, so we simply have

$$\mathbf{F}_i = -\frac{\partial \Psi}{\partial \mathbf{r}_i}. \quad (2.13)$$

Fortunately, then, no need exists to compute variations of the moments μ_k with respect to spatial displacements of the particles, which would have been a severely complicating feature.

Upon carrying out the derivative indicated in Eq. (2.13), one finds that the force \mathbf{F}_i has the following character:

$$\mathbf{F}_i = \sum_{j(\neq i)} (\mathbf{F}_{ij}^{(2)} + \mathbf{F}_{ij}^{(\mu q)} + \mathbf{F}_{ij}^{(\nu q)} + \mathbf{F}_{ij}^{(\nu \mu)}). \quad (2.14)$$

The first of these contributions is the direct central force, arising from Φ_i , that particle j exerts on particle i :

$$\mathbf{F}_{ij}^{(2)} = -\nabla_i \phi_{ij}(r_{ij}). \quad (2.15)$$

The remaining contributions arise from the polarization interaction Φ_{II} , and have the following forms:

$$\begin{aligned} \mathbf{F}_{ij}^{(\mu q)} &= -\frac{1}{2} \frac{\partial}{\partial \mathbf{r}_i} \left\{ \frac{(\mu_i \cdot \mathbf{r}_{ij}) q_j}{r_{ij}^3} [1 - L_j(r_{ij})] \right. \\ &\quad \left. + \frac{(\mu_j \cdot \mathbf{r}_{ji}) q_i}{r_{ji}^3} [1 - L_i(r_{ij})] \right\}, \end{aligned} \quad (2.16)$$

$$\begin{aligned} \mathbf{F}_{ij}^{(\nu q)} &= -\frac{1}{2} \frac{\partial}{\partial \mathbf{r}_i} \left\{ \frac{(\nu_i \cdot \mathbf{r}_{ij}) q_j}{r_{ij}^3} [1 - K_j(r_{ji})] \right. \\ &\quad \left. + \frac{(\nu_j \cdot \mathbf{r}_{ji})}{r_{ji}^3} [1 - K_i(r_{ij})] \right\}, \end{aligned} \quad (2.17)$$

$$\begin{aligned} \mathbf{F}_{ij}^{(\nu \mu)} &= -\frac{1}{2} \frac{\partial}{\partial \mathbf{r}_i} \left\{ \frac{\nu_j \cdot \mathbf{T}_{ij} \cdot \mu_i}{r_{ji}^3} [1 - K_j(r_{ji})] \right. \\ &\quad \left. + \frac{(\nu_i \cdot \mathbf{T}_{ij} \cdot \mu_j)}{r_{ij}^3} [1 - K_i(r_{ij})] \right\}. \end{aligned} \quad (2.18)$$

Recall that the spatial derivatives are carried out with fixed μ 's and ν 's.

It is noteworthy that the entire set of forces acting on particle i [shown in Eq. (2.14)] may formally be associated with specific pairs ij . However, the occurrences of the μ 's and ν 's in the polarization forces $\mathbf{F}_{ij}^{(\mu q)}$, $\mathbf{F}_{ij}^{(\nu q)}$, and $\mathbf{F}_{ij}^{(\nu \mu)}$ renders these three types nonsimple in the sense that they cannot be strictly resolved into pairwise additive contributions.

Expressions (2.14)–(2.18) suffice to construct numerical solutions for Newton's equations (2.10), thereby permitting molecular dynamics simulation of the polarization model by digital computer.

III. VIRIAL THEOREM

We now examine the implication of the preceding force calculation for the virial theorem of Clausius.⁴ In the present context, this theorem may be written as follows⁵:

$$pV = Nk_B T + \frac{1}{3} \sum_{i=1}^N \langle \mathbf{r}_i \cdot \mathbf{F}_i \rangle. \quad (3.1)$$

Here, p is the pressure in the system, V is its volume,

k_B is Boltzmann's constant, and T is the absolute temperature. The averaging denoted in Eq. (3.1) by $\langle \dots \rangle$ stands for an average over long-time behavior of an isolated quasiergodic single system (microcanonical ensemble), or equally well over a thermostatted collection of equivalently prepared systems (canonical ensemble).

The leading term in the right member of Eq. (3.1) is obviously the ideal gas pressure attributable to N independent particles in volume V . In the case of HF or H₂O, forces are present in the polarization model that will cause spontaneous self-assembly of intact molecules. This will be the case even at large system volumes where the resulting molecular aggregates would form a dilute gas. In this circumstance, the system may well behave as an ideal gas composed not of N particles, but of $\frac{1}{2}N$ (for HF) or $\frac{1}{3}N$ (for H₂O). The virial of intramolecular forces evidently induces this shift.⁶

In view of the result (2.14) for F_{ij} , we can write

$$pV = Nk_B T - \frac{1}{3} \sum_{i < j=1}^N \langle \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \rangle, \quad (3.2)$$

where

$$\begin{aligned} \mathbf{r}_{ij} &= \mathbf{r}_j - \mathbf{r}_i, \\ \mathbf{F}_{ij} &= \mathbf{F}_{ij}^{(2)} + \mathbf{F}_{ij}^{(\mu q)} + \mathbf{F}_{ij}^{(\nu q)} + \mathbf{F}_{ij}^{(\nu \mu)}, \end{aligned} \quad (3.3)$$

and where we have recognized that

$$\mathbf{F}_{ij} = -\mathbf{F}_{ji}. \quad (3.4)$$

It will be convenient to combine all equivalent terms in the sum in Eq. (3.2). For this purpose, we can let σ and τ stand for species indices. The total number N of particles is thus composed of species numbers

$$N = \sum_{\sigma} N_{\sigma}. \quad (3.5)$$

The virial equation of state (3.2) thereupon reduces to

$$pV = Nk_B T - \frac{1}{6} \sum_{\sigma, \tau} N_{\sigma}(N_{\tau} - \delta_{\sigma\tau}) \langle \mathbf{r}_{12} \cdot \mathbf{F}_{12} \rangle_{\sigma\tau}. \quad (3.6)$$

The subscripted brackets $\langle \dots \rangle_{\sigma\tau}$ serve as a reminder that particles named for convenience 1 and 2 are presumed to have species σ and τ , respectively.

Although Eq. (3.6) has the same outward appearance as it would for a conventional mixture with pairwise additive central forces, we must continue to keep in mind that now \mathbf{F}_{12} includes the effect of many-body polarization interactions.

IV. DISTRIBUTION FUNCTIONS

The form derived for the virial theorem within the polarization model context [Eq. (3.6)] suggests that it would be helpful and instructive to introduce a new set of particle distribution functions. These distribution functions describe the local geometric and polarization structure in the system.

Within the regime of classical canonical ensemble theory, the configurational probability for the N -particle system is given by

$$Z^{-1} \exp(-\Phi/k_B T), \quad (4.1)$$

where Z is the configurational integral

$$Z = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \exp(-\Phi/k_B T). \quad (4.2)$$

By integration, this configurational probability can be contracted to a set of distribution functions $P_{\sigma \cdots \omega}^{(N)}(\mathbf{r}_1 \cdots \mathbf{r}_N)$ that give the joint probabilities for simultaneous occurrence of particles with specified species ($\sigma \cdots \omega$) at specified positions ($\mathbf{r}_1 \cdots \mathbf{r}_N$), with specified moments ($\mu_1 \cdots \mu_N$) and quasimoments ($\nu_1 \cdots \nu_N$). In particular, we have

$$P_{\sigma \cdots \omega}^{(n)}(\mathbf{r}_1, \mu_1, \nu_1 \cdots \mathbf{r}_n, \mu_n, \nu_n) = (C_{\sigma \cdots \omega} / Z) \int d\mathbf{r}_{n+1} \cdots \int d\mathbf{r}_N \times \exp[-\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)/k_B T] \prod_{i=1}^n \delta(\mu'_i - \mu_i) \delta(\nu'_i - \nu_i), \quad (4.3)$$

in this expression, μ'_i and ν'_i are vectors determined by Eqs. (2.4) and (2.8) for particle positions $\mathbf{r}_1 \cdots \mathbf{r}_N$, and $C_{\sigma \cdots \omega}$ is the number of distinct ways that the N available particles can be distributed over positions $\mathbf{r}_1 \cdots \mathbf{r}_n$ in a manner consistent with the respective species $\sigma \cdots \omega$. This combinatorial factor will have the form

$$C_{\sigma \cdots \omega} = \prod_{\xi} (N_{\xi}! / n_{\xi}!), \quad (4.4)$$

where among the n species labels $\sigma \cdots \omega$, we suppose that species ξ occurs precisely n_{ξ} times.

Conventional distribution functions $\rho_{\sigma \cdots \omega}^{(n)}$ for particle positions⁷ can be obtained from the $P_{\sigma \cdots \omega}^{(n)}$ by integrating the latter over the vector variables $\mu_1 \cdots \mu_n$:

$$\rho_{\sigma \cdots \omega}^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n) = \int d\mu_1 \cdots \int d\mu_n P_{\sigma \cdots \omega}^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n, \mu_1 \cdots \mu_n). \quad (4.5)$$

Using the newly introduced distribution functions for $n=2$, the virial equation of state (3.6) may be put into an alternative form;

$$pV = Nk_B T - \frac{1}{6} \sum_{\sigma, \tau} \int d\mathbf{r}_1 \int d\mu_1 \int d\nu_1 \int d\mathbf{r}_2 \times \int d\mu_2 \int d\nu_2 \mathbf{r}_{12} \cdot \mathbf{F}_{12} P_{\sigma\tau}^{(2)}(\mathbf{r}_1 \cdots \nu_2). \quad (4.6)$$

Evidently, the pressure is affected by many-body interactions in the system insofar as they affect the particle pair distribution functions, as well as \mathbf{F}_{12} .

The same situation surrounds the thermodynamic energy E . Starting from expressions (2.1)–(2.3) for Φ , one easily derives the following:

$$E = \frac{3}{2} Nk_B T + \frac{1}{2} \sum_{\sigma, \tau} \int d\mathbf{r}_1 \int d\mu_1 \int d\nu_1 \int d\mathbf{r}_2 \times \int d\mu_2 \int d\nu_2 \psi_{\sigma\tau}(\mathbf{r}_1 \cdots \mu_2) P_{\sigma\tau}^{(2)}(\mathbf{r}_1 \cdots \nu_2), \quad (4.7)$$

$$\begin{aligned} \psi_{\sigma\tau}(\mathbf{r}_1 \cdots \mu_2) &= \phi_{\sigma\tau}(\mathbf{r}_{12}) + \frac{(\mu_1 \cdot \mathbf{r}_{12})q_{\tau}}{2r_{12}^3} [1 - L_{\sigma}(r_{12})] \\ &\quad + \frac{(\mu_2 \cdot \mathbf{r}_{21})q_{\sigma}}{2r_{21}^3} [1 - L_{\tau}(r_{21})]. \end{aligned} \quad (4.8)$$

Since the "effective" pair interaction $\psi_{\sigma\tau}$ does not depend on quasimoments ν_1 and ν_2 , these variables may immediately be integrated in Eq. (4.7).

We note in passing that in the conventional infinite system limit the particle distribution functions also yield expressions for the isothermal compressibility.⁷ It has been pointed out before⁸ that the distribution functions contain information sufficient to determine the degree of molecular dissociation.

V. DIELECTRIC PROPERTIES

Because the polarization model permits dissociation of molecules into ionic fragments, the system in principle will be electrically conducting at any nonzero temperature. The response of the system to an externally supplied electric field perturbation then would have to be described by a complex dielectric function even in the zero frequency limit. However, in many cases, it is appropriate to inquire about the purely real dielectric response of an undissociated collection of polar molecules. In fact, that will be our viewpoint now. Either the temperature and density conditions will be such that dissociation is negligible from the outset, or else we can mathematically restrict attention just to that region of configuration space which exhibits fully intact molecules.

The external electric field applied to the molecular system will be created by a set of suitably arranged point charges. The precise nature of these charges is irrelevant; since they lie well outside the system, the $1 - K_i$ and $1 - L_i$ factors that occur in the polarization model for their interaction with the system particles will all have reduced to unity, to yield standard electrostatic behavior.

One of the major advances in understanding polar dielectrics was due to Kirkwood,⁹ who first elucidated the role of local molecular orientational correlations. However, Kirkwood's treatment of molecular polarizability was improper, as Harris and Alder have pointed out.¹⁰ In fact, the simultaneous incorporation of static moments, electronic polarization, and nuclear deformation is a tricky matter which the polarization model may help to clarify.

In order to examine the static dielectric behavior of the polarization model, we shall assume for simplicity that only one type of molecule is present. Generalization to mixtures is conceptually straightforward. We suppose that the system constitutes a macroscopic sphere located in a vacuum region which, when it was empty, possessed a constant electric field E_0 . With the dielectric sphere in place, the macroscopic electric field within that sphere is related to E_0 and the static dielectric constant ϵ by

$$E = \left(\frac{3}{\epsilon + 2} \right) E_0. \quad (5.1)$$

This field and ϵ are also related to the polarization density P by the familiar formula

$$(\epsilon - 1) E = 4\pi P. \quad (5.2)$$

Connection between these macroscopic relations and the microscopic structure in the molecular system is established through the fluctuating system total moment

M . On the one hand,

$$P = \langle M \rangle / V, \quad (5.3)$$

where V is the volume of the spherical sample, while on the other hand, $\langle M \rangle$ can in principle be calculated from the general principles of statistical mechanics. If e is a unit vector in the direction of E_0 , we can write

$$\left(\frac{\epsilon - 1}{\epsilon + 2} \right) E_0 = \frac{4\pi}{3V} \langle M \cdot e \rangle. \quad (5.4)$$

The moment M depends both on all nuclear coordinates (to be denoted collectively by x) and on E_0 . We can write

$$M(x, E_0) = M(x, 0) + M_1(x, E_0), \quad (5.5)$$

where M_1 is the extra moment induced by E_0 with x held fixed. Since the polarization model contains only linear response, M_1 will strictly be linear in the components of E_0 . It is appropriate to identify M_1 as a manifestation of limiting high-frequency dielectric response, which can be described in terms of the high-frequency dielectric constant ϵ_∞ . Thus, we write

$$M_1(x, E_0) = \frac{3V}{4\pi} \left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right) E_0, \quad (5.6)$$

and we note in passing that M_1 and ϵ_∞ should be straightforward to evaluate in a computer simulation of the system, using the concepts presented in Sec. II above.

In accepting Eq. (5.6), it has been necessary to suppose that, for the great majority of nuclear configurations x , the polarization response fluctuates only negligibly from its most probable value (which is along E_0); this assumption is surely valid since the system is macroscopic.

Combining Eqs. (5.5) and (5.6) above yields

$$\left(\frac{\epsilon - 1}{\epsilon + 2} \right) E_0 = \left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right) E_0 + \frac{4\pi}{3V} \langle M(x, 0) \cdot e \rangle. \quad (5.7)$$

The remaining average in Eq. (5.7) can be carried out with the aid of the canonical distribution. This distribution has the same form as that shown earlier in Eq. (4.1) except that potential energy Φ must be augmented by the interaction of the molecular system with the external field. The total potential energy now has the form

$$U(x, E_0) = \Phi(x) - M(x, 0) \cdot E_0 + O(E_0^2). \quad (5.8)$$

Thus,

$$\begin{aligned} \langle M(x, 0) \cdot e \rangle &= \frac{1}{Z} \int dx [M(x, 0) \cdot e] \exp(-U/k_B T) \\ &= \langle [M(x, 0) \cdot e]^2 \rangle_0 (E_0/k_B T) + O(E_0^3) \\ &= \langle [M(x, 0)]^2 \rangle_0 (E_0/3k_B T) + O(E_0^3). \end{aligned} \quad (5.9)$$

The notation $\langle \dots \rangle_0$ implies an average for $E_0 = 0$, in other words with canonical distribution (4.1). The last form in Eq. (5.9) relies upon isotropy of the dielectric. We are only interested in linear response, so that terms denoted by $O(E_0^3)$ in Eq. (5.9) may be disregarded. Consequently, we have

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi}{9Vk_B T} \langle [M(x, 0)]^2 \rangle_0. \quad (5.10)$$

The mean squared system moment appearing in the last equation may be transformed into several different but equivalent versions. Since only intact molecules are present, \mathbf{M} can be resolved into the separate molecular moments \mathbf{m}_k :

$$\mathbf{M} = \sum_{k=1}^{N_0} \mathbf{m}_k, \quad (5.11)$$

where N_0 stands for the number of molecules in the system. Each \mathbf{m}_k consists of a vector sum of permanent charge and induced moment contributions (the latter due to intramolecular and intermolecular interactions). Since all of the N_0 molecules are equivalent, Eq. (5.10) can be rewritten as

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi N_0}{9Vk_B T} \langle \mathbf{m}_1 \cdot \mathbf{M} \rangle_0. \quad (5.12)$$

As the next step, Kirkwood's procedure⁹ would replace \mathbf{M} in the last equation by a strictly local moment \mathbf{m}_1^* . This latter quantity comprises \mathbf{m}_1 as well as the additional moment, present in the immediate surroundings of molecule 1, that is attributable to short-range intermolecular correlations. Both Kirkwood, and later Harris and Alder,¹⁰ agree that

$$\langle \mathbf{m}_1 \cdot \mathbf{M} \rangle_0 = \frac{9\epsilon}{(2\epsilon + 1)(\epsilon + 2)} \langle \mathbf{m}_1 \cdot \mathbf{m}_1^* \rangle_0. \quad (5.13)$$

Buckingham¹¹ has expressed reservations about the validity of relation (5.13) when molecular polarizability is present. His concern is that, upon fixing \mathbf{m}_1^* to perform the average required by Eq. (5.13), one automatically constrains the field near molecule 1 arising from molecules outside of the region defining \mathbf{m}_1^* . However, it is our present position that this field averages to zero (to within terms of order V^{-1}) for fixed \mathbf{m}_1^* ; since we deal at present only with linear polarization response, the apparent constraint should have no significant effect. If *nonlinear* polarizability were present, it is possible that Buckingham's effect could exert a significant influence. Once again, it might be stressed that computer simulation could be used to test directly the validity of Eq. (5.13) for the polarization model if doubts persist.

If Eq. (5.13) is accepted, our dielectric constant expression then becomes

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi N_0}{Vk_B T} \left[\frac{\epsilon}{(2\epsilon + 1)(\epsilon + 2)} \right] \langle \mathbf{m}_1 \cdot \mathbf{m}_1^* \rangle_0. \quad (5.14)$$

Under the influence of normal molecular motions, \mathbf{m}_1 will fluctuate. These fluctuations arise both from nuclear motions within molecule 1 itself, as well as from the fluctuating fields of neighbors to which molecule 1 is subject. The polarization model provides a definite prescription for evaluating these phenomena. The collective local moment \mathbf{m}_1^* likewise will fluctuate, in a manner correlated strongly with \mathbf{m}_1 . A proper description of these correlated variations would be based upon the generalized distribution functions $P_{\sigma \dots \omega}^{(n)}$ introduced in Sec. IV. Computer simulations of polar substances using the respective polarization models should have

great benefit in quantitative study of the statistical behavior of these moments over a wide range of temperature and density conditions.

The Kirkwood orientational correlation factor g_K may now formally be introduced by the identity

$$\langle \mathbf{m}_1 \cdot \mathbf{m}_1^* \rangle \equiv g_K \langle m_1^2 \rangle_0. \quad (5.15)$$

Therefore, we have

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi N_0}{Vk_B T} \left[\frac{\epsilon}{(2\epsilon + 1)(\epsilon + 2)} \right] g_K \langle m_1^2 \rangle_0. \quad (5.16)$$

There is no elementary and reliable way to relate $\langle m_1^2 \rangle_0$ in a condensed phase to its value for isolated molecules. Once again, the use of the polarization models in extensive computer studies may be the most informative technique available for investigation of this molecular quantity, and of the historically important Kirkwood factor g_K .

VI. CONCLUSION

Although the many-body interaction Φ_{II} makes the polarization models more complicated than the models usually studied in the statistical mechanics of condensed phases, we have shown in this paper that the complication is still manageable. Furthermore, the inclusion of interactions of the type Φ_{II} is a physical necessity in order to produce an adequate description of dielectric behavior. We have stressed that the statistical mechanics entails a new set of distribution functions $P_{\sigma \dots \omega}^{(n)}$ which involve positions, moments, and quasimoments. We suggest that these distribution functions be studied both by computer simulation for polarization models, and by derivation, closure, and numerical solution of hierarchy equations analogous to those that have been central to the study of simple liquids.¹² Finally, it has been emphasized that the polarization model offers a means to achieve greater understanding of dielectric behavior in condensed polar media.

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