

Space and time dependent polarization fluctuations in dielectric media*

U. M. Titulaer and J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 23 November 1973)

Molecular dipole moments in a dielectric medium are statistically correlated over large distances. In this paper we derive an expression for the correlation function of two molecular dipoles at different times and at different points in space in the limit of large separation. The result is obtained by means of a purely macroscopic treatment. For the case of equal times our results agree with those obtained by Nienhuis and Deutch from a microscopic theory of a fluid of rigid dipoles; in particular we see the same dependence on the shape of the dielectric sample and on the nature of its surroundings. The methods used in deriving the expression for the dipole correlation function may also be used to calculate the fluctuations in the higher electric multipole moments of small spherical regions in a dielectric sample. A number of results of this type are presented.

I. INTRODUCTION AND SURVEY

As a consequence of the long range of electric dipole-dipole forces, molecular dipole moments in a dielectric sample are correlated over large distances. Moreover, the precise form of the correlation function depends on the shape of the sample and the nature of its surroundings. In a liquid of rigid permanent dipoles the correlation function for molecular dipoles is closely related to the distribution function for the molecular orientations. Nienhuis and Deutch¹ derived an expression for the latter quantity for a general finite sample surrounded by a medium of arbitrary dielectric constant. The results of the molecular theory of Nienhuis and Deutch were obtained by diagrammatic techniques, and they are restricted to equal time correlations in orientation of different molecules.

In this paper we present a completely macroscopic theory of the correlations between the electric polarization at different points in space and at different times in an equilibrium fluid. Our results are obtained by an application of the techniques of linear response theory. The same method was used in an earlier paper² in a discussion of the relation between the frequency dependent dielectric constant of a material and the autocorrelation function of the net dipole moment of a macroscopic spherical region inside such a material.

In Sec. II we derive an expression for the equilibrium time correlation function of the dipole moments of two small spherical regions in a dielectric sample. The two small spherical regions are large compared to intermolecular distances. In Sec. III we deduce from this macroscopic time correlation function the asymptotic form of the time correlation function of molecular dipole moments when the distance between the molecules becomes large. The value of this correlation function for equal times is shown to be consistent with the result obtained by Nienhuis and Deutch on the basis of their molecular theory for a fluid of rigid dipoles. The expressions obtained in Secs. II and III contain a reaction field tensor, which depends on sample shape and surroundings. This tensor is evaluated in Sec. IV for the case of a spherical sample. In the course of the derivation we use some results about solutions of Maxwell's equations in spherical coordinates, which are assembled in an Appendix.

In Secs. V and VI we examine more closely some of the assumptions made in the course of the derivation in Sec. II. For example, we suppose in Sec. II that inhomogeneities in the external electric field do not influence the relation between the external field and the dipole moment it induces in a small spherical region. In Sec. V we show that, as long as the radius of the spherical region is small compared to the wavelength of the electromagnetic radiation with frequency ω , the space derivatives of the field are not related to the induced dipole moment of a sphere, but only to its higher multipole moments. By means of the usual arguments of linear response theory we obtain from this analysis expressions for the autocorrelation functions of higher multipole moments of a single spherical region in an infinite dielectric continuum.

In Sec. VI we discuss the corrections to the relation between the external field and the multipole moments induced in a small spherical region, which arise due to the finite size of the sample. The corrections depend on the shape of the sample and on the position of the spherical region in the sample. The general analysis justifies the procedure in Sec. II, where we neglected those corrections. Explicit expressions are only possible for some special geometries; as an example we discuss the case of a small spherical region at the center of a larger spherical sample. In the limit in which the radius of the larger sphere is small compared to the wavelength of electromagnetic radiation with frequency ω we obtain for this system a rather complete picture of the possible fluctuations in the electric multipole moments and their correlations at different times. This is discussed in the final section.

The intrinsic interest of the higher multipole moments of small macroscopic regions is probably less than that of their net dipole moments; e.g., the leading term in the expression for the net quadrupole moment is not the sum of the molecular quadrupoles, but a weighted sum of molecular dipoles. Nevertheless, relations of the type studied in Secs. VI and VII are sometimes useful; as an example we note the analysis by Buckingham and Graham³ of the birefringence of a polar fluid in an electric field gradient.

II. LINEAR RESPONSE RESULTS FOR CORRELATIONS IN THE ELECTRIC POLARIZATION

We consider an arbitrary sample V of a dielectric medium with dielectric constant $\epsilon_2(\omega)$. The sample is embedded in an infinite dielectric medium with dielectric constant $\epsilon_1(\omega)$. A spatially homogeneous external field, oscillating with frequency ω , acts on a spherical region with radius a with its center at \mathbf{r} ; the spherical region is entirely within the sample V (see Fig. 1). This space and time dependence of the external field $\mathbf{E}_0(\mathbf{R}, t)$ may be expressed by means of the formula

$$\mathbf{E}_0(\mathbf{R}, t) = \mathbf{E}_0(t)h(\mathbf{R}; \mathbf{r}) = \mathbf{E}_0 \exp(-i\omega t)h(\mathbf{R}; \mathbf{r}), \quad (2.1)$$

in which $h(\mathbf{R}; \mathbf{r})$ denotes the characteristic function of the sphere with radius a around \mathbf{r} :

$$\begin{aligned} h(\mathbf{R}; \mathbf{r}) &= 1 & \text{for } |\mathbf{R} - \mathbf{r}| \leq a, \\ h(\mathbf{R}; \mathbf{r}) &= 0 & \text{for } |\mathbf{R} - \mathbf{r}| > a. \end{aligned} \quad (2.2)$$

As a consequence of the imposed field (2.1) another physical region in the sample V , of radius a with its center at \mathbf{r}' , will exhibit a net dipole moment $\langle \mathbf{m}(\mathbf{r}', t) \rangle_{\mathbf{E}_0}$, which depends linearly on the components of \mathbf{E}_0 :

$$\langle \mathbf{m}(\mathbf{r}', t) \rangle_{\mathbf{E}_0} = \mathbf{X}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{E}_0 \exp(-i\omega t). \quad (2.3)$$

In this equation the net dipole moment $\mathbf{m}(\mathbf{r}', t)$ of the spherical region around \mathbf{r} may be expressed formally as

$$\mathbf{m}(\mathbf{r}', t) = \int_V d\mathbf{R} \sum_i \delta[\mathbf{R} - \mathbf{r}_i(t)] \mu_i(t) h(\mathbf{R}; \mathbf{r}'), \quad (2.4)$$

where the sum is over all the molecules in the sample and $\mathbf{r}_i(t)$, $\mu_i(t)$ denote the position and dipole moment, respectively, of the i th molecule. The tensor $\mathbf{X}(\mathbf{r}', \mathbf{r}; \omega)$, which is defined by the relation (2.3), is related to the Laplace transform of the autocorrelation function of the net dipole moments of the two spherical regions in the absence of any external field. The relation follows immediately from the basic formula of linear response theory⁴:

$$\langle \mathbf{m}(\mathbf{r}', t) \rangle_{\mathbf{E}_0} = \frac{-1}{kT} \int_0^\infty \mathbf{E}_0(t-t') \frac{d}{dt'} \langle \mathbf{m}(\mathbf{r}, 0) \mathbf{m}(\mathbf{r}', t') \rangle dt'. \quad (2.5)$$

By comparing the expressions (2.3) and (2.5) for $\langle \mathbf{m}(\mathbf{r}', t) \rangle_{\mathbf{E}_0}$ we obtain the relation

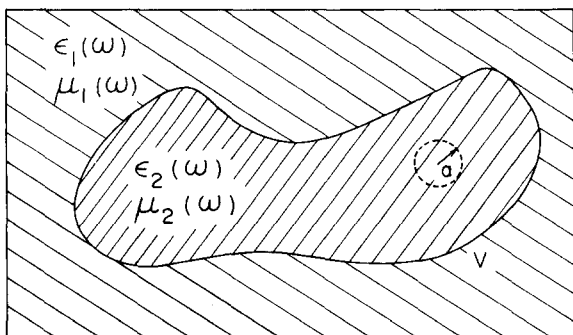


FIG. 1. The system discussed in Sec. II: a sample V with material coefficients $\epsilon_2(\omega)$ and $\mu_2(\omega)$ is embedded in an infinite continuum with material coefficients $\epsilon_1(\omega)$ and $\mu_1(\omega)$. We discuss in particular a sphere of radius a around the point \mathbf{r} .

$$\mathcal{L} \left[-\frac{d}{dt} \langle \mathbf{m}(\mathbf{r}, 0) \mathbf{m}(\mathbf{r}', t) \rangle \right] = kT \mathbf{X}(\mathbf{r}, \mathbf{r}'; \omega). \quad (2.6)$$

The symbol $\mathcal{L}[f(t)]$ denotes the Laplace transform of $f(t)$ with variable $z = -i\omega$. (The convention used for the sign of ω differs from that of Ref. 2.)

For certain values of the radius a we can calculate the tensor $\mathbf{X}(\mathbf{r}, \mathbf{r}'; \omega)$ by means of a purely macroscopic electromagnetic calculation, using the frequency dependent dielectric constant $\epsilon_2(\omega)$. The conditions are (i) the radius a is large compared to the average distance between molecules; otherwise a description in terms of a local dielectric constant is not justified; (ii) the radius a is small compared to the wavelength of electromagnetic radiation of frequency ω ; otherwise a spatially homogeneous field that varies harmonically in time does not even approximately obey Maxwell's equations; (iii) the radius a is small compared to the distance from \mathbf{r} to the boundary of the dielectric sample V .

We start our calculation of $\mathbf{X}(\mathbf{r}, \mathbf{r}'; \omega)$ with the observation that the field \mathbf{E}_0 in Eqs. (2.3) and (2.5) is not the ordinary Maxwell field, but the cavity field that would be present if the sphere around \mathbf{r} were removed from the sample. In general, the relation between the external field \mathbf{E}_0 and the Maxwell field is rather complicated; it depends upon the shape of the sample V and the values of ϵ_1 and ϵ_2 . However, for the case in which the sample V is infinite the relation between \mathbf{E}_0 and \mathbf{E} is simple. In this section we shall make use of the relation between \mathbf{E}_0 and \mathbf{E} for the case of a spherical cavity of radius a in an infinite dielectric. A justification for this step, which seems reasonable provided that the radius of the cavity is small compared to the distance from the center of the cavity to the boundary of the sample V , is postponed until Sec. VI. In all other stages of the calculation it is not justified to neglect the effects of the finite size of the sample V .

Fröhlich⁵ has shown, for the case of a spherical cavity in an infinite dielectric, that the Maxwell field $\mathbf{E}(t)$ inside the sphere is given by

$$\mathbf{E}(t) = \{ [2\epsilon_2(\omega) + 1] / 3\epsilon_2(\omega) \} \mathbf{E}_0(t). \quad (2.7)$$

According to the constitutive relations the resulting average net dipole moment of the sphere surrounding \mathbf{r} is

$$\langle \mathbf{m}(\mathbf{r}, t) \rangle_{\mathbf{E}_0} = \{ [\epsilon_2(\omega) - 1] / 4\pi \} \left(\frac{4}{3} \pi a^3 \right) \mathbf{E}(t). \quad (2.8)$$

Since this dipole moment is embedded in a dielectric, the field arising outside of the sphere is that of an apparent dipole moment $\mathbf{m}_*(\mathbf{r}, t)$ related to $\mathbf{m}(\mathbf{r}, t)$ by the expression

$$\langle \mathbf{m}_*(\mathbf{r}, t) \rangle_{\mathbf{E}_0} = \{ 3\epsilon_2(\omega) / [2\epsilon_2(\omega) + 1] \} \langle \mathbf{m}(\mathbf{r}, t) \rangle. \quad (2.9)$$

By combining Expressions (2.7)–(2.9) one obtains

$$\langle \mathbf{m}_*(\mathbf{r}, t) \rangle_{\mathbf{E}_0} = \frac{1}{3} [\epsilon_2(\omega) - 1] a^3 \mathbf{E}_0(t). \quad (2.10)$$

The relations (2.7)–(2.10) are valid for a spherical region in an infinite dielectric continuum. In the remaining part of the calculation the finite sample size must be taken into account explicitly. The apparent dipole $\langle \mathbf{m}_*(\mathbf{r}, t) \rangle_{\mathbf{E}_0}$ at \mathbf{r} gives rise to an electric field

$\mathbf{E}_*(\mathbf{r}', t)$ at \mathbf{r}' , which may be denoted by

$$\mathbf{E}_*(\mathbf{r}', t) = [\epsilon_2(\omega)]^{-1} \mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \langle \mathbf{m}_*(\mathbf{r}, t) \rangle_{\mathbf{E}_0}. \quad (2.11)$$

According to Eq. (2.8) this field gives rise to a net dipole moment in a small spherical region of radius a about \mathbf{r}' given by

$$\langle \mathbf{m}(\mathbf{r}', t) \rangle_{\mathbf{E}_0} = \{[\epsilon_2(\omega) - 1]/4\pi\} (\frac{4}{3}\pi a^3) \mathbf{E}_*(\mathbf{r}', t). \quad (2.12)$$

By combining Eqs. (2.11) and (2.12) we obtain the relation

$$\langle \mathbf{m}(\mathbf{r}', t) \rangle_{\mathbf{E}_0} = \frac{\epsilon_2(\omega) - 1}{3\epsilon_2(\omega)} a^3 \mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \langle \mathbf{m}_*(\mathbf{r}, t) \rangle_{\mathbf{E}_0}. \quad (2.13)$$

The relation (2.12) is valid provided that the field \mathbf{E}_* is homogeneous over the sphere around \mathbf{r}' . In Sec. V we shall see that inhomogeneities do not alter this result if the radius a is much smaller than the wavelength of the field in V .

Elimination of $\langle \mathbf{m}_*(\mathbf{r}, t) \rangle_{\mathbf{E}_0}$ in Eq. (2.13) by use of Eq. (2.10) leads to a relation between $\langle \mathbf{m}(\mathbf{r}', t) \rangle_{\mathbf{E}_0}$ and \mathbf{E}_0 of the form

$$\langle \mathbf{m}(\mathbf{r}', t) \rangle_{\mathbf{E}_0} = \frac{1}{\epsilon_2(\omega)} \left[\frac{\epsilon_2(\omega) - 1}{3} a^3 \right]^2 \mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{E}_0(t). \quad (2.14)$$

Comparison of Eqs. (2.3) and (2.14) gives an expression for the susceptibility $\mathbf{X}(\mathbf{r}, \mathbf{r}'; \omega)$; according to Eq. (2.6) we obtain the desired expression for the equilibrium time correlation of the net dipole moments of spherical regions around \mathbf{r} and \mathbf{r}' at times that are an amount t apart. The result is

$$\mathcal{L} \left[-\frac{d}{dt} \langle \mathbf{m}(\mathbf{r}, 0) \mathbf{m}(\mathbf{r}', t) \rangle \right] = \frac{kT}{\epsilon_2(\omega)} \left\{ \frac{1}{3} a^3 [\epsilon_2(\omega) - 1] \right\}^2 \mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega). \quad (2.15)$$

The result (2.15) is valid under the condition that a is large compared to intermolecular distances but small compared to both the wavelength of electromagnetic radiation of frequency ω in the medium and the distance from \mathbf{r} to the boundary of the sample V . In the next section we consider the consequences of this expression for the orientational correlation function of molecular dipoles in a substance in which the molecules may be represented as rigid dipoles.

The tensor $\mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega)$ defined by Eq. (2.11) is determined by a macroscopic calculation and depends upon the shape of the sample V and the dielectric constant of the external region $\epsilon_1(\omega)$. The tensor $\mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega)$ may be written as the sum of two terms:

$$\mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega) = \mathbf{D}_\infty(\mathbf{r}, \mathbf{r}'; \omega) + \mathbf{R}_V(\mathbf{r}, \mathbf{r}'; \omega). \quad (2.16)$$

The term \mathbf{D}_∞ represents the direct field,⁶

$$\mathbf{D}_\infty(\mathbf{r}, \mathbf{r}'; \omega) = -\left(\frac{\partial}{\partial \mathbf{r}'} \frac{\partial}{\partial \mathbf{r}} - k_2^2 \mathbf{I} \right) \frac{\exp(ik_2 |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.17)$$

The symbol k_2 denotes the wavenumber of a wave with frequency ω in the medium with dielectric constant $\epsilon_2(\omega)$ and magnetic permeability $\mu_2(\omega)$,

$$k_2 = [\omega/c][\epsilon_2(\omega)\mu_2(\omega)]^{1/2}. \quad (2.18)$$

When $|\mathbf{r} - \mathbf{r}'|$ is small compared to k_2 the expression (2.10) reduces to

$$\lim_{\omega \rightarrow 0} \mathbf{D}_\infty(\mathbf{r}, \mathbf{r}'; \omega) = -\frac{\partial}{\partial \mathbf{r}'} \frac{\partial}{\partial \mathbf{r}} \frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.19)$$

which is identical to the usual expression for the dipole-dipole tensor $\mathbf{T}(\mathbf{r}, \mathbf{r}')$;

$$\lim_{\omega \rightarrow 0} \mathbf{D}_\infty(\mathbf{r}, \mathbf{r}'; \omega) = \mathbf{T}(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|^3} \left[\frac{3(\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^2} - \mathbf{I} \right]. \quad (2.20)$$

The contribution $\mathbf{D}_\infty(\mathbf{r}, \mathbf{r}'; \omega)$ is the only term present in the limit of an infinite sample. For a finite sample V there is an additional term $\mathbf{R}_V(\mathbf{r}, \mathbf{r}'; \omega)$, which depends on the size and shape of the sample V and on the constants $\epsilon(\omega)$ and $\mu(\omega)$ of both the sample and the surroundings. In general it is not possible to find a closed expression for the tensor $\mathbf{R}_V(\mathbf{r}, \mathbf{r}'; \omega)$; however, an explicit expression for the case of a spherical sample V will be presented in Sec. IV. The physical interpretation of the term \mathbf{R}_V is that of a "reaction field"; a unit dipole \mathbf{p} oscillating with frequency ω at point \mathbf{r} will give rise to polarization near the boundary of the sample V , which in turn produces a field $[\epsilon_2(\omega)]^{-1} \mathbf{R}_V \cdot \mathbf{p}$ at the point \mathbf{r}' .

III. ORIENTATIONAL CORRELATIONS FOR INDIVIDUAL DIPOLES IN A POLAR MEDIUM

The average net dipole moment of a spherical region is just the sum of the average dipole moments of the individual molecules. In the same way the correlation function of two spherical regions, which was calculated in the preceding section, is the sum of correlation functions of the dipole moments of individual molecules. When the two regions are so far apart that the field tensor $\mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega)$ does not vary appreciably over a distance a , we may assume that those molecular correlation functions are all essentially equal, and we obtain their value by dividing the expression (2.15) by the square of the average number of molecules in each sphere, $\frac{4}{3}\pi\rho a^3$:

$$\mathcal{L} \left[-\frac{d}{dt} \langle \mu(\mathbf{r}, 0) \mu(\mathbf{r}', t) \rangle \right] = \frac{kT}{\epsilon_2(\omega)} \left[\frac{\epsilon_2(\omega) - 1}{4\pi\rho} \right]^2 \mathbf{D}(\mathbf{r}, \mathbf{r}'; \omega). \quad (3.1)$$

In this formula $\mu(\mathbf{r}, t)$ is the dipole moment at time t of a molecule which is at the position \mathbf{r} . The expression (3.1) is valid for distances large compared to intermolecular distances (and the range of short range forces) and for a medium which can be characterized by a local frequency dependent dielectric constant $\epsilon_2(\omega)$ and magnetic permeability $\mu_2(\omega)$.

The equal time correlation function $\langle \mu(\mathbf{r}, 0) \mu(\mathbf{r}', 0) \rangle$ may be obtained from Eq. (3.1) by taking the limit $\omega \rightarrow 0$. The result is

$$\langle \mu(\mathbf{r}, 0) \mu(\mathbf{r}', 0) \rangle = \frac{kT}{\epsilon_2(0)} \left[\frac{\epsilon_2(0) - 1}{4\pi\rho} \right]^2 \mathbf{D}(\mathbf{r}, \mathbf{r}'; 0). \quad (3.2)$$

By using Eqs. (2.16) and (2.20) we may express the tensor $\mathbf{D}(\mathbf{r}, \mathbf{r}'; 0)$ in the form

$$\mathbf{D}(\mathbf{r}, \mathbf{r}'; 0) = \mathbf{T}(\mathbf{r}, \mathbf{r}') + \mathbf{R}_V(\mathbf{r}, \mathbf{r}'; 0). \quad (3.3)$$

This expression for the equal time correlation function, which has been obtained completely from macroscopic considerations, can be compared to the results of the

microscopic theory of Nienhuis and Deutch.¹ The microscopic expression of the static correlation function Eq. (3.1) is

$$\langle \mu(\mathbf{r}, 0) \mu(\mathbf{r}', 0) \rangle = \int \int d\omega d\omega' \mu(\omega) G(\mathbf{r}, \omega; \mathbf{r}', \omega') \mu(\omega') \rho^{-2}, \quad (3.4)$$

where $\omega[\omega']$ refers to the Euler angles specifying the orientation of the dipole at position $\mathbf{r}[\mathbf{r}']$ and $G(\mathbf{r}, \omega; \mathbf{r}', \omega')$ is the reduced two particle correlation function for positions and orientations. The factor ρ^{-2} is included since we are assuming the molecules are at specified positions. From their microscopic theory Nienhuis and Deutch provided an explicit expression for the long-range part of G . This quantity, denoted by $G^{(1)}$, was determined from a graphical analysis¹ to be

$$G^{(1)}(\mathbf{r}, \omega; \mathbf{r}', \omega') = \frac{1}{\epsilon_2(0) \Omega^2 k T} \mu_{\text{eff}}(\omega) \cdot \mathbf{D}(\mathbf{r}, \mathbf{r}') \cdot \mu_{\text{eff}}(\omega'), \quad (3.5)$$

where the "effective" dipole moment μ_{eff} is related to the dielectric constant by

$$\epsilon_2(0) - 1 = (4\pi\rho/3kT) \mu \cdot \mu_{\text{eff}} \quad (3.6)$$

and $\Omega = \int d\omega$ is the phase space volume associated with the molecular orientations. The tensor \mathbf{D} obtained by Nienhuis and Deutch was calculated only for the case in which the sample V is surrounded by vacuum ($\epsilon_1 = 1$). Their result was expressed as

$$\mathbf{D}(\mathbf{r}, \mathbf{r}') = \mathbf{T}(\mathbf{r}, \mathbf{r}') + \mathbf{R}_V^*(\mathbf{r}, \mathbf{r}'; \epsilon_2^{-1}). \quad (3.7)$$

In this formula \mathbf{R}_V^* denotes the reaction field tensor calculated for the "inverse geometry": the space occupied by the sample V is empty, while the space outside V is filled with a medium of dielectric constant $[\epsilon_2(0)]^{-1}$. Thus $\mathbf{R}_V^*(\mathbf{r}, \mathbf{r}'; \epsilon_2^{-1}) \cdot \mathbf{p}$ has the physical interpretation of the field established at point \mathbf{r}' by a dipole \mathbf{p} at point \mathbf{r} when the sample volume V is empty and the surrounding is filled by a dielectric continuum of dielectric constant $\epsilon_2^{-1}(0)$. One may show that the reaction field tensor \mathbf{R}_V of Eq. (3.3), for the special case $\epsilon_1(0) = 1$, is equal to the reaction field tensor \mathbf{R}_V^* for the "inverse geometry." The expressions for the tensors \mathbf{D} appearing in Eqs. (3.3) and (3.7) are identical. This point is discussed more fully in the next section.

When the expression for the long-range part of the correlation function G , Eq. (3.5), is substituted into Eq. (3.4), and use is made of Eq. (3.7) and the relation

$$\Omega^{-1} \int d\omega \mu(\omega) \mu_{\text{eff}}(\omega) = \frac{1}{3} \mu \cdot \mu_{\text{eff}}, \quad (3.8)$$

one obtains exactly the macroscopic expression Eq. (3.2). Accordingly we have demonstrated that, for separations large compared to molecular distances, the results of the macroscopic theory presented here and the microscopic Nienhuis-Deutch theory lead to exactly the same expression for $\langle \mu(\mathbf{r}) \mu(\mathbf{r}') \rangle$. The expression (3.2) agrees with a calculation of Ben-Naim and Stillinger⁷ for the special case of an infinite system, where $\mathbf{D} = \mathbf{T}$ and $\mathbf{R}_V = 0$, if we substitute the appropriate expression for Kirkwood's g factor in a fluid of rigid dipoles:

$$(4\pi\rho/9kT) \mu^2 g = [\epsilon_2(0) - 1] [2\epsilon_2(0) + 1] / 3\epsilon_2(0). \quad (3.9)$$

An earlier calculation by Kuni⁸ differs by a factor of $3[2\epsilon_2(0) + 1]^{-1}$.

The important result of this section is the new expression for the equilibrium space-time correlation function presented in Eq. (3.2). This expression, which is valid for separations of the dipoles large compared to the range of short-range forces, contains a reaction field contribution that depends on the sample shape and the nature of the surroundings. For the special case of equal time correlations we have demonstrated that the result is consistent with the microscopic theory. In the next section we explicitly evaluate the dipole space-time correlation function for the special case of a spherical sample V embedded in a dielectric continuum of dielectric constant $\epsilon_1(\omega)$.

IV. EXPLICIT EXPRESSIONS FOR ORIENTATIONAL CORRELATIONS IN A SPHERICAL SAMPLE

In the present section we determine the reaction field tensor $\mathbf{R}_V(\mathbf{r}, \mathbf{r}'; \omega)$, defined in Eq. (2.16), for the case of a spherical sample V of radius R , characterized by a dielectric constant $\epsilon_2(\omega)$ and a magnetic permeability $\mu_2(\omega)$. The sample is embedded in a medium characterized by $\epsilon_1(\omega)$ and $\mu_1(\omega)$. See Fig. 2. For the purpose of our calculation it is convenient to start by considering the electric Hertz vector⁹ associated with a dipole of strength \mathbf{m}_* at \mathbf{r} ,

$$\Pi(\mathbf{r}') = \frac{1}{\epsilon_2(\omega)} \frac{\exp(ik_2|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \mathbf{m}_* \exp(-i\omega t). \quad (4.1)$$

From this expression the electric and magnetic fields are obtained by means of the formulas

$$\mathbf{E}(\mathbf{r}') = \nabla \times \nabla \times \Pi(\mathbf{r}'); \quad \mathbf{H}(\mathbf{r}') = \frac{\epsilon(\omega)}{c} \nabla \times \frac{\partial \Pi(\mathbf{r}')}{\partial t}. \quad (4.2)$$

The expressions (4.1) and (4.2) do not satisfy the correct boundary conditions at the surface of the sphere; for that purpose we must add a reaction field which is regular at $\mathbf{r} = \mathbf{r}'$. As a first step towards the determination of this reaction field we expand the expression (4.1) in terms of a set of vector solutions of Helmholtz's equation, which are singular at the origin (chosen at the center of the spherical sample under consideration).

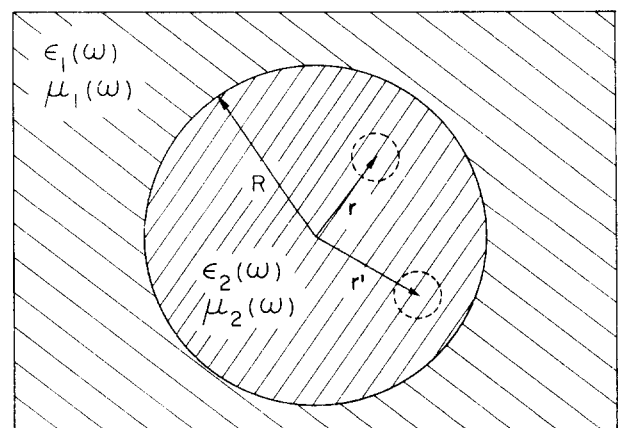


FIG. 2. A special case of the situation in Fig. 1: The sample V is taken to be a sphere with radius R . Two spherical regions with radius a around \mathbf{r} and \mathbf{r}' are discussed in particular.

The specific form of those solutions, $\mathbf{L}^{(3)}$, $\mathbf{M}^{(3)}$, and $\mathbf{N}^{(3)}$, is given in the Appendix [Eq. (A2) with $i=3$]. The basic expansion theorem was given by Hansen¹⁰; in our notation it is

$$\frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} = \sum_{l,m} \frac{4\pi ik}{l(l+1)} [\mathbf{L}_{klm}^{(3)}(\mathbf{r}')\mathbf{L}_{klm}^{(1)*}(\mathbf{r}) + \mathbf{M}_{klm}^{(3)}(\mathbf{r}')\mathbf{M}_{klm}^{(1)*}(\mathbf{r}) + \mathbf{N}_{klm}^{(3)}(\mathbf{r}')\mathbf{N}_{klm}^{(1)*}(\mathbf{r})] \quad (4.3)$$

The electric field of a dipole \mathbf{m}_* at \mathbf{r} at points \mathbf{r}' with $|\mathbf{r}'| > |\mathbf{r}|$ can be determined by means of Eqs. (4.1)–(4.3) and the relations

$$\nabla \times \mathbf{L}_{klm}^{(i)} = 0; \quad \nabla \times \mathbf{M}_{klm}^{(i)} = k\mathbf{N}_{klm}^{(i)}; \quad \nabla \times \mathbf{N}_{klm}^{(i)} = k\mathbf{M}_{klm}^{(i)}. \quad (4.4)$$

Application of these relations gives for the electric field in Eq. (4.2)

$$\mathbf{E}(\mathbf{r}') = \frac{4\pi ik_2^3}{\epsilon_2(\omega)} \sum_{l,m} \frac{1}{l(l+1)} [\mathbf{M}_{k_2lm}^{(3)}(\mathbf{r}')\mathbf{M}_{k_2lm}^{(1)*}(\mathbf{r}) + \mathbf{N}_{k_2lm}^{(3)}(\mathbf{r}')\mathbf{N}_{k_2lm}^{(1)*}(\mathbf{r})] \cdot \mathbf{m}_* \exp(-i\omega t). \quad (4.5)$$

The reaction field corresponding to this field is found by comparing this expression with the standard solutions of the Maxwell equations with boundary conditions, given by Eq. (A10) in the Appendix; the resulting expression is

$$\mathbf{E}^{(r)}(\mathbf{r}') = \frac{4\pi ik_2^3}{\epsilon_2(\omega)} \sum_{l,m} \frac{1}{l(l+1)} [R_l^{(m)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1)\mathbf{M}_{k_2lm}^{(1)}(\mathbf{r}')\mathbf{M}_{k_2lm}^{(1)*}(\mathbf{r}) + R_l^{(e)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1)\mathbf{N}_{k_2lm}^{(1)}(\mathbf{r}')\mathbf{N}_{k_2lm}^{(1)*}(\mathbf{r})] \cdot \mathbf{m}_* \exp(-i\omega t); \quad (4.6)$$

the coefficients $R_l^{(m)}$ and $R_l^{(e)}$ are given in Eq. (A11). A comparison with Eqs. (2.8) and (2.5) shows that the reaction field tensor \mathbf{R}_\odot for a sphere is given by

$$\mathbf{R}_\odot(\mathbf{r}, \mathbf{r}'; \omega) = 4\pi ik_2^3 \sum_{l,m} \frac{1}{l(l+1)} [R_l^{(m)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1)\mathbf{M}_{k_2lm}^{(1)}(\mathbf{r}')\mathbf{M}_{k_2lm}^{(1)*}(\mathbf{r}) + R_l^{(e)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1)\mathbf{N}_{k_2lm}^{(1)}(\mathbf{r}')\mathbf{N}_{k_2lm}^{(1)*}(\mathbf{r})]. \quad (4.7)$$

For the case $k_2R \ll 1$ we find by substitution of the asymptotic expressions that the terms containing $\mathbf{M}(\mathbf{r}')\mathbf{M}^*(\mathbf{r})$ disappear, while the other terms may be expressed in the gradients of the scalar potentials $\phi_{k_2lm}^{(1)}(\mathbf{r}', t)$ in Eq. (A8a) [and of $\phi_{k_2lm}^{(1)*}(\mathbf{r}, t)$]. By also substituting the asymptotic expression (A12b) for $R_l^{(e)}$ we obtain

$$\mathbf{R}_\odot(\mathbf{r}, \mathbf{r}'; \omega) = -\frac{\partial}{\partial \mathbf{r}'} \frac{\partial}{\partial \mathbf{r}} \sum_{l,m} \frac{4\pi}{2l+1} \left(\frac{k_2^*}{k_2}\right)^{l-1} \frac{(l+1)(\epsilon_2 - \epsilon_1)}{l\epsilon_2 + (l+1)\epsilon_1} \frac{r^l (r')^l}{R^{2l+1}} Y_{lm}(\theta', \phi') Y_{lm}^*(\theta, \phi). \quad (4.8)$$

The factor $(k_2^*/k_2)^{l-1}$ approaches unity for low k when $\text{Im}[\epsilon(\omega)]$ is linear at $\omega=0$; the difference is of order k^2 and should, therefore, be neglected in this approximation. Furthermore the summation over m may be carried out (this is just the addition theorem for spherical harmonics¹¹) and we obtain

$$\mathbf{R}_\odot(\mathbf{r}, \mathbf{r}'; \omega) = -\frac{\partial}{\partial \mathbf{r}'} \frac{\partial}{\partial \mathbf{r}} \sum_l \frac{(l+1)(\epsilon_2 - \epsilon_1)}{l\epsilon_2 + (l+1)\epsilon_1} \frac{(rr')^l}{R^{2l+1}} P_l(\cos\gamma), \quad (4.9)$$

in which γ is the angle between the vectors \mathbf{r} and \mathbf{r}' .

The limiting expression no longer depends on ϵ_1 and ϵ_2 separately, but only on their ratio. This implies that the reaction field tensor \mathbf{R}_\odot for the case $\epsilon_1(\omega)=1$ has the same low frequency limit as that for the “inverse geometry” $\epsilon_2'(\omega)=1$, $\epsilon_1'(\omega)=[\epsilon_2(\omega)]^{-1}$. This result is a special case of one stated, without proof, in the course of our demonstration of the consistency of our result (3.2) with the result obtained by Nienhuis and Deutch from a microscopic theory. For that purpose we needed the equality of the reaction tensors in “inverse geometries” for arbitrary shape of the sample V.

It is easy to see that the reaction field tensors for the actual and the inverse geometry are the same, irrespective of the shape of the sample. The reaction field is determined by constructing a solution of the free field equations, which obeys the boundary conditions at the surface of the sample and exhibits a singularity at $\mathbf{r}=\mathbf{r}'$ corresponding to a dipole of unit strength. In the zero frequency case this is also a solution for the inverse geometry: the free field equation is just Poisson’s equation, which does not contain the dielectric constant as a parameter, while the boundary conditions involve only the ratio of the dielectric constants of the two regions.

This completes our proof of the consistency of our results with those of Nienhuis and Deutch. It is perhaps worthwhile to point out that the equality of the reaction field tensor to that of the inverse geometry does not hold for nonzero frequencies; then the free field equation is Helmholtz’s equation, which contains the parameter $k^2 = \omega^2 c^{-2} \epsilon(\omega) \mu(\omega)$, and the equivalence with the inverse geometry is destroyed.

V. TIME CORRELATION FUNCTIONS FOR HIGHER MULTIPOLE MOMENTS OF A SPHERE

In this section we discuss the response of a small spherical region in a dielectric to an inhomogeneous external electric field. Via the algorithm of linear response theory this leads to expressions for the autocorrelation function of the net electric multipole moments of that region in the absence of any external field. We will consider fields that vary with frequency ω and assume that the radius a is small compared to the wavelength of electromagnetic waves with frequency ω . This means that the electric field may be described in very good approximation as minus the gradient of a scalar potential [cf. the discussion in the Appendix preceding Eq. (A8)]. The most general form for such a potential is

$$\phi(\mathbf{r}) = \sum_{l,m} \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_{lm}(\theta, \phi) [-r^l E_{lm} + r^{-l-1} m_{lm}] \exp(-i\omega t). \quad (5.1)$$

with arbitrary coefficients E_{lm} and m_{lm} . The singular terms between the square brackets are the potentials of an electric 2^l pole at the origin. The normalization is chosen in such a way that the energy of this collection of multipole moments in a regular inhomogeneous electric

field is precisely equal to

$$H = - \sum_{l,m} E_{lm} m_{l,-m} \quad (5.2)$$

By means of the standard procedure of matching solutions at the boundary we can calculate the multipole moments that are induced in a sphere of radius a with dielectric constant $\epsilon_2(\omega)$, surrounded by vacuum, when it is placed in an inhomogeneous field derived from the potential

$$\phi(\mathbf{r}) = - \sum_{l,m} \left(\frac{4\pi}{2l+1} \right)^{1/2} r^l E_{lm}^{(0)} Y_{lm}(\theta, \phi) \exp(-i\omega t) \quad (5.3)$$

See Fig. 3(a). The induced multipole moments turn out to be

$$m_{lm} = [l(\epsilon_2 - 1)/(l\epsilon_2 + l + 1)] a^{2l+1} E_{lm}^{(0)} \quad (5.4)$$

Evidently the moment m_{lm} depends only on the component of the field with the angular symmetry denoted by the same indices l and m .

When the sphere with radius a is embedded in an infinite medium with dielectric constant $\epsilon_1(\omega)$ it feels a reaction field proportional to its own multipole moments, in addition to the external field (5.3). See Fig. 3(b). This reaction field is again easily calculated by standard boundary value matching techniques, and we find

$$E_{lm}^{(r)} = - \frac{(l+1)(\epsilon_1 - 1)}{[(l+1)\epsilon_1 + l] a^{2l+1}} m_{lm} \quad (5.5)$$

Now we can replace $E_{lm}^{(0)}$ in Eq. (5.4) by $E_{lm}^{(0)} + E_{lm}^{(r)}$ and solve the resulting linear equation. The result is

$$m_{lm} = \frac{l(\epsilon_2 - 1)[(l+1)\epsilon_1 + l] a^{2l+1}}{(2l+1)[(l+1)\epsilon_1 + l\epsilon_2]} E_{lm}^{(0)} \quad (5.6)$$

For the case $\epsilon_1 = 1$ this, of course, reduces to Eq. (5.4).

From Eq. (5.6) we can obtain an expression for the correlation functions of the multipole moments of a spherical region of dielectric constant ϵ_2 embedded in a medium of dielectric constant ϵ_1 :

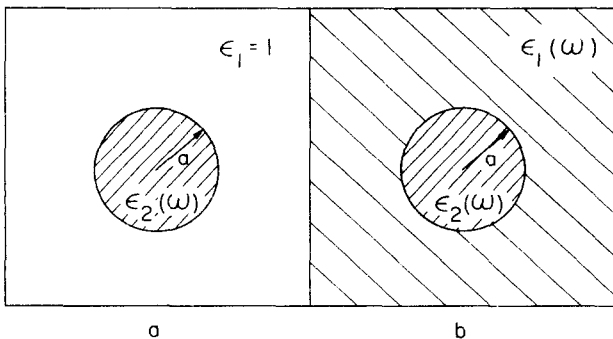


FIG. 3. A small sphere of dielectric constant $\epsilon_2(\omega)$ placed either in vacuum (a) or inside an infinite dielectric continuum with dielectric constant $\epsilon_1(\omega)$ (b). The autocorrelation functions of the electric multipole moments of the sphere in both cases are discussed in Sec. V.

$$\begin{aligned} \mathcal{L} \left[- \frac{d}{dt} \langle m_{lm}(0) m_{l',m'}(t) \rangle \right] \\ = \frac{l(\epsilon_2 - 1)[(l+1)\epsilon_1 + l]}{(2l+1)[(l+1)\epsilon_1 + l\epsilon_2]} a^{2l+1} k T \delta_{ll'} \delta_{m,-m'} \quad (5.7) \end{aligned}$$

This formula is the analog of Eq. (2.3); it is derived by taking the expression (5.2) as the perturbation Hamiltonian in the standard linear response argument. For the important case $\epsilon_1 = \epsilon_2 = \epsilon$ this expression becomes

$$\begin{aligned} \mathcal{L} \left[- \frac{d}{dt} \langle m_{lm}(0) m_{l',m'}(t) \rangle \right] \\ = \frac{l(\epsilon - 1)[(l+1)\epsilon + l]}{(2l+1)^2 \epsilon} a^{2l+1} k T \delta_{ll'} \delta_{m,-m'} \quad (5.8) \end{aligned}$$

The important result of this section is presented in Eq. (5.7); this expression relates the fluctuations in the electric moments of a spherical sample embedded in an infinite dielectric medium to the dielectric constants of the sample [$\epsilon_2(\omega)$] and the surroundings [$\epsilon_1(\omega)$]. The expression is valid for low frequencies for which the associated wavelength is large compared to the sample radius, and it represents a generalization to higher moments of the analysis presented in Ref. 2.

In principle one could now proceed from Eq. (5.6) to calculate the field around the position \mathbf{r}' due to an electric 2^l pole of type m_{lm} at the position \mathbf{r} . This would lead to expressions for $\mathcal{L}[-(d/dt)\langle m_{lm}(\mathbf{r}, 0) m_{l',m'}(\mathbf{r}', t) \rangle]$. The result would contain generalized reaction field tensors, dependent on sample shape and surroundings, which give the value of the coefficient $E_{l',m'}$ in the Taylor series (5.3) around the point \mathbf{r}' of the electrostatic potential due to an electric 2^l pole of type m_{lm} at site \mathbf{r} . (As argued in the Appendix, we can always represent the electric field *locally* as minus the gradient of an appropriately chosen scalar potential.) In general one would obtain nonvanishing correlations even for $l \neq l'$ and $m \neq -m'$. Since there is no obvious application for formal expressions of this type, we do not present them explicitly.

In our derivation of the expressions (5.6) and (5.7) we used an expression for the reaction field that is correct only for an infinite medium. In the next section we consider the corrections that occur when we consider a region inside a finite sample. Since we are mainly interested in an order of magnitude estimate we will carry out the calculation only for an especially convenient geometry, namely, a sphere of radius a located at the center of a larger spherical sample of radius R .

VI. CORRECTIONS ASSOCIATED WITH FINITE SAMPLE SIZE

In various calculations in Secs. II and V we approximated the multipole moments induced in a small spherical region inside a finite dielectric sample by those induced in a small spherical region inside an infinite dielectric medium; see, e.g., Eqs. (2.7) and (5.5). In order to estimate the errors made by this procedure we will now carry out the calculation without this approximation, but only for an especially favorable geometry, namely, a spherical region of radius a embedded in a spherical shell with external radius R . As always be-

fore we will assume that a (but not necessarily R) is small compared to the wavelength of an electromagnetic wave of frequency ω . The calculation is a generalization of that in our earlier paper for $kR \ll 1$ and $l=1$. At the end of this section we shall argue that the corrections for arbitrary sample shape are of the same order of magnitude.

We will carry out the calculations for the sphere for the slightly more general case in which the embedded sphere and the surrounding spherical shell can have different dielectric constants, $\epsilon_2(\omega)$ and $\epsilon_1(\omega)$, respectively. See Fig. 4. The region outside R is vacuum. Since $ka \ll 1$, the electric field in the immediate neighborhood of the origin may be described by means of a scalar potential. In order to find an expression for the reaction field coefficients $E_{lm}^{(r)}$ that generalizes Eq. (5.5) we consider the situation in which the sphere with radius a contains no medium, but an electric multipole of type m_{lm} is placed at the origin. For that case, the scalar potential is given by

$$\phi(\mathbf{r}) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{lm}(\theta, \phi) [r^{-l-1} m_{lm} - r^l E_{lm}^{(r)}] \times \exp(-i\omega t); \quad r \leq a, \quad (6.1a)$$

$$\phi(\mathbf{r}) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{lm}(\theta, \phi) [r^{-l-1} \hat{m}_{lm} - r^l \hat{E}_{lm}^{(r)}] \times \exp(-i\omega t); \quad r \geq a. \quad (6.1b)$$

The parameters \hat{m}_{lm} and $\hat{E}_{lm}^{(r)}$ are connected by means of the boundary conditions at $r=R$. The field derived from the potential (6.1b) must be the small \mathbf{r} approximation of a solution of type (A10b). By substituting the asymptotic expressions (A8) we find the relation

$$\hat{E}_{lm}^{(r)} = [-i(l+1)k_1^{2l+1}/l(2l-1)!!(2l+1)!!] R_l^{(e)}(\epsilon_1, \mu_1; 1, 1) \hat{m}_{lm}, \quad (6.2)$$

where $R_l^{(e)}$ is defined by Eqs. (A10) and (A11). For the limiting case $kR \ll 1$ we find by means of the asymptotic relation (A12b) for $R_l^{(e)}(\epsilon_1, \mu_1; 1, 1)$ that

$$\hat{E}_{lm}^{(r)} \simeq \{(l+1)(\epsilon_1 - 1)/[(l+1)\epsilon_1 + l]R^{2l+1}\} \hat{m}_{lm}. \quad (6.3)$$

After substitution of Eqs. (6.2) or (6.3) into Eq. (6.1b) we can determine the relation between $E_{lm}^{(r)}$ and m_{lm} ; when we abbreviate Eq. (6.2) or (6.3) to

$$\hat{E}_{lm}^{(r)} = \alpha_l a^{-2l-1} \hat{m}_{lm} \quad (6.4)$$

the required relation replacing Eq. (5.5) becomes

$$E_{lm}^{(r)} = - \frac{(l+1)(\epsilon_1 - 1) + \alpha_l [l\epsilon_1 + l + 1]}{[(l+1)\epsilon_1 + l] + \alpha_l l(\epsilon_1 - 1)} \frac{m_{lm}}{a^{2l+1}}. \quad (6.5)$$

The corrections obtained compared to Eq. (5.5) are of the order α_l . In the limit $kR \ll 1$ we see from Eq. (6.3) that

$$\alpha_l \sim (a/R)^{2l+1}. \quad (6.6)$$

In the opposite limit, $kR \gg 1$, the coefficient $R_l^{(e)}$ becomes closely related to the reflection coefficient for an electromagnetic wave at the surface between two dielectrics, and it is at most of order unity. Consequently it follows from Eq. (6.2) that

$$\alpha_l \sim (k_1 a)^{2l+1}. \quad (6.7)$$

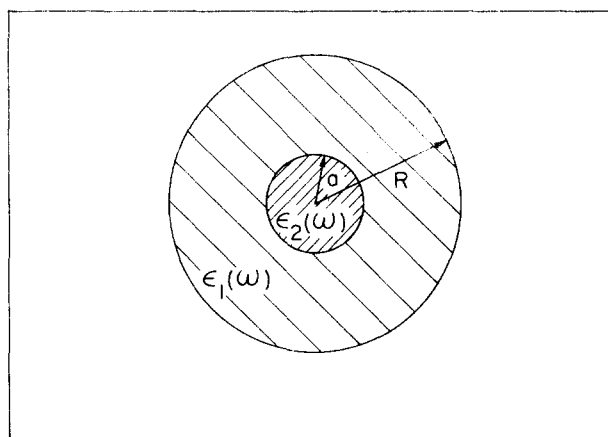


FIG. 4. A sphere with dielectric constant $\epsilon_2(\omega)$ embedded in a spherical shell of dielectric constant $\epsilon_1(\omega)$. The correlations between various electric multipole moments in this system are discussed in Sec. VII in the long wavelength limit.

This means that the error we make in neglecting the terms in the reaction field proportional to α_l is certainly smaller than the error inherent in the description of the local electric field by means of a scalar potential. The use of Eq. (6.5) instead of Eq. (5.5) is meaningful only in the long wavelength limit. Such a calculation will be carried out in the last section. We conclude this section with two remarks concerning the results just obtained.

First of all, the estimates (6.6) and (6.7) are expected to be correct irrespective of the particular geometry considered; k_1^{-1} and R are the only parameters of dimension length which are available to make α_l dimensionless in spite of the presence of the factor a^{2l+1} . Equations (6.6) and (6.7) state that α_l is of the order of the smallest available dimensionless parameter in the problem. For more general geometries one expects that the role of R will be taken over by the distance from the center of the small sphere to the boundary of the sample.

The observation made above completes the justification of the procedure used in Sec. II to calculate the correlation function for the electric polarization. The assumptions made in the beginning of that section, namely that a is small compared to both the wavelength k^{-1} and the distance to the boundary of the sample, are sufficient to justify neglecting the finiteness of the sample in the derivation of Eqs. (2.4), (2.5), and (2.7).

VII. CORRELATIONS OF MULTIPOLE MOMENTS FOR A SPHERE IN A SPHERICAL SHELL; LONG WAVELENGTH LIMIT

In this section we will complete the calculation for the autocorrelation functions of the electric multipoles of a sphere embedded in a spherical shell, in the limit in which the radii of both the sphere and the spherical shell are small compared to the wavelength of radiation with frequency ω . The autocorrelation function of any multipole moment follows immediately when we repeat the derivation of Eq. (5.7) using the expression (6.5) for the reaction field instead of Eq. (5.5). The result is

$$\mathcal{L}\left[-\frac{d}{dt}\langle m_{lm}(0)m_{l'm'}(t)\rangle\right] = kT\delta_{ll'}\delta_{m,-m'} \times \frac{l(\epsilon_2 - 1)\{[(l+1)\epsilon_1 + l](l\epsilon_1 + l + 1)R^{2l+1} - l(l+1)(\epsilon_1 - 1)^2 a^{2l+1}\}}{(2l+1)\{[(l+1)\epsilon_1 + l\epsilon_2](l\epsilon_1 + l + 1)R^{2l+1} + l(l+1)(\epsilon_1 - 1)(\epsilon_2 - \epsilon_1)a^{2l+1}\}} a^{2l+1}. \quad (7.1)$$

As expected, this reduces to Eq. (5.7) in the limit $R \gg a$.

In the limit $kR \ll 1$ we may consider a more general problem, in which not only the fluctuations in the embedded sphere, but also those in the surrounding shell are considered. The results obtained in this way, and the method used to obtain them, are direct generalizations of those in Sec. VI of Ref. 2. We first consider the spherical shell separately, in a situation in which it is subjected to several fictitious external electric fields in

addition to the multipole fields caused by the fluctuating multipole moments of the embedded sphere, which are now denoted by $m_{lm}^{(2)}$. The fictitious external fields are of two types: fields regular in the origin, which will be denoted by means of the parameters $E_{lm}^{(1)}$, and fields associated with fictitious multipoles μ_{lm} at the origin. The latter will be described by means of the parameters $E_{lm}^{(3)} = \mu_{lm} a^{-2l-1}$. The resulting expression for the scalar potential may be written as

$$\begin{aligned} \phi(\mathbf{r}) &= \sum_{l,m} \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_{lm}(\theta, \phi) [-r^l E_{lm}^{(1)} + r^{-l-1}(m_{lm}^{(1)} + m_{lm}^{(2)} - a^{2l+1} E_{lm}^{(3)})] \times \exp(-i\omega t) \quad \text{for } r \geq R; \\ \phi(\mathbf{r}) &= \sum_{l,m} \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_{lm}(\theta, \phi) [\epsilon_1(\omega)]^{-1} [-r^l A_{lm} + r^{-l-1} m_{*lm}] \times \exp(-i\omega t) \quad \text{for } R \geq r \geq a; \\ \phi(\mathbf{r}) &= \sum_{l,m} \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_{lm}(\theta, \phi) [-r^l B_{lm} + r^{-l-1}(m_{lm}^{(2)} - a^{2l+1} E_{lm}^{(3)})] \times \exp(-i\omega t) \quad \text{for } a \geq r. \end{aligned} \quad (7.2)$$

The parameters $m_{lm}^{(1)}$, m_{*lm} , A_{lm} , and B_{lm} are determined by applying the standard boundary conditions of electrostatics. In order to reach agreement with the definition of m_* in Sec. II we included a factor ϵ_1^{-1} in the expression for ϕ inside the shell; apart from this modification Eq. (7.2) is an immediate generalization of Eq. (3.14) of Ref. 2. The parameters $m_{lm}^{(1)}$ and B_{lm} have a direct physical significance: $m_{lm}^{(1)}$ is the multipole moment of the shell and B_{lm} describes the reaction field in the cavity with radius a .

The part of the field inside the medium proportional to m_{*lm} gives rise to a polarization density in the shell concentrated near the inner surface. In order to find convenient parameters to describe the "surface multipole moments" we consider the energy of the shell in the external fields described by $E_{lm}^{(1)}$ and $E_{lm}^{(3)}$. According to Landau and Lifshitz¹² this energy may be described by $-\int \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}_{\text{ext}}(\mathbf{r}) d\mathbf{r}$, in which $\mathbf{P}(\mathbf{r})$ denotes the polarization density, \mathbf{E}_{ext} denotes the sum of all external fields, and the integral extends over the volume of the spherical shell. It turns out that this quantity may be written in the form

$$H_{\text{shell}} = - \sum_{l,m} [m_{lm}^{(1)} E_{l,-m}^{(1)} + m_{lm}^{(3)} E_{l,-m}^{(3)}] \quad (7.3)$$

when we define the parameter $m_{lm}^{(3)}$ by

$$m_{lm}^{(3)} = - \frac{l+1}{2l+1} \frac{[\epsilon_1(\omega) - 1](R^{2l+1} - a^{2l+1})}{\epsilon_1(\omega) R^{2l+1}} m_{*lm}. \quad (7.4)$$

The total energy of the configuration in Fig. 4 is obtained by adding a term $-\sum_{l,m} E_{lm}^{(2)} m_{l,-m}^{(2)}$, which gives the energy of the embedded sphere due to the presence of an external field described by the parameters $E_{lm}^{(2)}$. In this

way we obtain

$$H = - \sum_{i=1}^3 \sum_{l,m} m_{lm}^{(i)} E_{l,-m}^{(i)}. \quad (7.5)$$

We recall that $m_{lm}^{(1)}$ denotes the multipole moment of the shell and $m_{lm}^{(2)}$ that of the embedded sphere. The multipole $m_{lm}^{(3)}$ arises in the shell near the boundary with the embedded sphere; accordingly it may be interpreted as a "surface fluctuation."

It is important to note that the definitions of $m_{lm}^{(i)}$ do not involve the frequency ω . The reduction of the energy to an expression of the type (7.5) makes it possible to derive expressions for the correlations of the moments $m_{lm}^{(i)}(0)$ and $m_{lm}^{(j)}(t)$ once we know the linear relations expressing the expectation values of $m_{lm}^{(i)}$ in terms of $E_{lm}^{(j)}$; from the relation

$$\overline{m_{lm}^{(i)}} = \sum_j \chi_{l;ij}(\omega) E_{lm}^{(j)}, \quad (7.6)$$

it follows that

$$\mathcal{L}\left[-\frac{d}{dt}\langle m_{lm}^{(i)}(0)m_{l'm'}^{(j)}(t)\rangle\right] = kT\chi_{l;ij}(\omega)\delta_{ll'}\delta_{m,-m'}. \quad (7.7)$$

The matrix $\chi_{l;ij}$ may be found from the relations between the parameters of the general expression (7.2) for the potential, obtained by applying the standard boundary conditions, and from the relation (5.4) for $m_{lm}^{(2)}$, in which the parameter $E_{lm}^{(0)}$ is replaced by the sum of the parameter $E_{lm}^{(2)}$, describing the imposed external field acting on the sphere, and the parameter B_{lm} , describing the reaction field. The resulting matrix is given here only for the case $\epsilon_1 = \epsilon_2 = \epsilon$. In this case we have

$$\chi_l(\omega) = \frac{\epsilon - 1}{(2l+1)^2 \epsilon R^{2l+1}} \times \begin{bmatrix} \frac{l\{(2l+1)^2 \epsilon R^{2l+1} + l(l+1)(\epsilon - 1)^2 a^{2l+1}\}(R^{2l+1} - a^{2l+1})}{l\epsilon + l + 1} & \dots & \dots \\ \frac{l^2(l+1)(\epsilon - 1)^2 (R^{2l+1} - a^{2l+1}) a^{2l+1}}{l\epsilon + l + 1} & \frac{l\{(l+1)\epsilon + l\}(l\epsilon + l + 1)R^{2l+1} - l(l+1)(\epsilon - 1)^2 a^{2l+1}}{l\epsilon + l + 1} & \dots \\ l(l+1)(\epsilon - 1)(R^{2l+1} - a^{2l+1}) a^{2l+1} & -l(l+1)(\epsilon - 1)(R^{2l+1} - a^{2l+1}) a^{2l+1} & (l+1)(l\epsilon + l + 1)(R^{2l+1} - a^{2l+1}) a^{2l+1} \end{bmatrix} \quad (7.8)$$

The matrix elements not indicated in this scheme follow from the symmetry of the matrix. The dependence of ϵ on ω is understood. In the same way as in the earlier paper² we can derive expressions for the free energy associated with equal time fluctuations in all variables $m_{lm}^{(i)}$ by inverting the matrix $\chi_l(0)$. In this way we obtain

$$\mathcal{F} = \frac{1}{2} \sum_{l,m} \left(\frac{l\epsilon_0 + l + 1}{l(\epsilon_0 - 1)(R^{2l+1} - a^{2l+1})} \overline{m_{lm}^{(1)} m_{l,-m}^{(1)}} + \frac{l\epsilon_0 + l + 1}{l(\epsilon_0 - 1)(R^{2l+1} - a^{2l+1})} \overline{m_{lm}^{(2)} m_{l,-m}^{(2)}} + \frac{[(l+1)\epsilon_0 + l]R^{2l+1}}{(l+1)(\epsilon_0 - 1)(R^{2l+1} - a^{2l+1})a^{2l+1}} \times \overline{m_{lm}^{(3)} m_{l,-m}^{(3)}} + \frac{2}{R^{2l+1} - a^{2l+1}} \overline{m_{lm}^{(1)} m_{l,-m}^{(3)}} + \frac{2}{a^{2l+1}} \overline{m_{lm}^{(2)} m_{l,-m}^{(3)}} \right) \quad (7.9)$$

The free energy associated with fluctuations in $m_{lm}^{(1)}$ and $m_{lm}^{(2)}$ may be obtained by inverting the 2×2 submatrix of Eq. (7.8) associated with those two variables. In the limit $R \gg a$ the result is

$$\mathcal{F} = \frac{1}{2} \sum_{l,m} \left\{ \frac{l\epsilon_0 + l + 1}{l(\epsilon_0 - 1)R^{2l+1}} \overline{m_{lm}^{(1)} m_{l,-m}^{(1)}} + \frac{2(l+1)(\epsilon_0 - 1)}{[(l+1)\epsilon_0 + l]R^{2l+1}} \times \overline{m_{lm}^{(1)} m_{l,-m}^{(2)}} + \frac{(2l+1)^2 \epsilon_0}{l(\epsilon_0 - 1)[(l+1)\epsilon_0 + l]a^{2l+1}} \overline{m_{lm}^{(2)} m_{l,-m}^{(2)}} \right\} \quad (7.10)$$

Apart from a factor of l in the last term this expression is identical to one derived earlier by Glarum.¹³

The time-dependent behavior of the fluctuating quantities $m_{lm}^{(i)}$ becomes more transparent when the matrix $\chi_l(\omega)$ of Eq. (7.8) is brought into diagonal form. This may be done by introducing the new fluctuating moments

$$\begin{aligned} \tilde{m}_{lm}^{(1)} &= m_{lm}^{(1)} + m_{lm}^{(2)} ; \\ \tilde{m}_{lm}^{(2)} &= \frac{-a^{2l+1}}{R^{2l+1} - a^{2l+1}} m_{lm}^{(1)} + m_{lm}^{(2)} - \frac{l}{l+1} \frac{R^{2l+1}}{R^{2l+1} - a^{2l+1}} m_{lm}^{(3)} ; \\ \tilde{m}_{lm}^{(3)} &= \frac{-a^{2l+1}}{R^{2l+1} - a^{2l+1}} m_{lm}^{(1)} + m_{lm}^{(2)} + \frac{R^{2l+1}}{R^{2l+1} - a^{2l+1}} m_{lm}^{(3)} . \end{aligned} \quad (7.11)$$

In terms of these new variables, and the external fields $\tilde{E}_{lm}^{(i)}$ obtained by applying the inverse transformation, the matrix χ_l is diagonal with matrix elements

$$\begin{aligned} \tilde{\chi}_{l,11} &= \frac{l(\epsilon - 1)R^{2l+1}}{l\epsilon + l + 1} , \\ \tilde{\chi}_{l,22} &= \frac{l(\epsilon - 1)R^{2l+1} a^{2l+1}}{(l+1)(R^{2l+1} - a^{2l+1})} , \\ \tilde{\chi}_{l,33} &= \frac{(\epsilon - 1)R^{2l+1} a^{2l+1}}{\epsilon(R^{2l+1} - a^{2l+1})} . \end{aligned} \quad (7.12)$$

As always before the matrix elements and the dielectric constant ϵ are frequency dependent.

The principal relaxation times of the system under consideration correspond to the poles of the matrix elements $\tilde{\chi}_{l,i,i}(\omega)$. In this connection it should be pointed out that the poles of $\tilde{\chi}_{l,11}(\omega)$ are at the point where $\epsilon(\omega) = -(l+1)/l$, and therefore dependent on l . The poles in

the other two diagonal matrix elements, $\tilde{\chi}_{l,22}$ and $\tilde{\chi}_{l,33}$, coincide with the poles and the zeros of $\epsilon(\omega)$ respectively; these obviously do not depend on the value of l . In the limit $R \gg a$ the matrix element $\chi_{l,22}$ from Eq. (7.12) reduces to the coefficient appearing in the expression (5.8) for the autocorrelation function of the moments of a sphere embedded in its own medium; the only relaxation times occurring are those connected with the zeros and poles of $\epsilon(\omega)$. The expression is probably more directly related to relaxation processes on a molecular level than the analogous quantity for a sphere in vacuum; accordingly it seems more suited as a starting point for an *ab initio* calculation of the frequency-dependent dielectric constant.

APPENDIX

In this Appendix we list the explicit form and some of the properties of a complete set of vector solutions of Maxwell's equations, that is appropriate for the discussion of problems with spherical symmetry. Essentially the same set is chosen in many textbooks¹⁴; the normalizations that are chosen here are somewhat different. It is convenient to start by giving a complete set of solutions of Helmholtz's equation for a vector field $\mathbf{f}(\mathbf{r})$,

$$\nabla^2 \mathbf{f}(\mathbf{r}) + k^2 \mathbf{f}(\mathbf{r}) = 0 . \quad (A1)$$

A complete set of solutions of this equation is obtained by taking the functions

$$\mathbf{L}_{klm}^{(i)}(\mathbf{r}) = k^{-1} [l(l+1)]^{1/2} \nabla [z_l^{(i)}(kr) Y_{lm}(\theta, \phi)] , \quad (A2a)$$

$$\mathbf{M}_{klm}^{(i)}(\mathbf{r}) = \nabla \times [\mathbf{r} z_l^{(i)}(kr) Y_{lm}(\theta, \phi)] , \quad (A2b)$$

$$\mathbf{N}_{klm}^{(i)}(\mathbf{r}) = k^{-1} \nabla \times \mathbf{M}_{klm}^{(i)}(\mathbf{r}) , \quad (A2c)$$

for all nonnegative l , all m between $-l$ and $+l$, and i between 1 and 4. The symbol $z_l^{(i)}(kr)$ denotes the spherical Bessel, Neumann, or Hankel functions,

$$\begin{aligned} z_l^{(1)}(kr) &= j_l(kr) , & z_l^{(2)}(kr) &= n_l(kr) , \\ z_l^{(3)}(kr) &= h_l^{(1)}(kr) , & z_l^{(4)}(kr) &= h_l^{(2)}(kr) . \end{aligned} \quad (A3)$$

The functions $Y_{lm}(\theta, \phi)$ are the spherical harmonics, normalized to unity on a sphere. The set (A2) with the index l running from 1 to 4 is overcomplete. In order to obtain a complete set one takes only two of the indices, usually 1 and 2. In this paper we encounter the solutions with $l=1$, which are regular at the origin, and

$$\begin{aligned} M_{klm}^{(i)}; r &= 0, & N_{klm}^{(i)}; r &= [l(l+1)/kr] Y_{lm}(\theta, \phi) z_l^{(i)}(kr), \\ M_{klm}^{(i)}; \theta &= (1/\sin\theta) [\partial Y_{lm}(\theta, \phi) / \partial \phi] z_l^{(i)}(kr), & N_{klm}^{(i)}; \theta &= (1/kr) [\partial Y_{lm}(\theta, \phi) / \partial \theta] \bar{z}_l^{(i)}(kr), \\ M_{klm}^{(i)}; \phi &= -[\partial Y_{lm}(\theta, \phi) / \partial \theta] z_l^{(i)}(kr), & N_{klm}^{(i)}; \phi &= (1/kr \sin\theta) [\partial Y_{lm}(\theta, \phi) / \partial \phi] \bar{z}_l^{(i)}(kr). \end{aligned} \quad (\text{A4})$$

In the expressions for $N^{(i)}$ we have used the abbreviation

$$\bar{z}_l^{(i)}(kr) = (1/r)(d/dr)[r z_l^{(i)}(kr)]. \quad (\text{A5})$$

We note that $M^{(i)}$ is a purely transversal field, while $N^{(i)}$ contains both a longitudinal and a transversal component.

With the set (A2) of solutions of Helmholtz's equations we can construct a complete set of solutions of Maxwell's equations as well. There are two types of solution:

solutions of magnetic type

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= A^{(m)} \mathbf{M}_{klm}^{(i)}(\mathbf{r}) \exp(-i\omega t); \\ \mathbf{H}(\mathbf{r}) &= A^{(m)} (kc/i\omega\mu) \mathbf{N}_{klm}^{(i)}(\mathbf{r}) \exp(-i\omega t); \end{aligned} \quad (\text{A6a})$$

solutions of electric type

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= A^{(e)} \mathbf{N}_{klm}^{(i)}(\mathbf{r}) \exp(-i\omega t); \\ \mathbf{H}(\mathbf{r}) &= A^{(e)} (kc/i\omega\mu) \mathbf{M}_{klm}^{(i)}(\mathbf{r}) \exp(-i\omega t). \end{aligned} \quad (\text{A6b})$$

The wave vector k is related to ω by means of the relation

$$k = \omega c^{-1}(\epsilon\mu)^{1/2}. \quad (\text{A7})$$

The symbols ϵ and μ always stand for the frequency-dependent quantities $\epsilon(\omega)$ and $\mu(\omega)$. For the solutions (A6a) the electric field is purely transversal; it is of order kr relative to the magnetic field. For the solutions (A6b) the situation is reversed; the magnetic field is purely transversal and near the origin the electric field is larger than the magnetic field by a factor $(kr)^{-1}$. Moreover, near the origin the electric field becomes asymptotically equal to minus the gradient of a scalar potential $\phi^{(i)}(\mathbf{r})$ equal to

$$\phi_{klm}^{(1)}(\mathbf{r}) = -A^{(e)} \frac{(l+1)k^{l-1}r^l}{(2l+1)!!} Y_{lm}(\theta, \phi) \exp(-i\omega t) \quad (\text{A8a})$$

or

$$\phi_{klm}^{(3)}(\mathbf{r}) = -A^{(e)} \frac{i l (2l-1)!!}{k^{l+2} r^{l+1}} Y_{lm}(\theta, \phi) \exp(-i\omega t). \quad (\text{A8b})$$

These expressions are obtained by substitution of the asymptotic expressions for the spherical Bessel and Hankel functions. The symbol $(2l+1)!!$ indicates the product of all odd integers up to $2l+1$,

$$(2l+1)!! = \prod_{s=1}^l (2s+1) = \frac{(2l+1)!}{2^l l!}. \quad (\text{A9})$$

those with $l=3$, which correspond to outgoing spherical waves.

The functions \mathbf{M} and \mathbf{N} are purely solenoidal in character; they are a natural basis for the description of electric and magnetic fields. We give for future use their components in spherical coordinates:

It is clear from Eq. (A8b) that the fields (A6b) for $l=3$ approach those radiated by an electric 2^l pole; similarly the fields (A6a) are those of a magnetic 2^l pole. The fields with $l=1$ are the regular fields that are capable of inducing magnetic or electric 2^l poles in a small spherical sample with its center at the origin (with a radius small compared to k^{-1}), as is demonstrated in Sec. V.

For the calculation of reaction fields inside a sphere we need solutions of Maxwell's equations for which the electric field has the form

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= A^{(m)} [\mathbf{M}_{k_2 l m}^{(3)}(\mathbf{r}) + R_l^{(m)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1) \mathbf{M}_{k_1 l m}^{(1)}(\mathbf{r})] \\ &\quad \times \exp(-i\omega t) \quad \text{for } r \leq R \end{aligned} \quad (\text{A10a})$$

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= A^{(m)} Q_l^{(m)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1) \mathbf{M}_{k_1 l m}^{(3)}(\mathbf{r}) \\ &\quad \times \exp(-i\omega t) \quad \text{for } r \geq R \end{aligned}$$

or

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= A^{(e)} [\mathbf{N}_{k_2 l m}^{(3)}(\mathbf{r}) + R_l^{(e)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1) \mathbf{N}_{k_1 l m}^{(1)}(\mathbf{r})] \\ &\quad \times \exp(-i\omega t) \quad \text{for } r \leq R \end{aligned} \quad (\text{A10b})$$

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= A^{(e)} Q_l^{(e)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1) \mathbf{N}_{k_1 l m}^{(3)}(\mathbf{r}) \exp(-i\omega t) \\ &\quad \text{for } r \geq R. \end{aligned}$$

The magnetic fields are constructed by analogy to Eq. (A6). By applying the standard boundary conditions at the surface of the sphere with radius R we obtain the values of the parameters Q and R . In particular

$$\begin{aligned} R_l^{(m)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1) &= -\frac{\mu_2 h_l^{(1)}(k_2 r) \bar{h}_l^{(1)}(k_1 r) - \mu_1 h_l^{(1)}(k_1 r) \bar{h}_l^{(1)}(k_2 r)}{\mu_2 j_l(k_2 r) \bar{h}_l^{(1)}(k_1 r) - \mu_1 h_l^{(1)}(k_1 r) \bar{j}_l(k_2 r)}, \end{aligned} \quad (\text{A11a})$$

$$\begin{aligned} R_l^{(e)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1) &= -\frac{\epsilon_2 h_l^{(1)}(k_2 r) \bar{h}_l^{(1)}(k_1 r) - \epsilon_1 h_l^{(1)}(k_1 r) \bar{h}_l^{(1)}(k_2 r)}{\epsilon_2 j_l(k_2 r) \bar{h}_l^{(1)}(k_1 r) - \epsilon_1 h_l^{(1)}(k_1 r) \bar{j}_l(k_2 r)}. \end{aligned} \quad (\text{A11b})$$

In the limit $kR \ll 1$ these expressions reduce to

$$R_l^{(m)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1) \approx i \frac{(2l+1)!! (2l-1)!!}{(k_2 R)^{2l+1}} \frac{l(\mu_2 - \mu_1)}{l\mu_2 + (l+1)\mu_1}, \quad (\text{A12a})$$

$$R_l^{(e)}(\epsilon_2, \mu_2; \epsilon_1, \mu_1) \approx i \frac{(2l+1)!! (2l-1)!!}{(k_2 R)^{2l+1}} \frac{l(\epsilon_2 - \epsilon_1)}{l\epsilon_2 + (l+1)\epsilon_1}. \quad (\text{A12b})$$

This asymptotic form is used in Secs. IV and VI.

*Supported in part by the National Science Foundation.

¹G. Nienhuis and J. M. Deutch, *J. Chem. Phys.* **55**, 4213 (1971).

²U. M. Titulaer and J. M. Deutch, *J. Chem. Phys.* **60**, 1502 (1974).

³A. D. Buckingham and C. Graham, *Mol. Phys.* **22**, 335 (1971).

⁴R. Kubo, in *Statistical Mechanics of Equilibrium and Non-Equilibrium*, edited by J. Meixner (North-Holland, Amsterdam, 1965), p. 81.

⁵H. Fröhlich, *Theory of Dielectrics* (Clarendon, Oxford, 1958), 2nd Ed., Appendix B.

⁶J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), Chap. 9.

⁷A. Ben-Naim and F. H. Stillinger, in *Water and Aqueous Solu-*

tions, Structure, Thermodynamics, and Transport Processes, edited by R. A. Horne (Wiley-Interscience, New York, 1972).

⁸F. M. Kuni, *Phys. Lett. A* **26**, 305 (1968).

⁹See, e.g., J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), Sec. 1.11.

¹⁰W. W. Hansen, *Phys. Rev.* **47**, 139 (1934).

¹¹See, e.g., Ref. 6, Sec. 3.5.

¹²L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960), Sec. 11.

¹³S. H. Glarum, *Mol. Phys.* **24**, 1327 (1972).

¹⁴See, e.g., Ref. 9, Sec. 7.1 or P. M. Morse and H. Feshbach, *Methods of Theoretical Physics, Part II* (McGraw-Hill, New York, 1953), Chap. 13. See also Ref. 10.