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Collective Excitations of Dipolar Systems*

ROBERTO LOBO† AND SERGIO RODRIGUEZ
Department of Physics, Purdue University, Lafayette, Indiana and Argonne National Laboratory, Argonne, Illinois

AND

JOHN E. ROBINSON
Argonne National Laboratory, Argonne, Illinois

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A system of neutral molecules having permanent electric dipole moments should exhibit self-sustained longitudinal polarization waves analogous to the plasma vibrations of an electron gas. To study these long-wavelength collective modes (dipolar plasmons), we adapt some techniques successful in many-electron problems to systems whose Hamiltonians include kinetic energy both of center-of-mass and of rotational motion, the interaction between rigid dipoles, and short-range interactions which we need not specify in detail. A canonical transformation plus a random-phase approximation (RPA) is used to display the collective modes explicitly in the Hamiltonian, and it is shown that the ground state of the system is adequately described in the RPA. The dipolar plasmon frequency so found is also obtained by linearizing equations of motion for Fourier components of the polarization charge density, and is affected statistically by short-range forces through a constant factor. Linear dielectric response theory yields a simple exact sum rule and, in a self-consistent-field approximation, a dielectric function in which dynamical effects of short-range forces can be retained. The classical dielectric function for linear and spherical rotators is evaluated in closed form when short-range forces are neglected. Its static limit is the Onsager expression for rigid dipoles, and it vanishes at the dipolar plasmon frequency.

I. INTRODUCTION

COLLECTIVE excitations in charged plasmas have been studied extensively, both theoretically and experimentally.[1–3] The best known are the long-wavelength plasma oscillations, for example, in the electron gas. Similar collective oscillations must also exist in systems of neutral molecules having permanent electric dipole moments, but no detailed analysis of such modes seems to be available. In a system of identical interacting dipoles, we anticipate the existence of self-sustained polarization waves whose frequency in the long-wavelength limit tends to a finite value of order $(N\mu^2/I\Omega)^{1/2}$, where N is the number of molecules in the system of volume Ω, μ is the dipole moment, and I is a suitable average moment of inertia of each molecule. The purpose of this work is to give a theoretical description of the dynamics of such modes.

We concentrate primarily on the influence of the long-range dipolar fields. Short-range dipole-dipole correlations are, of course, extremely important for the dielectric properties at low frequencies. However, we are here interested not in the static dielectric constant, but in the response of the system at frequencies of the order of 10^{13}–10^{14} sec^{-1}. The frequency of the collective dipolar mode (dipolar plasmon) does, of course, depend on the nature of the short-range forces, but primarily their effect upon the equilibrium distribution of dipole moments in the system. We shall show in Sec. II that the frequency ω_k of the dipolar plasmon, in the long-wavelength limit $k=0$, is given by

$$\omega_0^2=(4\pi N\mu^2/\Omega I)\,\langle\sin^2\theta\rangle, \tag{1}$$

where θ is the angle formed by one dipole moment with the direction of propagation, and the brackets indicate an average over all dipoles at equilibrium. If, for example, at equilibrium the dipoles are oriented at random, this average is $\frac{2}{3}$. On the other hand, if the system is completely polarized at equilibrium, this average is unity for propagation at right angles to the direction of polarization. Accordingly, the effect of short-range forces can be taken into account in performing the average in Eq. (1).

There exist alternative ways to arrive at a description of the dipolar plasmons and to derive their frequency. The approximations we use are similar to those common in treating the electron gas. In Sec. II A, we employ a canonical transformation to separate the Hamiltonian of the system into parts corresponding to single-particle and to collective motions, and discuss the conditions under which the residual coupling between these parts may be neglected. In Sec. II B we introduce collective coordinates which are Fourier coefficients of the polarization charge density, and obtain their equations of motion. Section III contains a discussion of the dielectric function within the linear-response theory.

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[1] See, for example, D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1961), and references cited therein.

[2] R. Brout and P. Carruthers, *Lectures on the Many-Electron Problem* (John Wiley & Sons, Inc., New York, 1963).

[3] See the articles by D. Bohm and by D. Pines, in *The Many-Body Problem*, edited by C. Dewitt (Dunod Cie., Paris, 1959), pp. 401–540.

II. DYNAMICS OF AN ASSEMBLY OF PERMANENT ELECTRIC DIPOLES

A. Canonical Transformations and the Random-Phase Approximation

We consider a system of identical molecules each of which has a permanent electric dipole. We shall in this section take these to be linear molecules, thus neglecting the moment of inertia about the direction of the dipole. The coordinates of the lth molecule are then the position $\mathbf{R}_l$ of its center-of-mass system and polar and azimuthal angles Θ_l, Φ_l, specifying the orientation of the dipole moment in an arbitrary reference frame. The classical Hamiltonian of the system is

$$\mathcal{H}=\sum_l \{(P_l^2/2M)+(2I)^{-1}(P_{l\Theta}^2+(\sin^2\Theta_l)^{-1}P_{l\Phi}^2)\}+\tfrac{1}{2}\sum_{l\neq l'}(V_{ll'}+U_{ll'}). \quad (2)$$

The single sum is the kinetic energy, M being the mass of one molecule, and $\mathbf{P}_l$, $P_{l\Theta}$, $P_{l\Phi}$ the momenta canonically conjugate to $\mathbf{R}_l$, Θ_l, Φ_l, respectively. The interaction between the molecules l and l' is separated into two parts: $V_{ll'}$ is the dipole-dipole interaction and $U_{ll'}$ is a short-range interaction whose form we need not specify. It is convenient to rewrite the total interaction energy as a Fourier series. We take $V_{ll'}$ to be the interaction of two finite dipoles and go to the limit of point dipoles after effecting the Fourier expansion, obtaining

$$V_{ll'}=\sum_k (4\pi/\Omega k^2)\,\mathbf{k}\cdot\boldsymbol{\mu}_l\mathbf{k}\cdot\boldsymbol{\mu}_{l'}\exp[i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_{l'})]. \quad (3)$$

It is to be understood that in this and all subsequent summations over $\mathbf{k}$, the term $\mathbf{k}=0$ is to be omitted.

Let us now introduce further degrees of freedom which can be regarded as being associated with the self-consistent electromagnetic field in the dipolar system.[4] Instead of using as field variables the Fourier components of the vector potential of the electromagnetic field, we use the scalar field

$$\bar{\Psi}(\mathbf{R})=\Omega^{-1/2}\sum_{k<k_c}\bar{\Psi}_k\exp(-i\mathbf{k}\cdot\mathbf{R}), \quad (4)$$

where the summation is over all $\mathbf{k}$ having magnitude less than that of a cutoff wave number k_c. There is, in principle, no need to introduce a cutoff. However, we wish to describe the system in terms of separated and relatively simple single-particle and collective motions. Such simple collective modes can exist only for wavelengths greater than the intermolecular spacing which, therefore, provides an upper limit to k_c. In practice, we impose the more restrictive condition on k_c that the number of additional variables $\bar{\Psi}_k$ be small compared to the number of degrees of freedom in the system. We introduce also a field $\bar{\pi}(\mathbf{R})$ canonically conjugated to $\bar{\Psi}(\mathbf{R})$ and write

$$\bar{\pi}(\mathbf{R})=\Omega^{-1/2}\sum_{k<k_c}\bar{\pi}_k\exp(i\mathbf{k}\cdot\mathbf{R}). \quad (5)$$

Since $\bar{\Psi}(\mathbf{R})$ and $\bar{\pi}(\mathbf{R})$ are taken to be real,

$$\bar{\pi}_k=\bar{\pi}_{-k}{}^*$$

and

$$\bar{\Psi}_k=\bar{\Psi}_{-k}{}^*.$$

The Hamiltonian can now be written as

$$\begin{aligned}\mathcal{H}=&\sum_l (P_l^2/2M)+(2I)^{-1}\sum_l[P_{l\Theta}^2+(\sin^2\Theta_l)^{-1}P_{l\Phi}^2]\\&+\tfrac{1}{2}\sum_{|\mathbf{k}|<k_c}\Big|\bar{\pi}_k+\sum_l i\hat{k}\cdot\boldsymbol{\mu}_l(4\pi/\Omega)^{1/2}\exp(i\mathbf{k}\cdot\mathbf{R}_l)\Big|^2\\&+\tfrac{1}{2}\sum_{l\neq l'}U_{ll'}-(2\pi/\Omega)\sum_{l,k}(\hat{k}\cdot\boldsymbol{\mu}_l)^2\\&+\tfrac{1}{2}\sum_{ll'}\sum_{|\mathbf{k}|\geq k_c}(4\pi/\Omega)(\hat{k}\cdot\boldsymbol{\mu}_l)(\hat{k}\cdot\boldsymbol{\mu}_{l'})\exp[i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_{l'})].\end{aligned} \quad (6)$$

We require that the Hamiltonian in Eq. (6) be identical to the one in Eq. (2). Thus we have the subsidiary conditions

$$\bar{\pi}_k=0, \quad (7)$$

for $|\mathbf{k}|<k_c$. In the quantum theory we impose the condition that the solutions of the Schrödinger equation $\mathcal{H}u=Eu$ be such that $\bar{\pi}_k u=0$, where $\bar{\pi}_k$ is to be regarded as a quantum-mechanical operator.

We shall now carry out a canonical transformation generated by the function

$$\begin{aligned}S=&-\sum_l\sum_{|\mathbf{k}|<k_c} i\bar{\Psi}_k(4\pi/\Omega)^{1/2}(\hat{k}\cdot\boldsymbol{\mu}_l)\exp(i\mathbf{k}\cdot\mathbf{R}_l)\\&+\sum_{|\mathbf{k}|<k_c}\pi_k\bar{\Psi}_k+\sum_l(p_{\theta l}\Theta_l+p_{\phi l}\Phi_l+\mathbf{p}_l\cdot\mathbf{R}_l).\end{aligned} \quad (8)$$

This transformation takes us from the old variables $\mathbf{R}_l$, $\mathbf{P}_l$, Θ_l, $P_{\Theta l}$, Φ_l, $P_{\Phi l}$, $\bar{\Psi}_k$, $\bar{\pi}_k$ to the new variables $\mathbf{r}_l$, $\mathbf{p}_l$, θ_l, $p_{\theta l}$, ϕ_l, $p_{\phi l}$, Ψ_k, π_k. The canonical transformation is given in the following explicit form:

$$\Psi_{\mathrm{k}}=\partial S/\partial\pi_{\mathrm{k}}=\bar{\Psi}_{\mathrm{k}}, \quad (9)$$

$$\theta_l=\partial S/\partial p_{\theta l}=\Theta_l, \quad (10)$$

$$\phi_l=\partial S/\partial p_{\phi l}=\Phi_l, \quad (11)$$

$$\mathbf{r}_l=\partial S/\partial\mathbf{p}_l=\mathbf{R}_l, \quad (12)$$

and the corresponding equations for the generalized momenta. To obtain the expressions for the new momenta, we need to define the polar angles of $\mathbf{k}$. These are designated by α_k and β_k, where α_k is the angle formed by $\mathbf{k}$ and the polar axis and β_k is an azimuthal

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[4] D. Bohm and D. Pines, Phys. Rev. 92, 609 (1953).

angle of the vector **k**. Then

$$\boldsymbol{\mu}_l\cdot\hat{k}=\mu[\cos\Theta_l\cos\alpha_k+\sin\Theta_l\sin\alpha_k\cos(\Phi_l-\beta_k)],\tag{13}$$

and

$$P_{\Phi l}=\partial S/\partial\Phi_l=p_{\phi l}+\sum_{|\mathbf{k}|<k_c} i\Psi_k\mu(4\pi/\Omega)^{1/2}\exp(i\mathbf{k}\cdot\mathbf{r}_l)\sin\theta_l\sin\alpha_k\sin(\phi_l-\beta_k),\tag{14}$$

$$P_{\theta l}=\partial S/\partial\Theta_l=p_{\theta l}+\sum_{|\mathbf{k}|<k_c} i\mu(4\pi/\Omega)^{1/2}\Psi_k\exp(i\mathbf{k}\cdot\mathbf{r}_l)[\sin\theta_l\cos\alpha_{\mathbf{k}}-\cos\theta_l\sin\alpha_k\cos(\phi_l-\beta_k)],\tag{15}$$

$$\mathbf{P}_l=\partial S/\partial\mathbf{R}_l=\mathbf{p}_l+(4\pi/\Omega)^{1/2}\sum_{|\mathbf{k}|<k_c}\mathbf{k}\Psi_k\mu\exp(i\mathbf{k}\cdot\mathbf{r}_l)[\cos\theta_l\cos\alpha_k+\sin\theta_l\sin\alpha_k\cos(\phi_l-\beta_k)],\tag{16}$$

and

$$\bar{\pi}_k=\partial S/\partial\bar{\Psi}_k=\pi_k-i\mu(4\pi/\Omega)^{1/2}\sum_l\exp(i\mathbf{k}\cdot\mathbf{r}_l)[\cos\theta_l\cos\alpha_k+\sin\theta_l\sin\alpha_k\cos(\phi_l-\beta_k)],\tag{17}$$

where in Eqs. (14)–(17) we have replaced the old variables by the new ones obtained in Eqs. (9)–(12). The new Hamiltonian is

$$K=\mathcal{H}+\partial S/\partial t=\mathcal{H}.\tag{18}$$

We now write

$$\begin{aligned}K=&\sum_l(p_l^2/2M)+(2I)^{-1}\sum_l(p_{\theta l}^2+(\sin^2\theta_l)^{-1}p_{\phi l}^2)+\sum_{|\mathbf{k}|<k}\tfrac{1}{2}\pi_k\pi_{-k}\\&-(2\pi\mu^2/I\Omega)\sum_{|\mathbf{k}|<k_c}\sum_{|\mathbf{k}'|<k_c}\sum_l\Psi_k\Psi_{k'}\exp[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_l]\{\sin\alpha_k\sin\alpha_{k'}\sin(\phi_l-\beta_k)\sin(\phi_l-\beta_{k'})\\&+[\cos\alpha_k\sin\theta_l-\cos\theta_l\sin\alpha_k\cos(\phi_l-\beta_k)][\cos\alpha_{k'}\sin\theta_l-\cos\theta_l\sin\alpha_{k'}\cos(\phi_l-\beta_{k'})]\\&-(I/M\mu^2)\mathbf{k}\cdot\mathbf{k}'(\boldsymbol{\mu}_l\cdot\hat{k})(\boldsymbol{\mu}_l\cdot\hat{k}')\}+K_{int}+\tfrac{1}{2}\sum_{|\mathbf{k}|\geq k_c}\sum_{l,l'}(4\pi/\Omega)\boldsymbol{\mu}_l\cdot\hat{k}\boldsymbol{\mu}_{l'}\cdot\hat{k}\exp[i\mathbf{k}\cdot(\mathbf{r}_l-\mathbf{r}_{l'})]\\&+\tfrac{1}{2}\sum_{l\neq l'}U_{ll'}-(2\pi/\Omega)\sum_k\sum_l(\boldsymbol{\mu}_l\cdot\hat{k})^2,\end{aligned}\tag{19}$$

where

$$\begin{aligned}K_{\text{int}}=&\sum_{|\mathbf{k}|<k_c}\sum_l(i\mu/I)(4\pi/\Omega)^{1/2}\Psi_kp_{\phi l}\exp(i\mathbf{k}\cdot\mathbf{r}_l)[\sin\alpha_k\sin(\phi_l-\beta_k)/\sin\theta_l]\\&+\sum_{|\mathbf{k}|<k_c}\sum_l(i\mu/I)(4\pi/\Omega)^{1/2}\Psi_kp_{\theta l}\exp(i\mathbf{k}\cdot\mathbf{r}_l)[\cos\alpha_k\sin\theta_l-\cos\theta_l\sin\alpha_k\cos(\phi_l-\beta_k)]\\&+\sum_{|\mathbf{k}|<k_c}\sum_l M^{-1}(4\pi/\Omega)^{1/2}\mathbf{p}_l\cdot\mathbf{k}\Psi_k\exp(i\mathbf{k}\cdot\mathbf{r}_l)\boldsymbol{\mu}_l\cdot\hat{k}.\end{aligned}\tag{20}$$

In Eq. (19) the first two terms represent, as before, the kinetic energy of the molecules. K_{int} couples the the collective oscillations described by the coordinates π_k and Ψ_k with the individual particle modes described by $\mathbf{r}_l$, $\mathbf{p}_l$, and $\boldsymbol{\mu}_l$. $U_{ll'}$ is the same as before with the new coordinates substituted in place of the old ones. The term containing a summation over wave vectors whose magnitudes exceed k_c is the short-range part of the dipole-dipole interaction. The last term is the self-energy of the electrical dipoles. The fourth term contains a sum over two wave vectors **k** and **k′**. This double summation can be divided into two parts, one with $\mathbf{k}=-\mathbf{k}'$ and the other with $\mathbf{k}\neq-\mathbf{k}'$. This latter part is negligible as we shall demonstrate later. After dropping these terms with $\mathbf{k}+\mathbf{k}'\neq0$, the Hamiltonian function becomes

$$\begin{aligned}K=&\sum_l(p_l^2/2M)+\sum_l[(p_{\theta l}^2/2I)+(p_{\phi l}^2/2I\sin^2\theta_l)]\\&+\sum_{|\mathbf{k}|<k_c}\tfrac{1}{2}(\pi_k\pi_{-k}+\omega_k^2\Psi_k\Psi_{-k})+K_{\text{int}}\\&+\tfrac{1}{2}\sum_{|\mathbf{k}|>k_c}(4\pi/\Omega)(\boldsymbol{\mu}_l\cdot\hat{k})(\boldsymbol{\mu}_{l'}\cdot\hat{k})\exp[i\mathbf{k}\cdot(\mathbf{r}_l-\mathbf{r}_{l'})]\\&+\tfrac{1}{2}\sum_{l\neq l'}U_{ll'}-(2\pi/\Omega)\sum_k\sum_l(\boldsymbol{\mu}_l\cdot\hat{k})^2,\end{aligned}\tag{21}$$

where

$$\omega_k^2=\left(\frac{4\pi\mu^2}{\Omega}\right)\sum_l\left(\frac{\sin^2(\mathbf{k},\boldsymbol{\mu}_l)}{I}+\frac{k^2\cos^2(\mathbf{k},\boldsymbol{\mu}_l)}{M}\right).\tag{22}$$

ω_k is regarded as the frequency of a collective dipolar excitation. Strictly speaking, the term in the Hamiltonian,

$$K_p=\sum_{|\mathbf{k}|<k_c}\tfrac{1}{2}(\pi_k\pi_{-k}+\omega_k{}^2\Psi_k\Psi_{-k}),\qquad(23)$$

does not give a completely satisfactory description of the collective excitations because ω_k depends, as is clear from Eq. (22), on the instantaneous angular orientation of all the dipoles in the system. However, it depends on this orientation only through terms of the form $\sum_l \sin^2(\mathbf{k},\boldsymbol{\mu}_l)$, so that to a high degree of accuracy they can be replaced by an average over all molecules [$(\mathbf{k},\boldsymbol{\mu}_l)$ designates the angle between $\mathbf{k}$ and $\boldsymbol{\mu}_l$]. The frequency ω_k is to be interpreted as a frequency analogous to the frequency of plasma oscillations in an electron gas. The frequency of long-wavelength plasma oscillations in an electron gas is given by $(4\pi Ne^2/m\Omega)^{1/2}$, where N is the number of electrons present. The analogous frequency for the fluctuation of the polarization field of a dipolar system is proportional to $(N\mu^2/I\Omega)^{1/2}$, and this is exactly the frequency given in Eq. (22). It is to be noticed, however, that this frequency depends on the average of $\sin^2(\mathbf{k},\boldsymbol{\mu}_l)$ over all the dipoles in the system. Thus the numerical factor in front of $(N\mu^2/I\Omega)^{1/2}$ depends on the nature of the short-range forces between the molecules since these will determine the value of that average.

From Eqs. (9) and (17) and remembering that $\alpha_{-k}=\pi-\alpha_k$ and $\beta_{-k}=\pi+\beta_k$ and that $\bar{\pi}(\mathbf{R})$ and $\bar{\Psi}(\mathbf{R})$ are real, we find that

$$\Psi_{-k}{}^*=\Psi_k,$$

and

$$\pi_{-k}{}^*=\pi_k.$$

The system is quantized in the usual fashion by requiring that canonically conjugate variables be operators satisfying the usual commutation relations. For example,

$$[\Psi_k,\pi_{k'}]=i\delta_{k,k'},\qquad(24)$$

where we take units such that $\hbar=1$. Let us now concentrate on the term K_p given in Eq. (23). We define the non-Hermitian operators a_k and $a_k{}^\dagger$ by means of

$$a_k{}^\dagger=(2\omega_k)^{-1/2}(\omega_k\Psi_{-k}-i\pi_k).\qquad(25)$$

Remembering that $\pi_k{}^\dagger=\pi_{-k}$, $\Psi_k{}^\dagger=\Psi_{-k}$, and $\omega_{-k}=\omega_k$, we find that

$$[a_k,a_{k'}{}^\dagger]=\delta_{kk'}.\qquad(26)$$

Substitution into K_p yields

$$K_p=\sum_k\omega_k(a_k{}^\dagger a_k+\tfrac{1}{2}).\qquad(27)$$

We now turn to the question of the justification of the neglect of the terms in Eq. (19) containing summations over $\mathbf{k}$ and $\mathbf{k}'$ with the restriction $\mathbf{k}+\mathbf{k}'\neq0$. This approximation will be called (in analogy to the similar one made for the free-electron gas) the random-phase approximation (RPA).[3] To be explicit, the terms we have in mind are

$$\begin{aligned}K'=-\frac{2\pi\mu^2}{I\Omega}\sum_{\mathbf{k},\mathbf{k}'}\sum_l\Psi_k\Psi_{k'}\exp[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_l]&\\ \times\{\sin\alpha_k\sin\alpha_{k'}\sin(\phi_l-\beta_k)\sin(\phi_l-\beta_{k'})&\\ +[\cos\alpha_k\sin\theta_l-\cos\theta_l\sin\alpha_k\cos(\phi_l-\beta_k)]&\\ \times[\cos\alpha_{k'}\sin\theta_l-\cos\theta_l\sin\alpha_{k'}\cos(\phi_l-\beta_{k'})]&\\ -(I/M\mu^2)\mathbf{k}\cdot\mathbf{k}'(\boldsymbol{\mu}_l\cdot\hat{k})(\boldsymbol{\mu}_l\cdot\hat{k}')\}.&\qquad(28)\end{aligned}$$

Here the summation over $\mathbf{k}$ and $\mathbf{k}'$ is restricted to those pairs of values of $\mathbf{k}$ and $\mathbf{k}'$ whose magnitude is less than k_c and satisfying the condition $\mathbf{k}+\mathbf{k}'\neq0$. We rewrite Eq. (28) as

$$K'=\sum_{\mathbf{k}\mathbf{k}'l}\left(\frac{4\pi\mu^2}{\Omega I}\right)\exp[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_l]\Psi_k\Psi_k{}'F_l(\mathbf{k},\mathbf{k}'),\qquad(29)$$

where the definition of the function $F_l(\mathbf{k},\mathbf{k}')$ is obvious from a comparison of Eqs. (28) and (29). Let us assume that the ground state of

$$K-K'-K_p-K_{\text{int}}=\Xi\qquad(30)$$

is of the form

$$\Phi_0=\prod_l\phi_0(l),\qquad(31)$$

where $\phi_0(l)$ is the ground-state wave function of the lth molecule in the Hartree self-consistent field of all other molecules (excluding long-range interactions). We now define

$$\begin{aligned}\Phi_m(\mathbf{K})=N^{-1/2}\sum_{l'}\exp(i\mathbf{K}\cdot\mathbf{r}_{l'})\phi_0(1)\cdots\phi_0(l'-1)&\\ \times\phi_m(l')\phi_0(l'+1)\cdots\phi_0(N).&\qquad(32)\end{aligned}$$

Here $\phi_m(l)$ is the mth rotational state of the lth molecule. It is assumed that the number of molecules excited above their ground state into excited rotational states is so small that it does not appreciably alter the Hartree self-consistent field in which each molecule is supposed to move. In the absence of interaction, $\Phi_m(\mathbf{K})$ has an energy W_m-W_0 above the ground-state energy of the system. (W_m is the energy of a single molecule in its mth stationary state in the self-consistent field arising from the short-range interaction of the other molecules.) The ground state of

$$\Xi+K_p$$

is of the form $\Phi_0\Lambda_0$, where Λ_0 is the state in which $a_k{}^\dagger a_k\Lambda_0=0$ for all $\mathbf{k}$; i.e., the state with no excitations of the collective motion. Of course, this is only valid when we can regard the ω_k as being independent of the position of the molecules. Strictly speaking, this is not rigorously correct; but there can be no doubt that it is valid to a high degree of accuracy. The term K' connects the ground state Λ_0 with states with two distinct excitations because

$$\Psi_k\Psi_{k'}=(4\omega_k\omega_{k'})^{-1/2}(a_k+a_{-k}^{\dagger})(a_{k'}+a_{-k'}^{\dagger}),\qquad(33)$$

and

$$\mathbf{k}+\mathbf{k}'\neq 0.$$

We now assume that excitation of one molecule does not alter the Hartree self-consistent field of other molecules or its own. Thus we have, in particular,

$$\langle\phi_m(l)\mid\phi_{m'}(l)\rangle=\delta_{mm'}.\qquad(34)$$

Clearly, this approximation breaks down if a considerable fraction of the molecules are excited, but we shall not be concerned with that case.

From Eqs. (29) and (34) it follows that the only nonzero matrix elements of K' between the ground state $\phi_0(1)\phi_0(2)\cdots\phi_0(l)\cdots$ and states of the form $\phi_m(1)\phi_{m'}(2)\cdots\phi_{m''}(l)\cdots$ are those in which the latter is such that only one molecule is excited. Let us define the quantity $f_m(\mathbf{k},\mathbf{k}')$ by

$$\langle\phi_m(l)\mid F_l(\mathbf{k},\mathbf{k}')\mid\phi_0(l')\rangle=f_m(\mathbf{k},\mathbf{k}')\delta_{ll'}.\qquad(35)$$

We have made the further assumption that $\phi_m(l)$ and $\phi_0(l')$ do not overlap. We now calculate the matrix elements of K' for states Φ_0 [Eq. (31)] and $\Phi_m(\mathbf{K})$ [Eq. (32)]. We have

$$\begin{aligned}\langle\Phi_m(\mathbf{K})\mid K'\mid\Phi_0\rangle&=\sum_{kk'l}(4\pi\mu^2/\Omega I)\Psi_k\Psi_{k'}\langle\Phi_m(\mathbf{K})\mid\exp[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_l]F_l(\mathbf{k},\mathbf{k}')\mid\Phi_0\rangle\\&=\sum_{kk'}(4\pi\mu^2/\Omega I)\Psi_k\Psi_{k'}N^{-1/2}\sum_{ll'}\langle\phi_0(1)\cdots\phi_m(l')\cdots\phi_0(N)\mid F_l(\mathbf{k},\mathbf{k}')\\&\qquad\times\exp[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_l-i\mathbf{K}\cdot\mathbf{r}_{l'}]\mid\phi_0(1)\cdots\phi_0(l')\cdots\phi_0(N)\rangle.\end{aligned}$$

The matrix elements involved here can be simplified considerably by writing down the explicit integrations. Let the element of volume of the configuration space of one molecule be $d\mathbf{r}_l dw_l$, where dw_l represents the contribution arising from the rotational degrees of freedom. We have, for $l\gg l'$,

$$\begin{aligned}&\langle\phi_0(1)\cdots\phi_m(l')\cdots\phi_0(N)\mid F_l(\mathbf{k},\mathbf{k}')\exp[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_l-i\mathbf{K}\cdot\mathbf{r}_{l'})\mid\phi_0(1)\cdots\phi_0(l')\cdots\phi_0(N)\rangle\\&\qquad=\int d\mathbf{r}_l\int d\mathbf{r}_{l'}\exp[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_l-i\mathbf{K}\cdot\mathbf{r}_{l'}]\int dw_l\int dw_{l'}\phi_m^*(l')\phi_0^*(l)F_l(\mathbf{k},\mathbf{k}')\phi_0(l')\phi_0(l)\\&\qquad=0,\end{aligned}$$

since, from Eq. (34),

$$\int dw_{l'}\phi_m^*(l')\phi_0(l')=\delta_{m0}=0.$$

For $l=l'$

$$\begin{aligned}&\langle\phi_0(1)\cdots\phi_m(l)\cdots\phi_0(N)\mid F_l(\mathbf{k},\mathbf{k}')\exp[i(\mathbf{k}+\mathbf{k}'-\mathbf{K})\cdot\mathbf{r}_l]\mid\phi_0(1)\cdots\phi_0(N)\rangle\\&\qquad=\int d\mathbf{r}_l\exp[i(\mathbf{k}+\mathbf{k}'-\mathbf{K})\cdot\mathbf{r}_l]\int dw_l\phi_m^*(l)F_l(\mathbf{k},\mathbf{k}')\phi_0(l)\\&\qquad=\delta_{\mathbf{K},k+k'}f_m(\mathbf{k},\mathbf{k}').\end{aligned}$$

There are, of course, N terms of this form. Thus,

$$\langle\Phi_m(\mathbf{K})\mid K'\mid\Phi_0\rangle=(4\pi\mu^2/\Omega I)N^{1/2}\sum_k\Psi_k\Psi_{K-k}f_m(\mathbf{k},\mathbf{K}-\mathbf{k}).\qquad(36)$$

We notice that this is still an operator containing $\Psi_k\Psi_{K-k}$ which connects Λ_0 with a state containing two collective excitations ($\mathbf{K}\neq 0$). The change in the ground-state energy to second order in K' is

$$\Delta'=\sum_m\sum_{\mathbf{k},\mathbf{k}'}\frac{|\langle\Phi_m(\mathbf{K})\Lambda(\mathbf{k},\mathbf{k}')\mid K'\mid\Phi_0\Lambda_0\rangle|^2}{\omega_k+\omega_{k'}+W_m-W_0}.\qquad(37)$$

Here ω_k is the energy of a collective excitation (dipolar plasmon) of wave vector $\mathbf{k}$, W_m-W_0 is the excitation energy of a single molecule in state m and $\Lambda(\mathbf{k},\mathbf{k}')$ is a wave function characterizing the system when it has two dipolar plasmons with wave vectors $\mathbf{k}$ and $\mathbf{k}'$. We wish to find an upper bound for Δ'. We have

$$\Delta'<(2\omega_0)^{-1}\sum_{m,k',k''K}|\langle\Phi_m(\mathbf{K})\Lambda(\mathbf{k}',\mathbf{k}'')\mid K'\mid\Phi_0\Lambda_0\rangle|^2.\qquad(38)$$

The matrix element is

$$\langle\Phi_m(\mathbf{K})\Lambda(\mathbf{k}',\mathbf{k}'')\,|\,K'\,|\,\Phi_0\Lambda_0\rangle=(4\pi\mu^2/I\Omega)N^{1/2}\sum_k(\omega_k\omega_{K-k})^{-1/2}f_m(\mathbf{k},\mathbf{K}-\mathbf{k})\,\delta_{k',-k}\delta_{k'',-K+k}.$$

Hence

$$\Delta'<(2\omega_0)^{-1}\sum_m\sum_{kK}(4\pi\mu^2/I\Omega)^2N(\omega_k\omega_{K-k})^{-1}\,|f_m(\mathbf{k},\mathbf{K}-\mathbf{k})|^2,$$

and *a fortiori*

$$\Delta'<\sum_m\sum_{kK}(4\pi\mu^2/I\Omega)^2(2\omega_0^3)^{-1}N\,|f_m(\mathbf{k},\mathbf{K}-\mathbf{k})|^2. \tag{39}$$

Replacing $4\pi N\mu^2/I\Omega$ by ω_0^2, which is of the same order of magnitude, we find

$$\Delta_1<\sum_m\sum_{k,K}(\omega_0/8N)\,|f_m(\mathbf{k},\mathbf{K}-\mathbf{k})|^2.$$

One can easily establish a sum rule for the $f_m(\mathbf{k},\mathbf{k}')$ as follows:

$$\sum_m|f_m(\mathbf{k},\mathbf{k}')|^2=\sum_m\langle\phi_0(l)\,|\,F_l(\mathbf{k},\mathbf{k}')\,|\,\phi_m(l)\rangle\langle\phi_m(l)\,|\,F_l(\mathbf{k},\mathbf{k}')\,|\,\phi_0(l)\rangle$$

$$=\langle\phi_0(l)\,|\,F_l^2(\mathbf{k},\mathbf{k}')\,|\,\phi_0(l)\rangle.$$

The maximum value (as a function of $\mathbf{k}$ and $\mathbf{k}'$) of this quantity will be designated by f_M. Now we let N' be the number of dipolar plasmon degrees of freedom so that $\sum_{k'<k_c}1=N'$. Then we have

$$\Delta'<(N'/8N)N'\omega_0f_M. \tag{40}$$

From Eq. (28) it is easy to see that

$$f_M\lesssim4.$$

Thus, the ratio of Δ' to the zero-point energy of the dipolar plasmons is

$$(2\Delta'/N'\omega_0)<(N'/4N)\ll1.$$

This procedure justifies the use of the RPA for the ground state of the system.

Furthermore, we may place an upper bound on the shift of the ground-state energy of the system arising from the term K_{int} in the Hamiltonian which couples dipolar plasmons with the individual particle motions. We calculate this shift by perturbation theory to second order in the plasmon field operators, and after carrying out the intermediate sum over one-plasmon states, have left an operator depending only on the single-particle momenta. By averaging this operator in the classical equilibrium ensemble at temperature T we obtain an upper bound to the shift. We find in this way that $\langle K_{\text{int}}\rangle<(k_BT/\omega_0)\,\Sigma_{k<k_c}(\omega_k/2)$, where k_B is the Boltzmann constant.

B. Equation of Motion of the Polarization Charge Density

In this section we treat the dynamics of the polarization charge density and discuss the conditions under which its Fourier components vary harmonically in time and, hence, are suitable collective coordinates of the system. The polarization charge density is

$$\rho(\mathbf{r})=-\nabla\cdot\mathbf{P}(\mathbf{r}), \tag{41}$$

and has Fourier components

$$\rho(\mathbf{k})=(-i/\Omega)\,\textstyle\sum_l\mathbf{k}\cdot\boldsymbol{\mu}_l\exp(-i\mathbf{k}\cdot\mathbf{r}_l). \tag{42}$$

The quantum-mechanical equation of motion for ρ is

$$\ddot{\rho}(\mathbf{k})=-[\mathcal{H},[\mathcal{H},\rho(\mathbf{k})]]. \tag{43}$$

The classical equation of motion is obtained by the correspondence, for any quantities A, B,

$$[A,B]\rightarrow i[A,B]_{\text{P.B.}}, \tag{44}$$

where P.B. means Poisson bracket. Using Eqs. (3) and (42), the Hamiltonian of Eq. (2) becomes

$$\mathcal{H}=\sum_l\left(\frac{P_{l\theta}^2}{2I}+\frac{P_{l\phi}^2}{2I\sin^2\theta_l}+\frac{\mathbf{P}_l^2}{2M}\right)+\sum_k\left(\frac{2\pi\Omega}{k^2}\right)\rho(\mathbf{k})\rho(-\mathbf{k})-\sum_{l,k}\left(\frac{2\pi}{\Omega}\right)(\boldsymbol{\mu}_l\cdot\hat{k})^2+\tfrac{1}{2}\sum_{l\neq l'}U_{ll'}. \tag{45}$$

The meanings of the terms in $\mathcal{H}$ are the same as in the previous sections. The third term on the right-hand side is the self-energy term for the dipoles and is a constant that we shall disregard. The fourth term is a short-range interaction between molecules, and can affect the frequency of the charge-density fluctuations only at large $\mathbf{k}$. Accordingly, since we concentrate on the long-wavelength limit, we neglect $U_{ll'}$. Choosing the polar axis parallel to $\mathbf{k}$, we find

$$\ddot{\rho}(\mathbf{k})=\frac{ik\mu}{\Omega}\sum_l \exp(-i\mathbf{k}\cdot\mathbf{r}_l)\biggl[\cos\theta_l(\mathbf{k}\cdot\mathbf{v}_l)^2+\cos\theta_l(\dot{\theta}_l)^2$$

$$+\frac{P_{l\phi}{}^2\cos\theta_l}{I^2\sin^2\theta_l}-2i(\mathbf{k}\cdot\mathbf{v}_l)\dot{\theta}_l\sin\theta_l\biggr]$$

$$-\sum_{l,k'}\frac{4\pi\mu^2k}{I\Omega k'}\exp\{i(\mathbf{k}-\mathbf{k})\cdot\mathbf{r}_l\}[\sin\theta_l\sin(\mathbf{k}',\boldsymbol{\mu}_l)$$

$$+(I\mathbf{k}\cdot\mathbf{k}'/M)\cos\theta_l\cos(\mathbf{k}',\boldsymbol{\mu}_l)]\rho(\mathbf{k}'),\quad(46)$$

where $\mathbf{v}_l$ is the velocity of the center of mass of the lth molecule. In the RPA, the summation in $\mathbf{k}'$ is replaced by the single term in which $\mathbf{k}'=\mathbf{k}$. We then have

$$\ddot{\rho}(\mathbf{k})=-\frac{4\pi\mu^2}{I\Omega}\sum_l\left(\sin^2\theta_l+\left(\frac{Ik^2}{M}\right)\cos^2\theta_l\right)\rho(\mathbf{k})$$

$$+\sum_l\exp(-i\mathbf{k}\cdot\mathbf{r}_l)(i/\Omega)\mathbf{k}\cdot\boldsymbol{\mu}_l\{(\dot{\theta}_l)^2+\phi_l{}^2\sin^2\theta_l$$

$$+(\mathbf{k}\cdot\mathbf{v}_l)^2-2i(\mathbf{k}\cdot\mathbf{v}_l)\dot{\theta}_l\tan\theta_l\}.\quad(47)$$

We now linearize Eq. (47) by taking averages in the equilibrium ensemble[5] as follows:

$$\ddot{\rho}(\mathbf{k})=-(4\pi\mu^2/I\Omega)\sum_l\langle\sin^2\theta_l+(k^2I/M)\cos^2\theta_l\rangle\rho(\mathbf{k})$$

$$-\sum_l(-i/\Omega)\mathbf{k}\cdot\boldsymbol{\mu}_l\exp(-i\mathbf{k}\cdot\mathbf{r}_l)$$

$$\times\langle\dot{\theta}_l{}^2+\phi_l{}^2\sin^2\theta_l+(\mathbf{k}\cdot\mathbf{v}_l)^2-2i(\mathbf{k}\cdot\mathbf{v}_l)\dot{\theta}_l\tan\theta_l\rangle.$$

Since the indicated averages are independent of l, we obtain

$$\ddot{\rho}(k)=-\{(4\pi N\mu^2/\Omega I)\langle\sin^2\theta+(k^2I/M)\cos^2\theta\rangle$$

$$+\langle\dot{\theta}^2+\dot{\phi}^2\sin^2\theta+(\mathbf{k}\cdot\mathbf{v})^2\rangle\}\rho(\mathbf{k}),\quad(48)$$

the averages being for one molecule. Since we have no velocity-dependent potentials, the classical average of the second term in Eq. (48) can be obtained using the equipartition principle. We then have

$$\ddot{\rho}(\mathbf{k})=-\omega_k{}^2\{1+(k_BT/I\omega_k{}^2)[2+(k^2/I/M)]\}\rho(\mathbf{k}),\quad(49)$$

where k_B is Boltzmann's constant and T the absolute temperature. The second term is negligible. For example, for water we should have $(I\omega_k{}^2/2k_B)=3000°\text{K}$. The quantum-mechanical average in the second term of Eq. (48) is always smaller than the classical, and hence we can always neglect this term. Finally then,

$$\ddot{\rho}(\mathbf{k})=-\omega_k{}^2\rho(\mathbf{k}),\quad(50)$$

with

$$\omega_k{}^2=(4\pi N\mu^2/I\Omega)\langle\sin^2\theta+(k^2I/M)\cos^2\theta\rangle.\quad(51)$$

III. DIELECTRIC RESPONSE OF A DIPOLAR SYSTEM

A. General Results

The dielectric behavior of a gas of interacting electrons is well known.[6,7] We first sketch the linear-response theory for a system having an arbitrary distribution of electric charge in order to emphasize the complete generality of the results, and then specialize to the present case of neutral dipoles.

We are concerned with the response of our system to a small perturbation produced by an external charge distribution $\rho_{\text{ext}}(\mathbf{r},t)$. To first order in the perturbation the induced charge ρ_{ind} is related to ρ_{ext} by

$$\epsilon^{-1}(\mathbf{k},\omega)-1=\{\rho_{\text{ind}}(\mathbf{k},\omega)/\rho_{\text{ext}}(\mathbf{k},\omega)\},\quad(52)$$

where $\rho(\mathbf{k},\omega)$ is the Fourier transform with respect to space and time of $\rho(\mathbf{r},t)$, and $\epsilon(\mathbf{k},\omega)$ is the dielectric function of the system. The external charge is assumed proportional to $\exp(i[\mathbf{k}\cdot\mathbf{r}-(\omega+i\delta)t])$, where δ is a positive infinitesimal which ensures that the perturbation is turned on adiabatically. The total charge density is the trace of the product of charge-density operator of Eq. (42) and the density matrix f of the system in the presence of the external perturbation. If we write $f=f_0+f_1(t)$, where f_0 is the equilibrium density matrix in the absence of ρ_{ext}, then we have

$$\exp[-i(\omega+i\delta)t]\rho_{\text{ind}}(\mathbf{k},\omega)=\text{Tr}\{\rho(\mathbf{k})f_1(t)\}.\quad(53)$$

$f_1(t)$ is obtained from the equation of motion

$$i(\partial f/\partial t)=[\mathcal{H}+\mathcal{H}',f],\quad(54)$$

where

$$\mathcal{H}'(t)=\int d^3r\,V_{\text{ext}}(\mathbf{r},t)\rho(\mathbf{r})$$

$$=\exp[-i(\omega+i\delta)t](4\pi\Omega/k^2)\rho(-\mathbf{k})\rho_{\text{ext}}(\mathbf{k},\omega)\quad(55)$$

is the interaction with the potential V_{ext} produced by ρ_{ext}. Note that in Eq. (55) $\rho_{\text{ext}}(\mathbf{k},\omega)$ is a c number while $\rho(-\mathbf{k})$ is an operator in the Schrödinger representation. Within linear response theory we have

$$i(\partial f_1/\partial t)=[\mathcal{H},f_1]+[\mathcal{H}',f_0],\quad(56)$$

whose solution is

$$f_1(t)=i\int_{-\infty}^{t}dt'\exp\{-i\mathcal{H}(t-t')\}[f_0,\mathcal{H}'(t')]$$

$$\times\exp\{i\mathcal{H}(t-t')\}.\quad(57)$$

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[5] See, e.g., D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1961), pp. 44–48.

[6] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, 8 (1954).

[7] P. Nozieres and D. Pines, Nuovo Cimento **9**, 470 (1958); also D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), Sec. 3.4.

Equations (52), (53), and (57) then give

$$\epsilon^{-1}(\mathbf{k},\omega)-1=(4\pi\Omega/k^2)\int_0^\infty dt\,\exp[i(\omega+i\delta)t] \times\langle i[\rho(-\mathbf{k},0),\rho(\mathbf{k},t)]\rangle. \tag{58}$$

Here, as usual,

$$\langle A\rangle=\mathrm{Tr}(f_0A) \tag{59}$$

and

$$\rho(\mathbf{k},t)=\exp(i\mathcal{H}t)\rho(\mathbf{k})\exp(-i\mathcal{H}t). \tag{60}$$

The asymptotic expansion of $\epsilon^{-1}(\mathbf{k},\omega)$ is obtained from Eq. (58) on integrating with respect to t by parts twice. Using Eq. (60) and noting that $[\rho(-\mathbf{k},0),\rho(\mathbf{k},0)]=0$ we find

$$\epsilon^{-1}(\mathbf{k},\omega)-1\sim-\frac{4\pi\Omega}{k^2}\frac{1}{\omega^2}\langle[\rho(-\mathbf{k}),[\rho(\mathbf{k}),\mathcal{H}]]\rangle +O(\omega^{-3}). \tag{61}$$

A sum rule then follows by exactly the same steps used for the electron gas, and is

$$\int_{-\infty}^\infty d\omega\,\omega\epsilon^{-1}(\mathbf{k},\omega)=2i\int_0^\infty d\omega\,\omega\mathrm{Im}\epsilon^{-1}(\mathbf{k},\omega) =i\pi(4\pi\Omega/k^2)\langle[\rho(-\mathbf{k}),[\rho(\mathbf{k}),\mathcal{H}]]\rangle. \tag{62}$$

That part of the total interaction energy at equilibrium which is due to the explicit intermolecular Coulomb interactions may be expressed in terms of $\epsilon(\mathbf{k},\omega)$. Understanding that self-energy terms [e.g., as in Eq. (45)] must eventually be subtracted, we write

$$E_c'\equiv\tfrac{1}{2}\sum_{\mathbf{k}}(4\pi\Omega/k^2)\langle\rho(-\mathbf{k})\,\rho(\mathbf{k})\rangle =\tfrac{1}{4}\sum_{\mathbf{k}}(4\pi\Omega/k^2)\langle\{\rho(-\mathbf{k},0),\rho(\mathbf{k},\eta)\}\rangle, \tag{63}$$

where the curly bracket indicates an anticommutator and η is a positive infinitesimal. Using only a fluctuation-dissipation theorem[8] and the symmetry of $\epsilon(\mathbf{k},\omega)$, we find[9]

$$E_c'=-\int_0^\infty\frac{d\omega}{2\pi}\sum_{\mathbf{k}}\hbar\coth(\tfrac{1}{2}\beta\hbar\omega)\,\mathrm{Im}\epsilon^{-1}(\mathbf{k},\omega), \tag{64}$$

where $\beta=(1/k_BT)$. We restore $\hbar$ in this and in succeeding interaction, energy formulas in order to make passage to the classical limit clearer. In the quantum limit $(T\rightarrow0)$,

$$E_c'=-\hbar\int_0^\infty\frac{d\omega}{2\pi}\sum_{\mathbf{k}}\mathrm{Im}\epsilon^{-1}(\mathbf{k},\omega), \tag{65}$$

which has the same form as occurs in the ground-state interaction energy of the electron gas.[10] In the classical limit $(\hbar\rightarrow0)$,

$$E_c'=-k_BT\int_0^\infty\frac{d\omega}{\pi\omega}\sum_{\mathbf{k}}\mathrm{Im}\epsilon^{-1}(\mathbf{k},\omega). \tag{66}$$

These expressions, in particular Eqs. (58), (61), (62), and (64), are completely general and hold for an arbitrary distribution of system change.

We now specialize to the present case, and, using Eqs. (2) and (42), we find

$$[\rho(-\mathbf{k}),[\rho(\mathbf{k}),\mathcal{H}]] =-(k^2\mu^2/I\Omega^2)\sum_l\{\sin^2\theta_l+(k^2I/M)\cos^2\theta_l\}. \tag{67}$$

Equations (61) and (62) become

$$\epsilon^{-1}(\mathbf{k},\omega)-1\rightarrow(\omega_k^2/\omega^2)+O(\omega^{-3}), \tag{68}$$

and

$$\int_0^\infty d\omega\,\omega\,\mathrm{Im}\epsilon^{-1}(\mathbf{k},\omega)=-\tfrac{1}{2}\pi\omega_k^2. \tag{69}$$

It is shown in Appendix A that Eqs. (67) through (69) hold for dipolar molecules of arbitrary rotational symmetry and dipole orientation when $(1/I)$ in Eq. (67) is supplanted by an appropriate average of the inverse principal moments of inertia. The dipole-dipole interaction energy at equilibrium is

$$E_{\mathrm{dipole}}=-\sum_{\mathbf{k}}\left\{\int_0^\infty\frac{d\omega}{2\pi}\hbar\coth(\tfrac{1}{2}\beta\hbar\omega)\,\mathrm{Im}\epsilon^{-1}(\mathbf{k},\omega) +2\pi(N/\Omega)\mu^2\langle\cos^2\theta\rangle\right\}. \tag{70}$$

In subtracting off the self-energy, we have assumed the system to be homogeneous. The dielectric function itself follows immediately on using Eq. (42) in Eq. (58).

We illustrate the connection of these expressions to the work of the preceding section by a simple example. Linearization of the equations of motion is, by Eqs. (43) and (50), equivalent to taking

$$[\mathcal{H},[\mathcal{H},\rho(\mathbf{k})]]\approx\omega_k^2\rho(\mathbf{k}). \tag{71}$$

It we assume Eq. (71) to be *exact*, then we easily find from Eq. (60)

$$\rho(\mathbf{k},t)=\cos(\omega_kt)\rho(\mathbf{k})+(1/\omega_k)\sin(\omega_kt)i[\mathcal{H},\rho(\mathbf{k})], \tag{72}$$

and, noting Eq. (67),

$$\frac{4\pi\Omega}{k^2}\langle i[\rho(-\mathbf{k},0),\rho(\mathbf{k},t)]\rangle =\frac{\sin(\omega_kt)}{\omega_k}\frac{4\pi\Omega}{k^2}\langle[\rho(-\mathbf{k}),[\rho(\mathbf{k}),\mathcal{H}]]\rangle =-\omega_k\sin(\omega_kt). \tag{73}$$

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[8] Only Eq. (B1) of Appendix B is required.

[9] See R. Brout and P. Carruthers [*Lectures on the Many-Electron Problem* (John Wiley & Sons, Inc., New York, 1963), p. 132] for a similar derivation for the electron gas.

[10] D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1961), p. 43.

We then have from Eq. (58)

$$\epsilon^{-1}(\mathbf{k},\omega)-1=\tfrac{1}{2}\omega_{\mathrm{k}}\{(\omega-\omega_{\mathrm{k}}+i\delta)^{-1}-(\omega+\omega_{\mathrm{k}}+i\delta)^{-1}\},$$

and hence

$$\mathrm{Im}\,\epsilon^{-1}(\mathbf{k},\omega)=-(\pi/2)\omega_k\{\delta(\omega-\omega_k)-\delta(\omega+\omega_k)\},\qquad(74)$$

$$\mathrm{Re}\,\epsilon(\mathbf{k},\omega)=1-(\omega_k^2/\omega^2).\qquad(75)$$

Equation (74) together with Eq. (70) gives the interaction energy associated with the dipolar plasmons as

$$E_{\mathrm{dipole,plasmon}}$$

$$=\sum_{|\mathrm{k}|<k_c}\{\tfrac{1}{4}\hbar\omega_{\mathrm{k}}\coth(\tfrac{1}{2}\beta\hbar\omega_k)-2\pi(N/\Omega)\mu^2\langle\cos^2\theta\rangle\}\qquad(76)$$

$$=\sum_{k<k_c}\{\tfrac{1}{4}\hbar\omega_k-2\pi(N/\Omega)\mu^2\langle\cos^2\theta\rangle\}\qquad(T\to0)\qquad(77)$$

$$=N'\{\tfrac{1}{2}k_BT-2\pi(N/\Omega)\mu^2\langle\cos^2\theta\rangle\}\qquad(\hbar\to0).\qquad(78)$$

Just as we should expect, the dipolar plasma frequency is a root of the dielectric function,[11] and interaction energy in the quantum limit is the exact analog of the corresponding expression for the electron gas.[10]

We shall carry the general discussion no further. We are dissuaded from attempting a diagrammatic analysis of the inverse dielectric function by the following circumstances: In a quantum-mechanical treatment, since the angular-momentum operators with which we must perforce deal have many eigenstates and do not have *c*-number commutators, no simple form of Wick's theorem or of a linked cluster expanlon exists. Some progress has recently been made in this respect, but not yet enough to facilitate the present work.[12] A similar complication of course carries over to the classical regime. Some graphical analysis of the *static* dielectric constant indeed exists,[13] but only up to the inclusion, for practical purposes, of ring or chain diagrams; and this results in a Clausius-Mosotti formula with concomitant peril of a ferroelectric catastrophe. Accordingly, we now turn to a simpler method of reducing calculations of $\epsilon(\mathbf{k},\omega)$ to tractable proportions.

B. Self-Consistent Field Approximation

In this section we address ourselves to reducing the general expression for $\epsilon(\mathbf{k},\omega)$ to a form on which practical calculation could be based. In the classical limit and for the static dielectric response this problem was long ago solved by the work of Onsager[14] and of Kirkwood,[15] and extension to finite frequency was later treated by Glarum.[16] Here we wish not only to retain quantum-mechanical validity, but also to allow for dispersion and center-of-mass motion. We must be careful to avoid introducing a spurious ferroelectric catastrophe, and commence by showing how this could most simply arise in the present formalism. It is sufficient to consider the classical limit of Eq. (58) for $\omega=0$, which with the help of Eq. (B3) of Appendix B is seen to be

$$\epsilon^{-1}(\mathbf{k},0)-1=-(4\pi\Omega/k^2)(1/k_BT)\langle\rho(-\mathbf{k})\rho(\mathbf{k})\rangle.\qquad(79)$$

If now all interactions between molecules were neglected, then

$$\epsilon^{-1}(\mathbf{k},0)-1=\epsilon^{-1}(0,0)-1=-(4\pi N\mu^2/3\Omega k_BT),\qquad(80)$$

which would indicate a ferroelectric Curie point at $T_c=(4\pi N\mu^2/3\Omega k_B)$. The precise parallel to this situation exists in the uniform electron gas, in which case neglect of all many-electron interactions would lead,[7] at long wavelength, to $\epsilon^{-1}(k,0)-1=(k_s^2/k^2)$ instead of the correct form $\epsilon(k,0)=1+(k_s^2/k^2)$. One well-known cure for this disease, in the electron gas, is to treat the electron-electron interactions by self-consistent first-order perturbation theory,[17] and we adopt this approach for the present case of dipolar systems.

The effective field to which a dipole responds is not the macroscopic field in the medium, in contrast to the case in the electron gas. As first pointed out by Onsager,[14] the reaction field[18] must be excluded. Hence we shall assume that each dipole responds to a generalized cavity field[18] which we further take to be of the form $\gamma(\mathbf{k},\omega)V_{\mathrm{SCF}}(\mathbf{k},\omega)$. We do not here enter into discussion of the form of γ for general $\mathbf{k}$, ω. We choose a form which is consistent with Glarum's results,[16] and for long wavelengths shall take

$$\gamma(\mathbf{k},\omega)=[2\epsilon_0+\epsilon(\mathbf{k},\omega)]/(2\epsilon_0+1),\qquad(81)$$

where ϵ_0 denotes the static dielectric constant at infinite wavelength. In the static limit ($\omega=0$), γ reduces to the proportionality constant $[3\epsilon_0/(2\epsilon_0+1)]$ of the Onsager cavity field.

Our self-consistent-field approximation consists of replacing the interactions with the external field together with those due to long-range dipole-dipole forces by an interaction of the charge density with the generalized cavity field. The induced charge in the system is then taken to be that produced by the linear response to an interaction of the form of Eq. (55) but with $\rho_{\mathrm{ext}}(\mathbf{k},\omega)$ replaced by $\gamma(\mathbf{k},\omega)\rho_{\mathrm{SCF}}(\mathbf{k},\omega)$, where $\rho_{\mathrm{SCF}}(\mathbf{k},\omega)$ produces the macroscopic field in the medium. In consequence we have

$$\rho_{\mathrm{ind}}(\mathbf{k},\omega)=-4\pi\gamma(\mathbf{k},\omega)\alpha(\mathbf{k},\omega)\rho_{\mathrm{SCF}}(\mathbf{k},\omega),\qquad(82)$$

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[11] D. Pines, Ref. 10, p. 42.

[12] B. Giovanni and S. Koide, Progr. Theoret. Phys. (Kyoto) **34**, 705 (1965); Y.-L. Wang and H. B. Callen, Phys. Rev. **148**, 433 (1966); T. Arai and B. Goodman, Bull. Am. Phys. Soc. **12**, 134 (1967).

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[14] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

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[16] S. H. Glarum, J. Chem. Phys. **33**, 1371 (1960).

[17] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

[18] For discussion of static reaction and cavity fields, see H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, London, 1958), 2nd ed.

where

$$\alpha(\mathbf{k},\omega)=-\left(\frac{\Omega}{k^2}\right)\int_0^\infty dt\, e^{i\omega t}\langle i[\rho(-\mathbf{k},0),\rho(\mathbf{k},t)]\rangle' \tag{83}$$

is the polarizability of the system. As indicated by the prime on the angular bracket, those long-range terms which have been incorporated into the self-consistent field are now to be omitted from the Hamiltonian used in generating the time evolution in $\rho(\mathbf{k},t)$ and in the density matrix involved in the thermal trace. For consistency we require

$$\rho_{\mathrm{SCF}}(\mathbf{k},\omega)=\rho_{\mathrm{ind}}(\mathbf{k},\omega)+\rho_{\mathrm{ext}}(\mathbf{k},\omega), \tag{84}$$

and hence obtain

$$\epsilon(\mathbf{k},\omega)=1+4\pi\gamma(\mathbf{k},\omega)\alpha(\mathbf{k},\omega), \tag{85}$$

as our expression for the dielectric function in the self-consistent-field approximation. Substitution of Eq. (81) into Eq. (85) gives

$$\frac{\epsilon(\mathbf{k},\omega)-1}{\epsilon(\mathbf{k},\omega)+2\epsilon_0}=\frac{4\pi\alpha(\mathbf{k},\omega)}{2\epsilon_0+1}. \tag{86}$$

The asymptotic expansion of $\epsilon(\mathbf{k},\omega)$ as obtained from that of $\alpha(\mathbf{k},\omega)$ and Eq. (86) is consistent with Eq. (61) and, in the case of linear molecules, agrees with Eq. (68). If we neglect short-range interactions, so that the polarizability given by Eq. (83) is that of free dipolar molecules, we find in the classical limit

$$\epsilon_0=1+\frac{3\epsilon_0}{2\epsilon_0+1}\frac{4\pi N\mu^2}{3\Omega k_BT}, \tag{87}$$

which is just Onsager's result for rigid dipoles.

The dipolar plasma frequencies are given by the zeros of $\epsilon(\mathbf{k},\omega)$ at given $\mathbf{k}$. To exhibit this behavior explicitly it suffices to neglect all short-range interactions and calculate the classical polarizability $\alpha_0(k,\omega)$ of a system of free rotators. Details of this calculation for linear and for spherically symmetric rotators are given in the Appendix B. It is there shown that for $\omega\gg(2k_BT/I)^{1/2}$

$$4\pi\left(\frac{N}{\Omega}\right)\alpha_0(k,\omega)\to-\frac{1}{\omega^2}\frac{8\pi N\mu^2}{3\Omega I}\left(1+\frac{k^2I}{2M}\right)\equiv-\frac{\omega_k^2}{\omega^2}. \tag{88}$$

The corresponding dipolar plasmon frequency is

$$\omega_{\mathrm{pl}}(k)=[2\epsilon_0/(2\epsilon_0+1)]^{1/2}\omega_k. \tag{89}$$

Indeed, we must expect Eq. (89) to hold for molecules of arbitrary rotational symmetry and dipole orientation, I then being a suitable average, as discussed below Eq. (69) and in Appendix A. In a system of free rotators the "natural frequencies" of significance in the equilibrium ensemble are measured by the thermal frequency $\omega_T\equiv(2k_BT/I)^{1/2}$, and the polarizability is adequately represented by its asymptotic expansion whenever $\omega\gg\omega_T$. As noted below Eq. (49), we commonly have $(\omega_k^2/\omega_T^2)\gg1$ in cases of interest, so that $\epsilon(k,\omega)$ will have a root given by Eq. (89). We see further that $\omega_{\mathrm{pl}}(k)$ is nearly equal to ω_k for condensed systems of such dipolar molecules. In systems for which (ω_k/ω_T) is only moderately large, the dipolar plasmon will still be a well-defined collective mode, but the frequency will be somewhat shifted by thermal damping effects.

We show in Fig. 1 the real and imaginary parts of the dielectric function, as given by the formulas of Appendix B, for $\epsilon_0=10$. In Fig. 2 we plot $\{-\mathrm{Im}\,\epsilon^{-1}(0,\omega)\}$ as a measure of the absorption, and in Fig. 3 plot the reflectivity. As the figures show, there is a substantial shift, due to thermal damping, of the frequency at peak absorption from $\omega_{\mathrm{pl}}(k)$, as given by Eq. (89). It should be borne in mind that these calculations assume rigid dipoles and hence do not apply quantitatively to real systems in which the polarizability of individual molecules must be taken into account. They do indicate, however, the effects of collective dipolar modes to be expected in the optical constants of dipolar systems such as HCl and SO_2. These modes should also be detectable in studies of Raman scattering in dipolar systems.

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APPENDIX A

We here evaluate the double commutator of Eq. (62) when the kinetic-energy operator has the form

$$T\equiv\sum_l\{(2M)^{-1}p_l^2+\sum_{j=1}^3(2I_j)^{-1}L_{l,j}^2\}, \tag{A1}$$

where I_j is a principal moment of inertia and $L_{l,j}$ the corresponding component of the angular momentum. Using (A1) and Eq. (42)

$$[\rho(-\mathbf{k}),[\rho(\mathbf{k}),T]]=(k^2/\Omega^2)\sum_l\{-(k^2/M)(k\cdot\boldsymbol{\mu}_l)^2$$
$$+[\hat{k}\cdot\boldsymbol{\mu}_l,[\hat{k}\cdot\boldsymbol{\mu}_l,\sum_j(2I_j)^{-1}L_{l,j}]]\}. \tag{A2}$$

Suppressing the index l, we first suppose $\boldsymbol{\mu}$ to be directed along a principal axis of inertia which we choose to be the 3 axis. On introducing Euler angles α, β, γ and expressing the L_j in terms of the conjugate momenta

p_α, p_β, p_γ,[19] we find

$$[L_1, \hat{k}\cdot\boldsymbol{\mu}]=i(\hat{k}\times\boldsymbol{\mu})_1,$$

$$[L_2, \hat{k}\cdot\boldsymbol{\mu}]=i(\hat{k}\times\boldsymbol{\mu})_2,$$

$$[L_3, \hat{k}\cdot\boldsymbol{\mu}]=i(k\times\boldsymbol{\mu})_3=0.$$

We can choose $\boldsymbol{\mu}$ to lie along each principal axis in turn and obtain the same result merely by relabeling axes, and hence we have

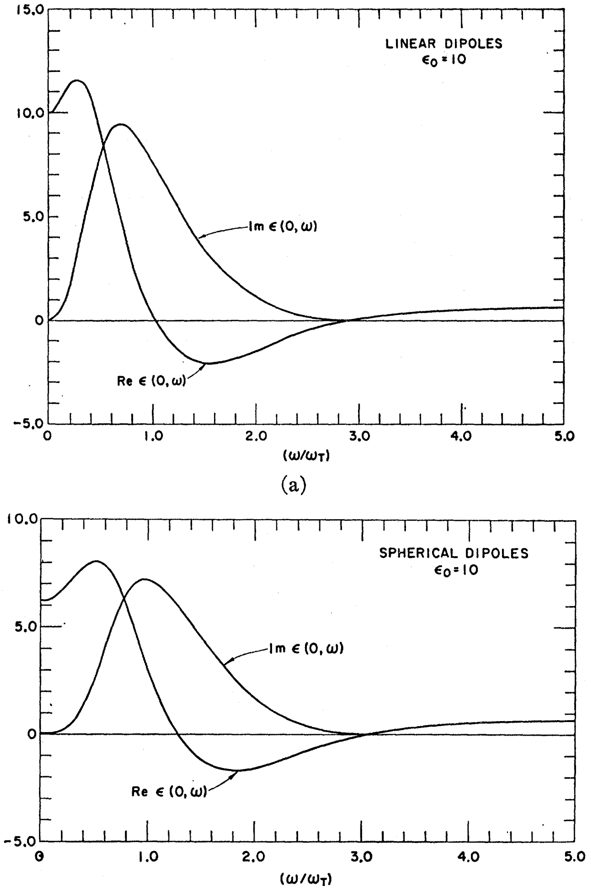
$$[L_j, \hat{k}\cdot\boldsymbol{\mu}]=i(\hat{k}\times\boldsymbol{\mu})_j \tag{A3}$$

for arbitrary orientation of $\boldsymbol{\mu}$ in its molecule. It follows directly that

$$[\hat{k}\cdot\boldsymbol{\mu}, [\hat{k}\cdot\boldsymbol{\mu}, \sum_j (2I_j)^{-1}L_j^2]]=-\sum_j (\hat{k}\times\boldsymbol{\mu})_j^2(I_j)^{-1}. \tag{A4}$$

The general sum rule for homogeneous dipolar systems is therefore

$$\frac{2}{\pi}\int_0^\infty d\omega\, \omega\, \mathrm{Im}\epsilon^{-1}(\mathbf{k}, \omega)=-\frac{4\pi N\mu^2}{\Omega}\left\{\frac{k^2}{M}\langle(\hat{k}\cdot\hat{u})^2\rangle + \langle(\hat{k}\times\hat{\mu})\cdot I^{-1}\cdot(\hat{k}\times\hat{\mu})\rangle\right\}, \tag{A5}$$



(a)

(b)

FIG. 1. Real and imaginary parts of the dielectric function at infinite wavelength, $\epsilon(0, \omega)$, for rigid dipoles calculated in the SCF approximation, Eq. (86), for a static dielectric constant $\epsilon_0=10$. $\omega_T=(2k_B\rangle T/I)^{1/2}$. Thermal damping shifts the zero of $\mathrm{Re}\epsilon(0,\omega)$ from the value $(\omega/\omega_T)=\sqrt{6}$ given by the asymptotic expansion, Eq. (88). (a) Linear rotators. (b) Spherical rotators. Note that in this case $6.3=\lim_{\omega\to 0} \epsilon(0, \omega) \neq \lim_{k\to 0} \epsilon(k, 0)=10$. (See Appendix B.)

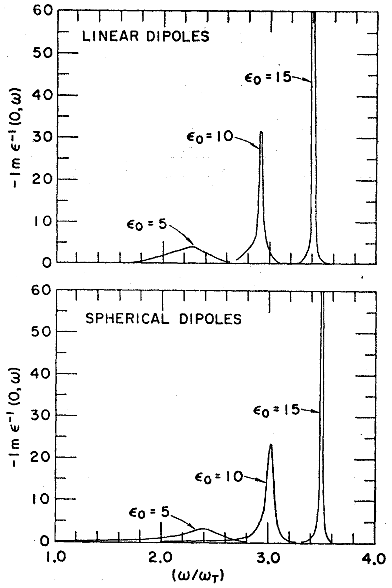


FIG. 2. Absorption at infinite wavelength for rigid dipoles, as measured by $\{-\mathrm{Im}\ \epsilon^{-1}(0,\omega)\}$ and for the indicated static dielectric constants. The height of the maximum for $\epsilon_0=15$ is 343.1 for linear rotators and 221.6 for spherical rotators.

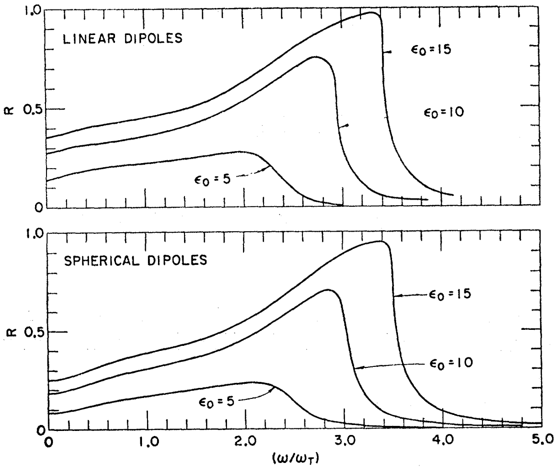


FIG. 3. Reflectivity of a system of rigid dipoles in the SCF approximation for the indicated static dielectric constants.

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[19] See, e.g., A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), Secs. 1.3 and 2.2.

where I^{-1} is the inverse inertial tensor. The quadratic form $(\hat{k}\times\hat{\mu})\cdot I^{-1}\cdot(\hat{k}\times\hat{\mu})$ is the inverse moment of inertia for an axis of rotation $(\hat{k}\times\hat{\mu})$ and is proportional to $|(\hat{k}\times\hat{\mu})|^2=\sin^2\theta$; it may be diagonalized as follows: Let ϑ, φ be the polar and azimuthal angles of $\hat{\mu}$ relative to the principal axes of inertia (1, 2, 3) with the 3 axis polar. Successive rotations by Euler angles $\alpha'=\varphi$, $\beta'=\vartheta$, $\gamma'=(\pi/4)$ produce a coordinate system $(1', 2', 3')$ with $\hat{\mu}$ as polar axis and in which

$$(\hat{k}\times\hat{\mu})\cdot I^{-1}\cdot(\hat{k}\times\hat{\mu})=(\hat{k}_{2'})^2(I^{-1})_{1'1'}+(\hat{k}_{1'})^2(I^{-1})_{2'2'}, \tag{A6}$$

where

$$(I^{-1})_{1'1'}=(1/2)\{(1/I_1)(\cos\vartheta\cos\varphi-\sin\varphi)^2 +(1/I_2)(\cos\vartheta\sin\varphi+\cos\varphi)^2+(\sin^2\vartheta/I_3)\}, \tag{A7a}$$

$$(I^{-1})_{2'2'}=(1/2)\{(1/I_1)(\cos\vartheta\cos\varphi+\sin\varphi)^2 +(1/I_2)(\sin\varphi-\cos\varphi)^2+(\sin^2\vartheta/I_3)\}, \tag{A7b}$$

and

$$\hat{k}_{1'}=\sin\theta\cos\varphi, \qquad \hat{k}_{2'}=\sin\theta\sin\varphi. \tag{A8}$$

Reductions in special cases are trivial. For example, for free rotation

$$\begin{aligned}\langle(\hat{k}\times\hat{\mu})\cdot I^{-1}\cdot(\hat{k}\times\hat{\mu})\rangle &=(1/3)\{(1/I_1)(1-\sin^2\vartheta\cos^2\varphi) +(1/I_2)(1-\sin^2\vartheta\sin^2\varphi)+(\sin^2\vartheta/I_3)\},\\ &=(1/3)\{(1/I_1)(1-\hat{\mu}_1^2)+(1/I_2)(1-\hat{\mu}_2^2) +(1/I_3)(1-\hat{\mu}_3)^2\}.\end{aligned} \tag{A9}$$

Equations (67) through (69) follow on taking $I_1=I_2=I$, $I_3=\infty$, and $\beta'=0$ in the relevant equations above.

APPENDIX B

We here calculate the polarizability $\alpha_0(\mathbf{k}, \omega)$ of a collection of identical, noninteracting dipoles in the classical limit. The calculation is considerably simplified by first making use of the relation, for any two operators A and B,

$$\int_{-\infty}^{\infty} dt\exp(i\omega t)\,\langle(i/\hbar)[A, B(t)]\rangle =-\tanh(\tfrac{1}{2}\beta\hbar\omega)\int_{-\infty}^{\infty} dt\exp(i\omega t)\,\langle(i/\hbar)\{A, B(t)\}\rangle, \tag{B1}$$

which is the heart of the fluctuation-dissipation theorem.[20] Equation (B1) implies the formal equivalence

$$\langle(1/i\hbar)[A, B(t)]\rangle =-(1/\hbar)\tan(\tfrac{1}{2}\beta\hbar(\partial/\partial t))\langle\{A, B(t)\}\rangle, \tag{B2}$$

which in the classical limit ($\hbar\rightarrow0$) is simply

$$\langle[A, B(t)]\rangle=-\beta(\partial/\partial t)\langle A\quad B(t)\rangle. \tag{B3}$$

In Eq. (B3) and throughout the remainder of this Appendix, a square bracket denotes a Poisson bracket. Using Eq. (42) and Eq. (B3) in the classical limit of Eq. (83), each dipole then independently contributes

$$\left(\frac{\Omega}{N}\right)\alpha_0(\mathbf{k}, \omega)=\left(\frac{\mu^2}{k_BT}\right) \times\left\{\langle(\hat{k}\cdot\hat{\mu})^2\rangle+i\omega_+\int_0^{\infty} dt\exp(i\omega_+t) \times\langle\exp\{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}(t))\}\hat{k}\cdot\hat{\mu}\;\hat{k}\cdot\hat{\mu}(t)\rangle\right\}, \tag{B4}$$

where $\omega_+=\omega+i\delta$. Remark that we could still retain short-range effects within a Hartree approximation and, for example, include the familiar single-particle hindered rotation. In the present case, the Hamiltonian for one dipolar rotator is $(p^2/2M)+H_R$, H_R being the rotational kinetic energy. The static polarizability is independent of k and is just the Langevin expression

$$\alpha_0(k, 0)=\alpha_0(0, 0)=(N\mu^2/3\Omega k_BT). \tag{B5}$$

The time evolution of $\boldsymbol{\mu}$ is given by

$$\boldsymbol{\mu}(t)=\exp(-itL_R)\,\boldsymbol{\mu}, \tag{B6}$$

where the Liouville operator L_R is defined by

$$iL_R\boldsymbol{\mu}\equiv[H_R, \boldsymbol{\mu}]. \tag{B7}$$

We shall often present our expressions in the reduced variables

$$\bar{k}\equiv k(I/M)^{1/2},$$

$$\bar{\omega}\equiv\omega(I/2k_BT)^{1/2}\equiv(\omega/\omega_T), \qquad \tau\equiv\omega_Tt, \tag{B8}$$

and will write

$$\alpha_0(k, \omega)\equiv(N\mu^2/3\Omega k_BT)\,A(\bar{k}, \bar{\omega}). \tag{B9}$$

Carrying out the trivial average over the translational center-of-mass motion gives

$$A(\bar{k}, \bar{\omega})=1+3i\omega_+\int_0^{\infty} dt\exp(i\omega_+t-\tfrac{1}{4}\bar{k}^2\omega_T{}^2t^2) \times\langle\hat{k}\cdot\hat{\mu}\;\hat{k}\cdot\hat{\mu}(t)\rangle. \tag{B10}$$

For linear dipoles

$$H_R=(p_\theta{}^2/2I)+(p_\phi{}^2/2I\sin^2\theta), \tag{B11}$$

and

$$\bar{k}\cdot\hat{\mu}\;\hat{k}\cdot\hat{\mu}(t)=\cos\theta\cos\theta(t). \tag{B12}$$

One finds immediately

$$iL_R\cos\theta=(1/I)\,p_\theta\sin\theta, \tag{B13}$$

$$(iL_R)^2\cos\theta=-(2H_R/I)\cos\theta, \tag{B14}$$

$$\equiv-\omega_R{}^2\cos\theta, \tag{B15}$$

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[20] See, e.g., W. Bernard and H. B. Callen, Rev. Mod. Phys. **31**, 1017 (1959); A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 986 (1962).

so that, after some transformation,

$$\cos\theta(t)=\cos\theta\cos\omega_R t-(p_\theta/I\omega_R)\sin\theta\sin\omega_R t. \qquad \text{(B16)}$$

The average over the rotational variables is straightforward and is

$$3\langle\cos\theta\cos\theta(t)\rangle=\Phi(1,\tfrac{1}{2};-\tfrac{1}{4}\tau^2) \qquad \text{(B17)}$$

$$=\exp(-\tfrac{1}{4}\tau^2)\Phi(-\tfrac{1}{2},\tfrac{1}{2};\tfrac{1}{4}\tau^2), \qquad \text{(B17}')$$

where

$$\Phi(a,c;z)={}_1F_1(a;c;z)=\sum_{n\geq 0}\{(a)_n z^n/(c)_n n!\}$$

is the Kummer confluent hypergeometric function.[21] For $k=0$, a closed form is obtained on inserting (B17) in (B10). We have

$$A(0,\bar{\omega})=1+i\bar{\omega}_+\int_0^\infty d\tau\exp(i\bar{\omega}_+\tau-\tfrac{1}{4}\tau^2)\Phi(-\tfrac{1}{2},\tfrac{1}{2};\tfrac{1}{4}\tau^2)$$

$$=1+\lim_{c\to\frac{1}{2}}\bar{\omega}_+(d/d\bar{\omega}_+)\int_0^\infty d\tau\exp(i\bar{\omega}_+\tau-\tfrac{1}{4}\tau^2)\tau^{2c-2}$$

$$\times\Phi(-c,c;\tfrac{1}{4}\tau^2)$$

$$=1-\bar{\omega}_+{}^2\exp(-\bar{\omega}_+{}^2)Ei(\bar{\omega}_+{}^2)$$

$$=1+\bar{\omega}_+{}^2\int_0^\infty dx\exp(-x)(x-\bar{\omega}_+{}^2)^{-1}. \qquad \text{(B18)}$$

These steps use the following equations in Ref. 21: 6.6 (11), 6.9.2 (25), 9.1 (2), 9.3 (3). Separating real and imaginary parts

$$\mathrm{Im}A(0,\bar{\omega})=\pi\bar{\omega}^2\exp(-\bar{\omega}^2), \qquad \text{(B19)}$$

$$\mathrm{Re}A(0,\bar{\omega})=1+\bar{\omega}^2\exp(-\bar{\omega}^2)\int_{-\omega 2}^\infty dx\,x^{-1}\exp(-x), \qquad \text{(B20)}$$

the integral in (B20) being a principal value. For all k we have, from (B10) and (B19),

$$\mathrm{Im}A(\hat{k},\bar{\omega})=\bar{\omega}\exp\{(\bar{k}^2/4)(d^2/d\bar{\omega}^2)\}(1/\bar{\omega})\,\mathrm{Im}A(0,\bar{\omega}),$$

$$=\pi\frac{\bar{\omega}^2}{(1+\bar{k}^2)^{3/2}}\exp\left(-\frac{\bar{\omega}^2}{1+\bar{k}^2}\right). \qquad \text{(B21)}$$

A power series in $\bar{k}^2$ for $\mathrm{Re}A(\bar{k},\bar{\omega})$ can be generated from $\mathrm{Re}A(0,\bar{\omega})$ in similar fashion, without, however, obtaining a closed form. For $\bar{\omega}\gg 1$, we find

$$\mathrm{Re}A(\bar{k},\bar{\omega})\sim-(1+\tfrac{1}{2}\bar{k}^2)(1/\bar{\omega}^2). \qquad \text{(B22)}$$

For spherically symmetric rotators,

$$H_R=(1/2I)L^2=\tfrac{1}{2}I\omega_R{}^2, \qquad \text{(B23)}$$

$$iL_R\boldsymbol{\mu}=-\boldsymbol{\omega}_R\times\boldsymbol{\mu}, \qquad \text{(B24)}$$

and on iterating Eq. (B24) we find

$$\hat{k}\cdot\hat{\mu}(t)=\cos(\omega_R t)\hat{k}\cdot\hat{\mu}+\{1-\cos(\omega_R t)\}(\hat{\omega}_R\cdot\hat{k})\hat{\omega}_R\cdot\hat{\mu})$$

$$+\sin(\omega_R t)(\hat{k}\times\hat{\omega}_R\cdot\hat{\mu}). \qquad \text{(B25)}$$

Averaging over the rotational variables gives the very simple result

$$3\langle\hat{k}\cdot\hat{\mu}\,\hat{k}\cdot\hat{\mu}(t)\rangle=\tfrac{1}{3}\{1+(2-\tau^2)\exp(-\tfrac{1}{4}\tau^2)\}. \qquad \text{(B26)}$$

The reduced polarizability,

$$A(\bar{k},\bar{\omega})=1+i\bar{\omega}_+\int_0^\infty d\tau\exp(i\bar{\omega}_+\tau-\tfrac{1}{4}\bar{k}^2\tau^2)$$

$$\times\tfrac{1}{3}\{1+(2-\tau^2)\exp(-\tfrac{1}{4}\tau^2)\}, \qquad \text{(B27)}$$

can be evaluated directly in closed form. Separating real and imaginary parts we obtain

$$\mathrm{Im}A(\bar{k},\bar{\omega})=\tfrac{1}{3}\sqrt{\pi}\left\{\frac{\bar{\omega}}{\bar{k}}\exp\left(-\frac{\bar{\omega}^2}{\bar{k}^2}\right)\right.$$

$$\left.+\frac{2\bar{\omega}}{(1+\bar{k}^2)^{3/2}}\left(\bar{k}^2+\frac{2\bar{\omega}^2}{1+\bar{k}^2}\right)\exp\left(-\frac{\bar{\omega}^2}{1+\bar{k}^2}\right)\right\}. \qquad \text{(B28)}$$

$$\mathrm{Re}A(\bar{k},\bar{\omega})=1-\frac{2}{3}\frac{\bar{\omega}^2}{\bar{k}^2}\Phi\left(1,\tfrac{3}{2};-\frac{\bar{\omega}^2}{\bar{k}^2}\right)-\frac{4}{3}\frac{\bar{\omega}^2}{(1+\bar{k}^2)^2}$$

$$\times\left\{\left(\bar{k}^2+\frac{2\bar{\omega}^2}{1+\bar{k}^2}\right)\Phi\left(1,\tfrac{3}{2};-\frac{\bar{\omega}^2}{1+\bar{k}^2}\right)-1\right\}. \qquad \text{(B29)}$$

The Φ function in Eq. (B29) is an error function, given by

$$x\Phi(1,\tfrac{3}{2};-x^2)=\exp(-x^2)\,\mathrm{Erf}i(x)=\int_0^x d\xi\exp(\xi^2-x^2). \qquad \text{(B30)}$$

For $k=0$ we have the simpler expressions

$$\mathrm{Im}A(0,\bar{\omega})=(4(\sqrt{\pi})/3)\bar{\omega}^3\exp(-\bar{\omega}^2), \qquad \text{(B31)}$$

$$\mathrm{Re}A(0,\bar{\omega})=\tfrac{2}{3}\{(1+2\bar{\omega}^4)-4\bar{\omega}^2\Phi(1,\tfrac{3}{2};-\bar{\omega}^2)\} \qquad \text{(B32)}$$

$$=\tfrac{2}{3}\Phi(1,-\tfrac{1}{2};-\bar{\omega}^2). \qquad \text{(B32}')$$

Note that the value obtained for $A(0,0)$ depends on the order in which limits are taken, in contrast to the case for linear dipoles. From Eqs. (B29) and (B30),

$$1=\lim_{k\to 0}\lim_{\omega\to 0}A(k,\omega)\neq\lim_{\omega\to 0}\lim_{k\to 0}A(k,\omega)=\tfrac{2}{3}.$$

The asymptotic expansion of Eq. (B29) for $\bar{\omega}^2\gg 1+\bar{k}^2$ again yields Eq. (B22).

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[21] A. Erdélyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953). Chapters 6 and 9 contain all formulas used in these derivations.