Analysis of conflicting theories of dielectric relaxation*

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Two different forms have been proposed for the relation between the frequency-dependent dielectric constant of a polar substance and the autocorrelation function for the net dipole moment of a small spherical region inside the dielectric. We find that one of them is correct, while the other one describes a spherical sample embedded in a medium with a frequency-independent dielectric constant equal to the static dielectric constant of the sample. A number of recent papers dealing with this question are analyzed. We discuss in particular the role played by fluctuations in the polarization of the surrounding medium near the surface of the embedded sphere.

I. INTRODUCTION

A. History of the problem

A controversy has developed concerning the precise relationship between the frequency-dependent dielectric constant of a polar medium and the spontaneous fluctuations of the dipole moment of a small spherical region in that medium. Kirkwood[1] derived a relation between the static dielectric constant of a polar substance and the mean square fluctuation in the net dipole moment of a spherical specimen, which is embedded in an infinite dielectric continuum with the same dielectric constant. Glarum[2] derived a similar expression for the frequency-dependent dielectric constant by applying the general formalism of linear response theory. The formalism was used to derive a relation between the dielectric constant and the autocorrelation function for the net dipole moment of a sphere in vacuum. The latter quantity was then related to the autocorrelation function of the net dipole moment of a sphere embedded in a medium with the same dielectric constant. In this way, he obtained the expression

$$\mathcal{L}\left[-\frac{d\phi}{dt}\right]=\frac{[\epsilon(\omega)-1]\cdot 3\epsilon_0}{[\epsilon_0-1][\epsilon(\omega)+2\epsilon_0]}\quad. \tag{1.1}$$

In this expression ϕ is the normalized autocorrelation function for the net dipole moment of an embedded sphere, $\mathcal{L}$ denotes a Laplace transform, and $\epsilon(\omega)$ and ϵ_0 are the frequency-dependent and the static dielectric constants of the medium. Glarum's theory was generalized by Cole[3] for the case that induced as well as permanent dipoles are present in the medium.

Glarum's derivation was criticized by Fatuzzo and Mason.[4] These authors arrived at a different relation between ϕ and $\epsilon(\omega)$:

$$\mathcal{L}\left[-\frac{d\phi}{dt}\right]=\frac{[\epsilon(\omega)-1][2\epsilon(\omega)+1]\epsilon_0}{(\epsilon_0-1)(2\epsilon_0+1)\epsilon(\omega)}\quad. \tag{1.2}$$

In the same paper Fatuzzo and Mason tentatively proposed a derivation of Eq. (1.2) by a direct application of the formulas of linear response theory to a sphere embedded in a medium. This direct treatment was also adopted by Klug, Kranbuehl, and Vaughan,[5] by Nee and Zwanzig,[6] and by Hill.[7] In these three papers the theory was generalized to include induced as well as permanent dipoles. In the present paper we will not treat the complications caused by induced dipoles; a clear exposition is found in Hill's paper.[7] Scaife treated aspects of the problem by calculations using the fluctuation-dissipation theorem.[8]

The derivations of Eq. (1.2) were attacked in a recent paper by Glarum.[9] In this paper he attributes the difference in the expressions (1.1) and (1.2) to differences in the treatment of the interface between the spherical sample and the surrounding dielectric continuum; Equation (1.2) is said to result when the interface is treated as a real physical surface rather than a mathematical construct; the fluctuations in the surface polarization that occur at a real surface are claimed to be responsible for the difference in the two expressions.

Two recent papers by Cole also concern the discrepancy between the two expressions (1.1) and (1.2). In the first one[10] he gives a molecular derivation of Glarum's original expression (1.1). The second one[11] aims to settle the issue by means of explicit calculations for a specific model of a polar solid, introduced by Zwanzig.[12] A straightforward calculation leads to an expression for $\phi(t)$ which disagrees with Glarum's prediction. However, Cole considers various features of this expression undesirable and proposes a modified treatment of the model, in which those undesirable features are absent; the modified treatment leads to agreement with Glarum's expression (1.1).

B. Survey of the present paper

The purpose of the present paper is to review and assess the arguments offered in favor of the rival expressions (1.1) and (1.2). In Sec. II we present the direct application of the linear response theory to a sphere embedded in an infinite dielectric medium. The treatment is slightly more general than that of earlier authors in that we allow for a difference in dielectric constant between the sphere and the surroundings. When the two dielectric constants are equal, the Fatuzzo–Mason expression is obtained. However, when the surrounding medium is given a frequency-independent dielectric constant equal to the static dielectric constant of the sphere, we obtain Glarum's relation.

Reservations have been expressed about the validity of this direct application of linear response theory. The cavity field, which enters as an external field in the linear response derivation, does in fact include a contribution due to the response of the surrounding medium

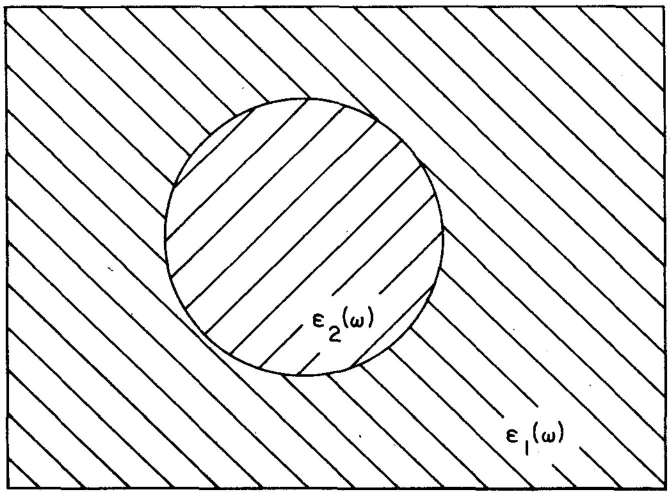

FIG. 1. The system discussed in Sec. II: a sphere with dielectric contant $\epsilon_2(\omega)$ embedded in an infinite dielectric continuum with dielectric constant $\epsilon_1(\omega)$.

to the true external field. This objection does not hold for the treatment in Sec. III. There we consider the problem of a sphere placed inside of a spherical shell. The response of this configuration to external fields is evaluated and the correlation functions for the spontaneous fluctuations in the net dipole moments follow via the fluctuation-dissipation theorem[13] in a manner similar to that employed by Scaife.[8] This fluctuation-dissipation calculation may be considered the time-dependent analogue of a free energy calculation carried out by Glarum.[9] In particular Glarum's prescriptions for the treatment of the internal surface are followed. Nevertheless, the calculations lead to the Fatuzzo–Mason expression (1.2). Glarum's relation (1.1) again results when we take the dielectric constant of the surrounding shell equal to the static dielectric constant of the sphere for all frequencies.

In Sec. IV we consider Cole's calculation for Zwanzig's model of a lattice of permanent dipoles. First we point out a simple way to determine the results to be expected on the basis of either Glarum's expression or the one found by Fatuzzo and Mason. It turns out that the result of the lattice calculation disagrees with Eq. (1.1) but shows full agreement with the prediction derived from Eq. (1.2). This latter comparison was not made explicitly by Cole.

In Sec. V we review Cole's derivation of Eq. (1.1) and his modified treatment of Zwanzig's lattice model. In both derivations there is a crucial step in which the reaction field exerted by molecules in the surrounding shell is replaced by an average reaction field. This average is calculated using the *instantaneous* values of the dipole moments of the molecules in the inner sphere. This amounts to replacing the frequency-dependent dielectric constant of the shell by the static one; it is therefore not surprising that this approximation leads to agreement with Glarum's result (1.1).

In the final section we discuss the fluctuations in the polarization near the inner surface of the external region. We show how to modify the treatment of Sec. III in such a way that these surface fluctuations are included. This more detailed description does not however lead to any modification of the results obtained in Sec. III. In particular the relation between the dielectric constant and the autocorrelation function of the net dipole moment of the inner sphere is not affected when surface fluctuations are included in the description. The more detailed description does however lead to a more transparent picture of the relaxation of the net dipole moments from initial nonequilibrium values. In the final part of Sec. VI we make some observations on the consequences for this relaxation behavior of choosing any one of two familiar approximate expressions for the frequency-dependent dielectric constant of a polar material.

The conclusion from our considerations is that the expression (1.2) of Fatuzzo and Mason is correct for the case of a sphere embedded in a medium with the same frequency-dependent dielectric constant. Glarum's expression (1.1) on the other hand correctly describes the fluctuations of a sphere embedded in a medium with a frequency-independent dielectric constant ϵ_0. The former is perhaps a more convenient starting point for undertaking microscopic model calculations.

II. SIMPLE LINEAR RESPONSE THEORY

Consider an isotropic molecular sample in a spherical volume of radius a, consisting of a material characterized by a frequency-dependent dielectric constant $\epsilon_2(\omega)$. This molecular sample is embedded in an infinite medium, which by assumption consists of a macroscopic dielectric continuum characterized by a dielectric constant $\epsilon_1(\omega)$. See Fig. 1. We further suppose than an electric field is present in the medium and that it approaches the constant value $\mathbf{E}^\infty(t)$ at large distances from the enclosure. The familiar algorithm of linear response theory[2,3,14] permits one to express the expectation value $\langle m_2(t)\rangle_{E^\infty}$ of the net dipole moment of the sphere in the presence of a field in terms of the autocorrelation function of the net dipole moment in the absence of a field:

$$\langle m_z(t)\rangle_{E^\infty} = \frac{-1}{kT}\int_0^\infty E_z^c(t-t')\,\frac{d}{dt'}\,\langle m_z(0)m_z(t')\rangle\,dt' \;. \tag{2.1}$$

In the linear response formalism the field E_z^c is the field in the macroscopic cavity of radius a, which would be present when the molecular sample were removed from the surrounding medium. For the special case in which $\mathbf{E}^\infty(t) = \hat{z}E^\infty(t) = E^\infty\hat{z}e^{i\omega t}$ we can express E_z^c in terms of E^∞ by means of a simple electrostatic boundary value calculation[15]; the result is

$$E_z^c(t) = \{3\epsilon_1(\omega)/[2\epsilon_1(\omega)+1]\}E^\infty(t) \;. \tag{2.2}$$

Of course this treatment is valid only when the spatial variation of the field is negligible, i.e., the wavelength associated with the frequency ω is large compared with the radius of the cavity. This condition is easily met for most polar substances, where the dielectric relaxation takes place at frequencies corresponding to those of radio waves. Dielectric relaxation in most nonpolar

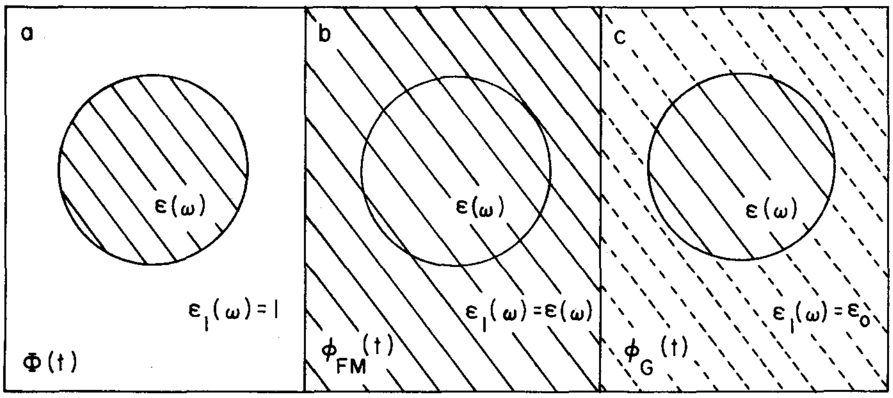

FIG. 2. Three special cases of the situation described in Fig. 1: (a) the surrounding continuum is replaced by vacuum; (b) the surrounding continuum has the same frequency-dependent dielectric constant as the embedded sphere; (c) the surrounding continuum has a frequency-independent dielectric constant equal to the static dielectric constant of the embedded sphere.

substances takes place at much higher frequencies and the simple theories presented in this paper cannot be applied without modification.

For uniform polarization geometries such as the one discussed here the net dipole moment per unit volume resulting from an external field with frequency ω is related to the frequency-dependent dielectric constant of the molecular medium $\epsilon_2(\omega)$ and the macroscopic electric field inside the spherical sample $E_z(t)$ by

$$\langle m_z(t)\rangle_{E^\infty}=\{[\epsilon_2(\omega)-1]/4\pi\}\cdot\tfrac{4}{3}\pi a^3E_z(t)\ . \qquad (2.3)$$

The quantity $E_z(t)$ may be expressed in terms of $E^\infty(t)$ by a macroscopic calculation[15]:

$$E_z(t)=\{3\epsilon_1(\omega)/[2\epsilon_1(\omega)+\epsilon_2(\omega)]\}E^\infty(t)\ . \qquad (2.4)$$

By equating the expressions (2.1) and (2.3) and substituing Eq. (2.2) and (2.4) we obtain the relation

$$-\frac{1}{kT}\int_0^\infty e^{-i\omega t'}\frac{d}{dt'}\langle m_z(0)m_z(t')\rangle\,dt'$$
$$=\frac{[\epsilon_2(\omega)-1][2\epsilon_1(\omega)+1]}{3\,[2\epsilon_1(\omega)+\epsilon_2(\omega)]}\,a^3\ . \qquad (2.5)$$

An analogous linear response calculation for a static field leads to the expression

$$\langle m_z(0)m_z(0)\rangle=\frac{[\epsilon_1(0)-1][2\epsilon_1(0)+1]}{3\,[2\epsilon_1(0)+\epsilon_2(0)]}\,a^3kT\ . \qquad (2.6)$$

where $\epsilon_1(0)$ $[\epsilon_2(0)]$ is the static dielectric constant of the outer [inner] region. When we define the normalized correlation function

$$\phi(t)=\langle m_z(0)m_z(t)\rangle/\langle m_z(0)m_z(0)\rangle \qquad (2.7)$$

and use the notation $\mathcal{L}[f(t)]$ to denote the Laplace transform of f with Laplace transform variable $z=i\omega$, we readily derive the relation

$$\mathcal{L}\left[-\frac{d}{dt}\,\phi(t)\right]=\frac{[\epsilon_2(\omega)-1][2\epsilon_1(\omega)+1][2\epsilon_1(0)+\epsilon_2(0)]}{[\epsilon_2(0)-1][2\epsilon_1(0)+1][2\epsilon_1(\omega)+\epsilon_2(\omega)]}\ . \qquad (2.8)$$

In Eq. (2.7) the bracket denotes an equilibrium average in the absence of any imposed field of the net dipole moment autocorrelation function. The average is performed over an equilibrium canonical ensemble. The classical Hamiltonian that occurs in the Boltzmann weighting factor includes both the direct interactions between the molecules in the spherical sample and the interactions between those molecules mediated by the surrounding polarizable medium. The same is true for the Liouville operator that governs the time dependence of $m_z(t)$. The result Eq. (2.8) clearly illustrates the dependence of the equilibrium time correlation function $\phi(t)$ upon the nature of the external continuum region, even in the absence of fields and irrespective of the size of the molecular sample. This situation is well known in the case of the static fluctuations,[16] e.g., Eq. (2.6). In polar systems both equilibrium- and time-dependent fluctuations in the net dipole moment depend upon the shape of the sample and the nature of external region.

The controversy concerning the various relationships between the correlation function $\phi(t)$ and $\epsilon_2(\omega)$ may be clarified by considering several special cases of Eq. (2.8); see Fig. 2. First we set $\epsilon_1(\omega)=1$, which corresponds to eliminating the external region; see Fig. (2a). In this case we recover the well-known result for the normalized autocorrelation function[2,3] of the net dipole moment of a sphere in vacuum. The function $\phi(t)$ for this special case is denoted by $\Phi(t)$, and it obeys

$$\mathcal{L}\left[-\frac{d}{dt}\,\Phi(t)\right]=\frac{[\epsilon(\omega)-1](\epsilon_0+2)}{[\epsilon(\omega)+2](\epsilon_0-1)}\ . \qquad (2.9)$$

In this expression we omitted the index 2 in $\epsilon_2(\omega)$ and wrote ϵ_0 for $\epsilon_2(0)$.

As a second special case we set $\epsilon_1(\omega)=\epsilon_2(\omega)=\epsilon(\omega)$. This corresponds to the physical situation of a molecular sample embedded in an infinite macroscopic medium characterized by the same dielectric constant; see Fig. 2b. For this case, which was considered by Fatuzzo and Mason,[4] we recover their result

$$\mathcal{L}\left[-\frac{d}{dt}\,\phi_{FM}(t)\right]=\frac{[\epsilon(\omega)-1][2\epsilon(\omega)+1]\epsilon_0}{(\epsilon_0-1)(2\epsilon_0+1)\epsilon(\omega)}\ ; \qquad (2.10)$$

we have denoted $\phi(t)$ for this special case by $\phi_{FM}(t)$. Fatuzzo and Mason in Sec. 4 of Ref. 4 express some reservations concerning the validity of this treatment, in view of the fact that the cavity field used in Eq. (2.1) is not a truly external field of the type required for Kubo's linear response treatment. We do not think the objection is a very grave one. However, the treatment in the next section, which leads to the same results, is not subject to this reservation.

Finally we consider the special case (to our knowledge not explicitly considered heretofore) in which $\epsilon_2(\omega)$

$=\epsilon(\omega)$ while $\epsilon_1(\omega)=\epsilon_0$ for all frequencies. This corresponds to the physical situation of a molecular medium characterized by a dielectric constant $\epsilon(\omega)$ embedded in an infinite macroscopic medium that responds instantaneously to fields of all frequencies as a static dielectric; see Fig. 2c. The resulting expression is

$$\mathcal{L}\left[-\frac{d}{dt}\phi_G(t)\right]=\frac{[\epsilon(\omega)-1]\cdot 3\epsilon_0}{[2\epsilon_0+\epsilon(\omega)](\epsilon_0-1)} . \qquad (2.11)$$

This formula corresponds precisely to the expression for $\phi(t)$ given by Glarum.[2] Accordingly we denote $\phi(t)$ for this case by $\phi_G(t)$.

Confusion between the second case where $\epsilon_1(\omega)=\epsilon_2(\omega)=\epsilon(\omega)$ and the third case where $\epsilon_1(\omega)=\epsilon_2(0)=\epsilon_0$ is responsible for part of the controversy on dielectric relaxation. Both equations, (2.10) and (2.11), are correct. One must recognize however that they correspond to entirely different physical situations: $\phi_{\mathrm{FM}}(t)$ corresponds to the fluctuating moment of a spherical molecular sample embedded in a medium of its own frequency-dependent dielectric constant, while $\phi_G(t)$ corresponds to the fluctuating moment of a spherical molecular sample embedded in a medium that is characterized by a frequency-independent dielectric constant equal to the static dielectric constant of the sphere. An exact calculation that takes into account this difference, if carried to completion for both $\phi_{\mathrm{FM}}(t)$ and $\phi_G(t)$, is expected on physical grounds to lead to identical results for $\epsilon(\omega)$. For model calculations it is likely that the second case, involving $\phi_{\mathrm{FM}}(t)$, will prove more useful. It is however definitely incorrect to identify $\phi_G(t)$ with the physical situation of a spherical molecular sample embedded in its own medium, characterized by $\epsilon(\omega)$. The only microscopic correlation function $\phi(t)$ which corresponds to this case is the Fatuzzo–Mason result $\phi_{\mathrm{FM}}(t)$.

The remainder of this article is devoted to establishing the correctness of Eqs. (2.10) and (2.11) for the two physical situations of interest by another method and to pointing out where previous analyses of the problem have gone astray.

III. APPLICATION OF THE FLUCTUATION-DISSIPATION THEOREM TO A SPHERE EMBEDDED IN A SPHERICAL SHELL

In this section we replace the infinite medium surrounding the small sphere by a spherical shell consisting of a molecular medium with dielectric constant $\epsilon_1(\omega)$ with external radius R and internal radius a. We will assume that both a and R are large on an atomic scale but small compared to any electromagnetic wavelength associated with a relevant frequency ω; see Fig. 3. The net dipole moments of the spherical shell and the embedded sphere will be designated by m_1 and m_2, respectively. The autocorrelation functions of m_1 and m_2 are related by means of the Wiener–Khinchin theorem to the spectral density of their fluctuations. The latter quantity is related to the energy dissipation in a periodic external field by means of the fluctuation-dissipation theorem. In this section we shall apply the fluctuation-dissipation theorem to the problem of dielectric relaxation. The calculation is very close in spirit to the linear response treatment of the preceding section. The main difference with the linear response discussion concerns the treatment of the exterior region and the presence of more than a single auxiliary external field.

For the purpose of our calculation we have to determine the energy dissipation for the case in which the spherical shell and the embedded sphere are subject to two distinct external fields $\mathbf{E}_1(t)$ and $\mathbf{E}_2(t)$. This leads to a rate of energy dissipation equal to[17]

$$Q=-\mathbf{m}_1\cdot(d\mathbf{E}_1/dt)-\mathbf{m}_2\cdot(d\mathbf{E}_2/dt) . \qquad (3.1)$$

Again we will assume that both $\mathbf{E}_1$ and $\mathbf{E}_2$ are in the z direction, and we will consider only z components of the various net dipole moments. Since no confusion can arise we will omit the subscript z in the remainder of this paper. The occurrence of quadratic quantities makes it mandatory to work with real fields; we therefore assume a time dependence for each field of the form

$$\mathbf{E}_i(t)=\tfrac{1}{2}[E_i(\omega)e^{i\omega t}+E_i^*(\omega)e^{-i\omega t}]\hat{z}, \quad i=1,2. \qquad (3.2)$$

The response of the net dipole moments m_i will exhibit the same oscillatory time dependence and their expectation values may be expressed in terms of $E_j(\omega)$ by means of a set of linear relations:

$$\bar{m}_i(\omega)=\sum_{j=1,2}\chi_{ij}(\omega)E_j(\omega) . \qquad (3.3)$$

Substitution of Eq. (3.2) and (3.3) in Eq. (3.1) and averaging over a period of oscillation leads to the expression

$$\bar{Q}=-(\omega/2)\sum_{i,j}E_i^*(\omega)\,\mathrm{Im}[\chi_{ij}(\omega)]E_j(\omega) . \qquad (3.4)$$

The fluctuation-dissipation theorem[13] enables us to determine from the relation (3.4) the spectral density of the fluctuations in the quantities m_1 and m_2 (valid pro-

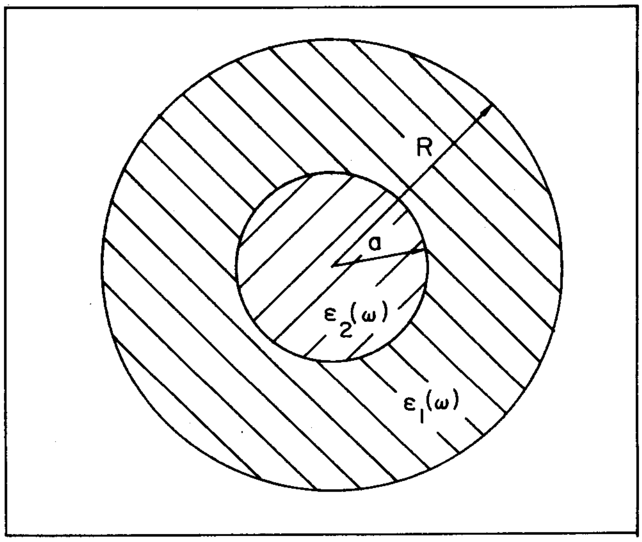

FIG. 3. The system discussed in Sec. III: a sphere with dielectric constant $\epsilon_2(\omega)$ embedded in a spherical shell with dielectric constant $\epsilon_1(\omega)$.

vided $kT \gg \hbar\omega$)

$$(m_i m_j)_\omega = -(kT/\pi\omega)\,\mathrm{Im}[\chi_{ij}(\omega)]\,, \tag{3.5}$$

where following Landau and Lifshitz[13] we introduced the notation

$$(m_i m_j)_\omega = (-1/2\pi)\int_{-\infty}^{+\infty} \langle m_i(0) m_j(t)\rangle\, e^{-i\omega t}\, dt\,. \tag{3.6}$$

The average is again a canonical one taken in the absence of any external fields. However, the Hamiltonian in the Boltzmann weighting factor and the Liouville operator governing the evolution of $m_j(t)$ now contain the direct interactions between molecules in both the inner sphere and the surrounding shell. The agreement we will find with the results of section II may be considered as a partial justification for the linear response procedure followed there. The equal time correlation of m_i and m_j in the absence of external fields follows immediately from Eqs. (3.5) and (3.6):

$$\begin{aligned}\langle m_i(0) m_j(0)\rangle &= -\int_{-\infty}^{+\infty} (m_i m_j)_\omega\, d\omega \\ &= -(kT/\pi)\int_{-\infty}^{+\infty} \omega^{-1}\,\mathrm{Im}[\chi_{ij}(\omega)]\, d\omega\,. \end{aligned} \tag{3.7}$$

Since the real and imaginary part of $\chi_{ij}(\omega)$ obey the Kramers–Kronig[18] relations this is equal to

$$\langle m_i(0) m_j(0)\rangle = kT\,\mathrm{Re}[\chi_{ij}(0)] = kT\chi_{ij}(0)\,. \tag{3.8}$$

The Laplace transform of the derivative of the correlation function $\langle m_i(0) m_j(t)\rangle$ is also expressible in terms of the spectral density of the fluctuations:

$$\begin{aligned}&\mathcal{L}[(d/dt)\langle m_i(0) m_j(t)\rangle] \\ &\quad = (-ikT/\pi)\int_0^{\infty} e^{-i\omega t}\, dt \int_{-\infty}^{+\infty} e^{i\omega' t}\,\mathrm{Im}[\chi_{ij}(\omega')]\, d\omega'\,. \end{aligned} \tag{3.9}$$

Using the identity

$$\int_0^{\infty} e^{i(\omega'-\omega)t}\, dt = iP(\omega' - \omega)^{-1} + \pi\delta(\omega' - \omega) \tag{3.10}$$

(in which P indicates that the principal value must be taken in the integration over ω') and once more using the Kramers–Kronig relations we obtain

$$\begin{aligned}&\mathcal{L}[(d/dt)\langle m_i(0) m_j(t)\rangle] \\ &\quad = -kT\{\mathrm{Re}[\chi_{ij}(\omega)] + i\,\mathrm{Im}[\chi_{ij}(\omega)]\} = -kT\chi_{ij}(\omega)\,. \end{aligned} \tag{3.11}$$

For the normalized correlation function

$$\phi_{ij}(t) = \langle m_i(0) m_j(t)\rangle / \langle m_i(0) m_j(0)\rangle \tag{3.12}$$

we find the result

$$\mathcal{L}[-(d/dt)\phi_{ij}(t)] = \chi_{ij}(\omega)[\chi_{ij}(0)]^{-1}, \tag{3.13}$$

where we have made use of Eq. (3.8).

We will now proceed to calculate $\chi_{ij}(\omega)$ by means of a macroscopic calculation. First we consider a spherical shell subjected to an external field E_1 and the field of a dipole m_2 placed in the center. All quantities vary harmonically in time with a factor $e^{i\omega t}$, and the coefficients in all subsequent formulae will be functions of ω; this dependence will often not be indicated explicitly.

The scalar potential for the hollow shell has the general form

$$\begin{aligned}\varphi &= z[-B + m_2 r^{-3}] && a > r; && \epsilon = 1 \\ \varphi &= z[-A + m_* r^{-3}] && R > r > a; && \epsilon = \epsilon_1 \\ \varphi &= z[-E_1 + (m_1 + m_2) r^{-3}] && r > R; && \epsilon = 1. \end{aligned} \tag{3.14}$$

The average values of A, B, m_*, and m_1 are related to E_1 and the average value of m_2 by means of the standard boundary conditions. After some algebra we obtain the relation

$$\begin{aligned}&\overline{m}_1[(2\epsilon_1 + 1)(\epsilon_1 + 2)R^3 - 2(\epsilon_1 - 1)^2 a^3] \\ &\quad = (\epsilon_1 - 1)(2\epsilon_1 + 1)R^3(R^3 - a^3)E_1 - 2(\epsilon_1 - 1)^2(R^3 - a^3)\overline{m}_2\,. \end{aligned} \tag{3.15}$$

We will also need the expression for the average cavity field $\overline{B}$,

$$a^3\overline{B} = R^3 E_1 - [(\epsilon_1 + 2)/(\epsilon_1 - 1)]\,\overline{m}_1\,. \tag{3.16}$$

Next we consider the inner sphere. In addition to the external field E_2 it feels the field $B - E_1$ due to the surrounding shell. A calculation like the one leading to Eq. (2.3) gives

$$\begin{aligned}\overline{m}_2 = [(\epsilon_2 - 1)/(\epsilon_2 + 2)]\{&E_2 a^3 + E_1(R^3 - a^3) \\ &- [(\epsilon_1 + 2)/(\epsilon_1 - 1)]\overline{m}_1\}\,. \end{aligned} \tag{3.17}$$

Equations (3.14) and (3.16) may be combined to give expressions for the coefficients $\chi_{ij}(\omega)$ in Eq. (3.3):

$$\begin{aligned}&\overline{m}_1[3(2\epsilon_1 + \epsilon_2)(\epsilon_1 + 2)R^3 + 6(\epsilon_2 - \epsilon_1)(\epsilon_1 - 1)a^3] \\ &\quad = (\epsilon_1 - 1)[3(2\epsilon_1 + \epsilon_2)R^3 + 2(\epsilon_1 - 1)(\epsilon_2 - 1)a^3](R^3 - a^3)E_1 \\ &\qquad - 2(\epsilon_1 - 1)^2(\epsilon_2 - 1)a^3(R^3 - a^3)E_2; \end{aligned} \tag{3.18a}$$

$$\begin{aligned}&\overline{m}_2[3(2\epsilon_1 + \epsilon_2)(\epsilon_1 + 2)R^3 + 6(\epsilon_2 - \epsilon_1)(\epsilon_1 - 1)a^3] \\ &\quad = (\epsilon_2 - 1)[(2\epsilon_1 + 1)(\epsilon_1 + 2)R^3 - 2(\epsilon_1 - 1)^2 a^3]a^3 E_2 \\ &\qquad - 2(\epsilon_1 - 1)^2(\epsilon_2 - 1)a^3(R^3 - a^3)E_1\,. \end{aligned} \tag{3.18b}$$

The limit $R \gg a$ corresponds to the physical situation considered in Sec. II. In this limit the expressions for $\chi_{11}(\omega)$ and $\chi_{22}(\omega)$ reduce to

$$\begin{aligned}\chi_{11}(\omega) &= [(\epsilon_1 - 1)/(\epsilon_1 + 2)]R^3, \\ \chi_{22}(\omega) &= [(\epsilon_2 - 1)(2\epsilon_1 + 1)/3(2\epsilon_1 + \epsilon_2)]a^3. \end{aligned} \tag{3.19}$$

These expressions in conjunction with Eq. (3.13) may be employed to obtain explicit expressions for the Laplace transform of the correlation functions of the net dipole moment. Thus Eq. (3.13) for $\chi_{11}(\omega)$ in the limit $R \gg a$ corresponds to the case of a sphere in vacuum and one obtains exactly the linear response result Eq. (2.9). In the limit $R \gg a$ Eq. (3.13) for $\chi_{22}(\omega)$ with $\epsilon_1(\omega) = \epsilon_2(\omega) = \epsilon(\omega)$ corresponds to the case of a sphere embedded in an infinite medium characterized by the same dielectric constant and one obtains exactly the Fatuzzo–Mason result Eq. (1.2). In the limit $R \gg a$ Eq. (3.12) for $\chi_{22}(\omega)$ with $\epsilon_1(\omega) = \epsilon_2(0) = \epsilon_0$ and $\epsilon_2(\omega) = \epsilon(\omega)$ corresponds to the case of a sphere embedded in an infinite medium characterized for all frequencies by a dielectric constant equal to the static dielectric constant of the inner sphere. The result is identical to Eq. (1.1). Accordingly we have demonstrated that the fluctuation-dissipation calculation leads to identical results for the various physical situations of interest as the linear response calculation. The two methods lead to the same relationship of $\epsilon(\omega)$ to the microscopic correlation functions $\phi(t)$.

In the limit $R \gg a$ the cross terms $\chi_{12}(\omega)$ take the form

$$\chi_{12}(\omega) = \chi_{21}(\omega) = -[2(\epsilon_1 - 1)^2(\epsilon_2 - 1)/3(2\epsilon_1 + \epsilon_2)(\epsilon_1 + 2)]a^3 . \tag{3.20}$$

This quantity is needed in order to calculate the decay of the polarization induced by the inner sphere in the surrounding shell. Fatuzzo and Mason[4] define the correlation function $\Phi_1(t)$ by the relation

$$\langle m_2(0) m_1(t)\rangle = \frac{2(\epsilon_0 - 1)^2}{(2\epsilon_0 + 1)(\epsilon_0 + 2)} \int_0^t \langle m_2(0) m_2(t')\rangle \frac{d\Phi_1(t - t')}{dt'}\, dt' . \tag{3.21}$$

Using Eq. (3.11) and the convolution property of the Laplace transform we find

$$\mathcal{L}\left[-\frac{d\Phi_1}{dt}\right] = \frac{\chi_{12}(\omega)\chi_{22}(0)}{\chi_{22}(\omega)\chi_{12}(0)} = \frac{2(\epsilon_1 - 1)^2}{(\epsilon_1 + 2)(2\epsilon_1 + 1)} \frac{(\epsilon_0 + 2)(2\epsilon_0 + 1)}{2(\epsilon_0 - 1)^2} , \tag{3.22}$$

which is exactly the result derived by Fatuzzo and Mason by a slightly different method. When the dielectric constant of the surrounding shell is frequency-independent, the function Φ_1 is equal to unity, as should be expected for a medium that responds instantaneously to any applied field.

Glarum[9] has presented a calculation of the equal time fluctuations of the net moment $\langle m_i(0) m_j(0)\rangle$ by examining the free energy of the configuration of a sphere inside a spherical shell, acted upon by two static homogeneous external fields. According to Landau and Lifshitz[17] this free energy may be written as

$$\mathfrak{F} = \tfrac{1}{2}[m_1 E_1 + m_2 E_2] , \tag{3.23}$$

in which m_1, m_2, E_1, and E_2 are now time-independent quantities. The expectation value of this expression may be written as

$$\overline{\mathfrak{F}} = \frac{1}{2} \sum_{i,j} E_i \chi_{ij}(0) E_j , \tag{3.24a}$$

or alternatively, in terms of the average dipole moments,

$$\overline{\mathfrak{F}} = \frac{1}{2} \sum_{i,j} \overline{m}_i [\chi(0)]^{-1}_{ij} \overline{m}_j . \tag{3.24b}$$

The expression (3.24b) may be evaluated by means of Eq. (3.18) and a matrix inversion. This leads to the expression

$$\overline{\mathfrak{F}} = \frac{1}{2}\left\{\overline{m}_1^2 \frac{(\epsilon_{10} + 2)(2\epsilon_{10} + 1)R^3 - 2(\epsilon_{10} - 1)^2 a^3}{(\epsilon_{10} - 1)(2\epsilon_{10} + 1)R^3(R^3 - a^3)} + 2\overline{m}_1\overline{m}_2 \frac{2(\epsilon_{10} - 1)}{(2\epsilon_{10} + 1)R^3} + \overline{m}_2^2 \frac{3(2\epsilon_{10} + \epsilon_{20})R^3 + 2(\epsilon_{10} - 1)(\epsilon_{20} - 1)a^3}{(\epsilon_{20} - 1)(2\epsilon_{10} + 1)R^3 a^3}\right\} , \tag{3.25}$$

where ϵ_{10} and ϵ_{20} refer to the static dielectric constants in the two regions. When we put $\epsilon_{10} = \epsilon_{20} = \epsilon_0$ and retain only terms of highest order in R^3/a^3, this expression reduces to one derived by Glarum in Ref. 9. Since the free energy associated with spontaneous fluctuations of m_1 and m_2 has the same form as Eq. (3.24), Glarum proceeds to calculate the correlations $\langle m_i(0) m_j(0)\rangle$. The results obtained from $\langle m_i(0) m_j(0)\rangle$ by Glarum's method or from Eq. (3.7) are identical. Accordingly for the equilibrium quantities $\langle m_i(0) m_j(0)\rangle$ there is no discrepency between the fluctuation-dissipation method and the approach through the free energy.

It is worthwile to point out that the expression (3.25) for the free energy and the Fatuzzo–Mason expression for the autocorrelation function are derived from the same physical picture. Glarum's assertion that the Fatuzzo–Mason expression somehow results from the introduction of artificial surface effects at the boundary of the inner sphere appears therefore questionable. We return to this point in Sec. VI.

IV. AN EXPLICIT MICROSCOPIC LATTICE MODEL CALCULATION

The calculations in the two preceding sections have been macroscopic in the sense that the only specific property of the medium that was used was a macroscopic one, the dielectric constant. In this section we will review a calculation on a specific microscopic model, which was undertaken by Cole[11] with the aim of resolving the controversy discussed in this paper. In this section we shall show how Cole's calculation supports the Fatuzzo–Mason result.

The model consists of a rigid cubic lattice with lattice constant $\rho^{-1/3}$, its sites occupied by rigid dipoles of strength μ. Each dipole separately undergoes rotational Brownian motion and in addition the dipoles interact with the familiar dipole–dipole forces. Zwanzig[12] was able to give a high-temperature expansion for the frequency-dependent susceptibility of a spherical sample with radius a formed out of such a material. His result may be written in the form

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \chi(\omega) a^{-3} = \tfrac{4}{3}\pi\left[\frac{\alpha\rho}{1 + i\omega\tau} - \alpha^3\rho^3\mathfrak{R}\left\{\frac{1}{1 + i\omega\tau} + \frac{i\omega\tau}{(1 + i\omega\tau)(4 + i\omega\tau)} + \frac{\tfrac{5}{2} i\omega\tau}{(1 + i\omega\tau)^2(4 + i\omega\tau)}\right\} + O(\alpha^4\rho^4)\right] . \tag{4.1}$$

In this expression τ is the molecular relaxation time associated with the rotational Brownian motion, α denotes $\mu^2/3kT$, and $\mathfrak{R}$ is the lattice sum

$$\mathfrak{R} = (1/3\rho^2)\,\mathrm{Tr}\left[\sum_{m \neq n} \mathbf{T}_{nm} \cdot \mathbf{T}_{mn}\right] , \tag{4.2}$$

in which $\mathbf{T}_{nm}$ is the dipole–dipole interaction tensor for the sites m and n:

$$\mathbf{T}_{nm} = (1/r_{nm}^3)[(3\mathbf{r}_{nm}\mathbf{r}_{nm}/r_{nm}^2) - \mathbf{1}] . \tag{4.3}$$

The expression (4.1) gives an explicit result for $\epsilon(\omega)$. According to Eq. (2.8) we may obtain an explicit expression for $\mathcal{L}[-(d/dt)\Phi(t)]$ for this microscopic model. Furthermore, since on physical grounds we expect $\epsilon(\omega)$ to be a property of the material independent of sample shape or surroundings, we can substitute the result (4.1) for $\epsilon(\omega)$ into Eq. (2.9) and Eq. (2.10) to obtain explicit expressions for $\mathcal{L}[-(d/dt)\phi_{FM}(t)]$ and $\mathcal{L}[-(d/dt)\phi_G(t)]$. We next proceed to obtain expressions for $\mathcal{L}[\phi_{FM}(t)]$ and $\mathcal{L}[\phi_G(t)]$. These two expressions may then be compared with Cole's direct calculation[11] of the high-temperature result for $\mathcal{L}[\phi(t)]$ in the case of a lattice of spherical shape embedded in a larger spherical region of the same material.

First we express the Laplace transform of $\phi_G(t)$ and $\phi_{FM}(t)$ in terms of the quantity $\chi(\omega)$ in Eq. (4.1) and its static analogue $\chi(0)$. In view of the fact that $\chi(\omega)$ is only determined up to third order in $\alpha\rho$ it is not necessary to keep the full expressions; for example the expression derived from Glarum's relation (1.1),

$$\mathcal{L}[\phi_G]=\frac{\chi(0)-\chi(\omega)}{i\omega\chi(0)}\cdot\frac{a^3+\chi(0)}{[a^3+\chi(0)-2a^{-3}\chi(0)\chi(\omega)]}\;, \tag{4.4}$$

may be replaced by

$$\mathcal{L}[\phi_G]=\frac{\chi(0)-\chi(\omega)}{i\omega\chi(0)}\,[1+2a^{-6}\chi(0)\chi(\omega)+O(\alpha^3\rho^3)]\;. \tag{4.5}$$

Similarly we obtain from the Fatuzzo–Mason expression (1.2)

$$\mathcal{L}[\phi_{FM}]=\frac{\chi(0)-\chi(\omega)}{i\omega\chi(0)}\,[1+2a^{-6}\{\chi(0)\chi(\omega)+\chi^2(\omega)\}+O(\alpha^3\rho^3)]\;. \tag{4.6}$$

When we substitute the result of Eq. (4.1) and retain only terms up to order $\rho^2\alpha^2$ the results are

$$\mathcal{L}[\phi_G]=\frac{\tau}{1+i\omega\tau}-\alpha^2\rho^2\mathcal{R}\left[\frac{\tau}{(1+i\omega\tau)(4+i\omega\tau)}+\frac{\frac{5}{2}\tau}{(1+i\omega\tau)^2(4+i\omega\tau)}\right]+\frac{(\frac{4}{3}\pi\rho\alpha)^2 2\tau}{(1+i\omega\tau)^2}+O(\alpha^3\rho^3) \tag{4.7}$$

and

$$\mathcal{L}[\phi_{FM}]=\frac{\tau}{1+i\omega\tau}-\alpha^2\rho^2\mathcal{R}\left[\frac{\tau}{(1+i\omega\tau)(4+i\omega\tau)}+\frac{\frac{5}{2}\tau}{(1+i\omega\tau)^2(4+i\omega\tau)}\right]+2\tau(\tfrac{4}{3}\pi\rho\alpha)^2\times\left[\frac{1}{(1+i\omega\tau)^2}+\frac{1}{(1+i\omega\tau)^3}\right]+O(\alpha^3\rho^3)\;. \tag{4.8}$$

The corresponding expression for a sphere in vacuum is[12]

$$\mathcal{L}[\Phi]=\frac{\tau}{1+i\omega\tau}-\alpha^2\rho^2\mathcal{R}\left[\frac{\tau}{(1+i\omega\tau)(4+i\omega\tau)}+\frac{\frac{5}{2}\tau}{(1+i\omega\tau)^2(4+i\omega\tau)}\right]+O(\alpha^3\rho^3)\;. \tag{4.9}$$

The direct calculation of $\mathcal{L}[\phi]$ by Cole gives exactly expression (4.8), and thereby supports the Fatuzzo–Mason relation. This fact was not noticed by Cole, who compared his result only with Glarum's expression. After noticing the discrepancy with that expression he proposed a different treatment of the model to which we will return in the next section. The results just presented clearly indicate however that Cole's microsopic model lattice calculation supports the Fatuzzo–Mason relation and not the Glarum relation (1.1).

In the remaining part of this section we will comment on the way in which the crucial term, that makes the difference between (4.7) and (4.8), arises in the course of Cole's calculation. For full details the reader is referred to Cole's paper.[11] The basic molecular expression for the correlation function $\langle m_2(0)m_2(t)\rangle$ is

$$\langle m_2(0)m_2(t)\rangle=\frac{\sum_i'\sum_j'\int d\hat{e}_1\cdots\int d\hat{e}_N e^{-\beta U(\{\hat{e}_n\})}\mu^2\hat{e}_1\cdot e^{iLt}\hat{e}_j}{\int d\hat{e}_1\cdots\int d\hat{e}_N e^{-\beta U(\{\hat{e}_n\})}}\;. \tag{4.10}$$

In this expression $\hat{e}_i$ is a unit vector in the direction of the ith dipole in the lattice, $d\hat{e}_i$ indicates an integration over the direction of the vector $\hat{e}_i$, and the primed summation is over all lattice points inside of a sphere with radius a (unprimed summations run over both the sphere and the surrounding spherical shell). The symbol $U(\{\hat{e}_n\})$ represents the dipole–dipole interaction energy:

$$U(\{\hat{e}_n\})=-(\mu^2/2)\sum_i\sum_{j\neq i}\hat{e}_i\cdot\mathbf{T}_{ij}\cdot\hat{e}_j\;, \tag{4.11}$$

in which $\mathbf{T}_{ij}$ is defined according to Eq. (4.3). It is assumed in Zwanzig's lattice model that inertial effects can be neglected and that the Brownian motion is described by a Smoluchowski equation. Consequently the momenta conjugate to $\hat{e}_j$ do not appear in Eq. (4.10). The quantity L in Eq. (4.10) denotes the diffusion operator of the system. We will not write it out fully but merely remark that it may be written as the sum of two terms

$$L=L^{(0)}+L^{(1)}=\sum_i L_i^{(0)}+\sum_i\sum_{j\neq i}L_{ij}^{(1)}\;. \tag{4.12}$$

The operator $L_i^{(0)}$ describes the free rotational Brownian motion of the dipole at site i, while $L_{ij}^{(1)}$ gives the effect on the time evolution of the dipole–dipole interaction between the dipoles at sites i and j. In order to get the series expansion of Eq. (4.1) we must disentangle the evolution operator:

$$e^{iLt}=e^{iL^{(0)}t}+\int_0^t dt_1 e^{iL^{(0)}(t-t_1)}L^{(1)}e^{iL^{(0)}t_1}+\int_0^t dt_1\int_0^{t_1}dt_2 e^{iL^{(0)}(t-t_1)}L^{(1)}e^{iL^{(0)}(t_1-t_2)}L^{(1)}e^{iL^{(0)}t_2}+\cdots\;, \tag{4.13}$$

and expand the exponentials $\exp[-\beta U(\{\hat{e}_n\})]$. The order of a term in the variable $\alpha\rho$ turns out to be equal to the number of times that either a factor $L^{(1)}$ or a factor U appears in the expression. The terms in (4.8) that contain the rapidly converging lattice sum $\mathcal{R}$ of Eq. (4.2) as a factor arise from the interaction of a molecule with the first few shells of neighbors. The terms containing a factor $(\frac{4}{3}\pi\rho\alpha)^2$ represent contributions from interactions with the surrounding shell. This is also clear from a comparison of Eq. (4.8) and (4.9).

The term that gives rise to the difference between Eq. (4.8) and (4.7) may be identified as a term which is of zeroth order in U and of second order in $L^{(1)}$; its specific form is

$$(4\pi)^{-2}\sum_i{}'\left[\sum_{k\neq i}-\sum_{k\neq i}{}'\right]\int d\hat{e}_i\int d\hat{e}_k\int_0^t dt_1\int_0^{t_1}dt_2\times\mu^2\hat{e}_i\cdot e^{iL_i^{(0)}(t-t_1)}L_{ik}^{(1)}e^{iL_k^{(0)}(t_1-t_2)}L_{ki}^{(1)}e^{iL_i^{(0)}t_2}\hat{e}_i\;. \tag{4.14}$$

[the factors 4π result from integrations over angles in the denominator of Eq. (4.10)]. The physical picture corresponding to Eq. (4.14) is the following: a dipole in the inner sphere interacts with a dipole in the surrounding shell at time t_2. The outer dipole executes rotational Brownian motion for a while and acts back on the original inner dipole *at a later time* t_1. On the other hand, the common quantity in the last term of Eqs. (4.7) and (4.8) is the Laplace transform of

$$(4\pi)^{-2}\sum_i{}' \left[\sum_{k\neq i} - \sum_{k\neq i}{}'\right] \int d\hat{e}_i \int d\hat{e}_k \int_0^t dt_1 \times \mu^4 \beta \hat{e}_i \cdot \mathbf{T}_{ik} \cdot \hat{e}_k \hat{e}_k \cdot e^{iL_k^{(0)}(t-t_1)} L_{ki}^{(1)} e^{iL_i^{(0)}t_1} \hat{e}_i \,. \tag{4.15}$$

In this case the outer dipole "acts back" on the inner dipole via the electrostatic correlation without any time lag. The picture emerging here is in agreement with our finding in Sec. II, that Glarum's expression applies to a sphere surrounded by a medium with a frequency-independent dielectric constant equal to the static dielectric constant of the enclosed sphere. The reaction field originated by such a shell will always correspond to the *instantaneous* value of the dipole moment of the enclosed sphere and will not exhibit any delay. In the next section we will come back to the role which this "lag of the reaction field" plays in various descriptions of dielectric relaxation. As far as the result of the present calculation is concerned, there is again no way in which the agreement with the relation of Fatuzzo and Mason can be ascribed to some artificial surface effects smuggled into the model. In this model lattice calculation all dipoles are treated in exactly the same way, both dynamically and statistically. The distinction between the inner sphere and the surrounding shell is only made at the end of the calculation when the summations over the dipoles are carried out.

V. MICROSCOPIC ARGUMENTS FAVORING GLARUM'S RELATION

In this section we review two recent calculations by Cole[10,11] presented in support of Glarum's relation between the dielectric constant and the autocorrelation function of the net dipole moment of an embedded sphere. One of them[10] is a derivation from the molecular equations of motion of Glarum's relation between the moment autocorrelation functions of a sphere in vacuum and a sphere embedded in its own medium. The second one[11] is a modified treatment of the lattice model discussed in the previous section; the modification, based on use of Kirkwood's diffusion equation,[19] leads to agreement with Glarum's formula.

In the course of the molecular derivation of Glarum's relation[11] Cole introduces an expression for the Liouville operator in which the n particles in the inner sphere of radius a and the particles in the surrounding shell play a completely different role [see Eqs. (11) and (13) of Ref. 11]:

$$L = L_n + \frac{2(\epsilon_0 - 1)}{(2\epsilon_0 + 1)a^3}\,\mathbf{m}_2 \cdot \sum_{i=1}^{n} q_i \frac{\partial}{\partial \mathbf{p}_i} \,, \tag{5.1}$$

where q_i is the formal charge, called e_i by Cole. In this equation L_n is the Liouville operator for the n dipoles in the inner sphere, $\mathbf{m}_2$ is the instantaneous net dipole moment of the n dipoles in the inner sphere, and ϵ_0 is the static dielectric constant of the material. The coordinates and momenta $\mathbf{p}_i$ of the particles of the inner sphere are treated in the usual way as dynamical variables. However, the coordinates and momenta of the particles in the surrounding shell do not enter at all into the description. The influence of the surrounding shell is represented by an average reaction field, proportional to the *instantaneous* value of the dipole moment of the inner sphere. The proportionality constant in Cole's expression, Eq. (5.1), contains only the *static* dielectric constant ϵ_0 of the surrounding shell. Clearly, Cole's Liouville operator does not describe the situation of a sphere embedded in its own medium, but instead that of a sphere embedded in a medium with an instantaneous dielectric response described by a frequency-independent dielectric constant equal to the static dielectric constant ϵ_0. The fact that this calculation leads to Glarum's relation is therefore entirely consistent with the physical picture developed in Secs. II and III.

Cole's modified treatment of Zwanzig's model of a polar lattice is subject to similar criticism. In Sec. 3 of Ref. 11 the equations of motion of the many-body system are replaced by two coupled equations of motion for the one- and two-particle orientational correlation functions according to the molecular diffusion theory of Kirkwood.[19] The forces exerted by all the other particles on the one or two particles occurring in the correlation functions under consideration are replaced by an average reaction force, determined by the instantaneous orientation of those one or two particles. Since the correlation functions are only integrated over the inner sphere, the particles in the surrounding shell can only enter into the picture via instantaneous reaction forces. This explains the fact that Glarum's relation rather than that of Fatuzzo and Mason is obeyed by the resulting expressions. In addition the introduction of averages in intermediate steps of the calculation leads to important modifications of the dipole-moment correlation function, even for a sphere in vacuum. For example comparison of the results of the direct high-temperature calculation and the high-temperature expansion of Cole's Kirkwood diffusion model indicates[11] that the shorter relaxation time $\tau/4$, present in the former, is completely absent in the latter. Both the occurrence of relaxation times which are a fraction of the basic relaxation time and their vulnerability to approximate treatments are well known phenomena in the theory of fluctuations in nonlinear systems. They appear, e.g., in van Kampen's discussion of Alkemade's diode model.[20]

The nonlinearity that causes the appearance of shorter relaxation times in this instance is in the relation between the electric field exerted by one dipole on a neighbor and the resulting change in the orientation of the dipole moment of that neighbor. Although the average value of this field is small, due to orientational disorder at high temperatures, the actual value in a polar substance is by no means small; nonlinear terms cannot be neglected, at least not for dipoles close to one another. The fact that he effect discussed results from interactions between relatively close neighbors is reflected in the appearance of the factor ℛ in front of the terms in Eqs. (4.1), (4.8), and (4.9) containing the shorter relaxation time. The quantity ℛ is a rapidly converging lattice sum, which depends on the lattice structure, but not on the sample shape or the nature of the surroundings (cf. the calculations by Rosenberg and Lax[21]).

The replacement of the full Liouville equation by the two coupled equations for one- and two-particle correlation functions is only justified by an analogy to Kirkwood's theory of transport processes in liquids.[19] However, that theory is based on the observation that in a liquid a molecule is virtually trapped in a cage formed by its neighbors. Consequently the position of the molecule hardly changes during the period of time needed for a complete randomization of its velocity.

When one writes down a Smoluchowski equation for the rotational Brownian motion of the dipoles, one similarly assumes that the autocorrelation function of the torque responsible for the rotational Brownian motion decays much faster than the autocorrelation function of the orientation of the dipoles. The autocorrelation of the dipolar forces, however, decays on the same time scale as the autocorrelation function of the orientation of the dipoles. Consequently, when dipolar forces are important it is no longer correct to describe the evolution of the system in the framework of Kirkwood's diffusion equations; at least the dipolar part of the interaction must be treated on a different level. This is done explicitly in the lattice calculations[12] described in the previous section, but not in Cole's modified treatment based on the Kirkwood diffusion equation.

VI. POLARIZATION FLUCTUATIONS NEAR THE INTERIOR SURFACE

It has been suggested[9] that the difference between Glarum's expression Eq. (1.1) and the expression (1.2) derived by Fatuzzo and Mason is caused by a difference in the treatment of polarization fluctuations near the surface between the interior and exterior regions. Glarum introduced in this context the distinction between the "Kirkwood" model, in which fluctuations of this kind are forbidden, and the "Onsager" model, in which they are allowed. He derived expressions for the free energy for each of the models and suggested that the two models lead to two expressions for the relation between the dielectric constant and the autocorrelation function of the net dipole moment of an embedded sphere: the "Kirkwood" model would lead to Glarum's expression, while the "Onsager" model would lead to the expression of Fatuzzo and Mason.

In this section we will show that the two expressions for the free energy do not correspond to two different physical situations, but rather to a more detailed and a less detailed description of the same physical situation. Accordingly both expressions lead to the same result for the correlation functions for the net dipole moments of the internal and/or the external region. However, when we consider the relaxation of the average net dipole moments for nonequilibrium initial values, the more detailed description leads to a clearer physical picture.

We would like to start our discussion by pointing out that no assumptions were made about surface fluctuations in the derivation presented in Sec. III. We used the boundary conditions at the interior surface only for the purpose of relating the *average* values of the parameters occurring in the general expression (3.14) to the value of the applied external fields. In order to gain information about the *fluctuations* of the surface polarization from a calculation such as the one in Sec. III we must introduce a third auxiliary external field which couples to these surface fluctuations. For this we choose the field of a dipole of strength μ, located in the center of the configuration. This auxiliary field acts only on the outer shell. The field $\mathbf{E}_\mu(\mathbf{r})$ caused by the dipole is of course an inhomogeneous one; it turns out to be convenient to introduce the parameter $E_3 = \mu a^{-3}$ as one of the parameters in an extended version of the calculation of Sec. III. The fluctuating quantity conjugate to E_3 may be found by evaluating the quantity $-\int \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}_\mu(\mathbf{r})\, d\mathbf{r}$, in which $\mathbf{P}(\mathbf{r})$ is the polarization density and the integral extends over the shell. Using the parametrization of Eq. (3.14) we obtain

$$-\int \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}_\mu(\mathbf{r})\, d\mathbf{r} = 2E_3 a^3[(\epsilon_1 - 1)/4\pi] \cdot \tfrac{1}{3} \circ 4\pi(a^{-3} - R^{-3}) m_* \ . \tag{6.1}$$

The coordinate m_3 conjugate to E_3 is therefore given by

$$m_3 = -\tfrac{2}{3}(\epsilon_1 - 1)[(R^3 - a^3)/R^3] m_* \ . \tag{6.2}$$

We can now determine the average values of m_1, m_2, and m_3 for given values of E_1, E_2, and E_3. Equation (3.16) remains valid in the presence of the external field $\mathbf{E}_\mu(\mathbf{r})$, while Eq. (3.15) can be adapted by replacing $\bar{m}_2$ by $\bar{m}_2 + a^3 E_3$. The third equation we need is found from direct application of the boundary conditions at the outer surface:

$$\bar{m}_* = -[(\epsilon_1 - 1)/3\epsilon_1] R^3 E_1 + [(\epsilon_1 + 2)/3\epsilon_1](\bar{m}_1 + \bar{m}_2 - E_3 a^3) \ . \tag{6.3}$$

Via some straightforward algebra we now derive the generalization of Eq. (3.18), which determines the matrix $\chi_{ij}(\omega)$. For simplicity we give the result only for the case $\epsilon_1 = \epsilon_2 = \epsilon$:

$$\begin{aligned}
\bar{m}_1 &= \frac{(\epsilon - 1)[9\epsilon R^3 + 2(\epsilon - 1)^2 a^3](R^3 - a^3)}{9\epsilon(\epsilon + 2)R^3} E_1 \\
&\quad - \frac{2(\epsilon - 1)^3 a^3 (R^3 - a^3)}{9\epsilon(\epsilon + 2)R^3} E_2 + \frac{2(\epsilon - 1)^2 a^3 (R^3 - a^3)}{9\epsilon R^3} E_3 \ , \\
\bar{m}_2 &= -\frac{2(\epsilon - 1)^3 a^3 (R^3 - a^3)}{9\epsilon(\epsilon + 2)R^3} E_1 + \\
&\quad + \frac{(\epsilon - 1)[(2\epsilon + 1)(\epsilon + 2)R^3 - 2(\epsilon - 1)^2 a^3] a^3}{9\epsilon(\epsilon + 2)R^3} E_2 \\
&\quad - \frac{2(\epsilon - 1)^2 a^3 (R^3 - a^3)}{9\epsilon R^3} E_3 \ , \\
\bar{m}_3 &= \frac{2(\epsilon - 1)^2 a^3 (R^3 - a^3)}{9\epsilon R^3} E_1 - \frac{2(\epsilon - 1)^2 a^3 (R^3 - a^3)}{9\epsilon R^3} E_2
\end{aligned} \tag{6.4}$$

$$+\frac{2(\epsilon-1)(\epsilon+2)a^3(R^3-a^3)}{9\epsilon R^3}E_3\;;$$

of course all ϵ in Eqs. (6.1) to (6.4) are frequency-dependent.

We see from Eq. (6.4) that the expressions for χ_{11}, χ_{12}, and χ_{22} and thus also those for $\langle m_1(0)m_1(t)\rangle$, $\langle m_1(0)m_2(t)\rangle$, and $\langle m_2(0)m_2(t)\rangle$ are the same as those found from the less detailed description in Eq. (3.18). As was noted in the introduction of this section, taking into account the surface fluctuations does not alter the results obtained for the fluctuations in the net dipole moments and their relations to the dielectric constant.

From the relations (6.4) we may derive expressions for the free energy analogous to the ones obtained in Eqs. (3.24). For example the analogue of Eq. (3.24b) for the case $\epsilon_{10}=\epsilon_{20}=\epsilon_0$ is

$$\bar{\mathfrak{F}}=\frac{1}{2}\left\{\frac{\epsilon_0+2}{(\epsilon_0-1)(R^3-a^3)}\bar{m}_1^2+\frac{\epsilon_0+2}{(\epsilon_0-1)a^3}\bar{m}_2^2+\frac{(2\epsilon_0+1)R^3}{2(\epsilon_0-1)a^3(R^3-a^3)}\bar{m}_3^2-\frac{2}{R^3-a^3}\bar{m}_1\bar{m}_3+\frac{2}{a^3}\bar{m}_2\bar{m}_3\right\}. \tag{6.5}$$

In order to make a comparison with Glarum's expression for the free energy of the "Onsager" model[9] we must express this result in terms of the variables m_1, m_2, and μ, using the relation $m_i=\sum_j\chi_{ij}(0)E_j$. In this way we obtain:

$$\bar{\mathfrak{F}}=\frac{1}{2}\left\{\frac{(2\epsilon_0+1)(\epsilon_0+2)R^3-2(\epsilon_0-1)^2a^3}{(2\epsilon_0+1)(\epsilon_0-1)R^3(R^3-a^3)}\bar{m}_1^2+\frac{4(\epsilon_0-1)}{(2\epsilon_0+1)R^3}\bar{m}_1\bar{m}_2+\frac{9\epsilon_0R^3+2(\epsilon_0-1)^2a^3}{(2\epsilon_0+1)(\epsilon_0-1)R^3(R^3-a^3)}\bar{m}_2^2+\frac{2(\epsilon_0-1)(R^3-a^3)}{(2\epsilon_0+1)R^3a^3}\mu^2\right\}\;. \tag{6.6}$$

In the limit $R\gg a$ this is exactly Glarum's expression for the "Onsager" model, Eq. (25) of Ref. 9 ($\bar{m}_1$, $\bar{m}_2$, and μ correspond with Glarum's M, m, and m^*-m).

Next we make some observations about the relaxation of the quantities $\bar{m}_i$ from initial nonequilibrium values $\bar{m}_i(0)$. Let us suppose that these nonequilibrium values are maintained at all negative times by applying external fields; the fields must be equal to

$$E_i(t)=\sum_j[\chi(0)]_{ij}^{-1}\bar{m}_j(0)\theta(-t)\;. \tag{6.7}$$

In this formula $\theta(-t)$ is the unit step function, which is equal to unity for negative times and equal to zero for positive times. The Fourier components of the fields (6.7) are

$$E_i(\omega)=\sum_j[\chi(0)]_{ij}^{-1}\bar{m}_j(0)[2\pi i(\omega+i\eta)]^{-1}\;, \tag{6.8}$$

in which η denotes an arbitrarily small positive number. From Eq. (6.8) we find the value of $m_i(t)$ for all times by application of Eq. (3.3) and Fourier transformation:

$$\bar{m}_i(t)=\sum_{j,k}A_{ij}(t)[\chi(0)]_{jk}^{-1}\bar{m}_k(0) \tag{6.9}$$

with

$$A_{ij}(t)=\int_{-\infty}^{+\infty}\chi_{ij}(\omega)e^{i\omega t}[2\pi i(\omega+i\eta)]^{-1}d\omega\;. \tag{6.10}$$

The quantity $\sum_j A_{ij}(t)[\chi(0)]_{jk}^{-1}$ is the relaxation function of the system. As a consequence of the causality principle $\chi_{ij}(\omega)$ is analytic in the lower half plane and $A_{ij}(t)=\chi_{ij}(0)$ for $t\leqslant 0$. The behavior of $A_{ij}(t)$ for $t>0$ is determined by the singularities of $\chi_{ij}(\omega)$ in the upper half-plane.

We will now compare the relaxation equations (6.9) with the results obtained by applying the transport equations from Onsager's theory of nonequilibrium behavior.[22] Since the elements of the matrix $\chi(0)^{-1}$ are second derivatives of the free energy $\mathfrak{F}$, the transport equations may be written in the form

$$(d/dt)\bar{m}_i(t)=-\sum_{j,k}\gamma_{ij}[\chi(0)]_{jk}^{-1}\bar{m}_k(t)\;. \tag{6.11}$$

The relaxation equations (6.9) are compatible with Eq. (6.11) only when the matrix **A** is equal to $\exp[-\gamma t]$. This imposes severe restrictions on the frequency dependence of $\chi_{ij}(\omega)$, and ultimately on that of $\epsilon(\omega)$. In order to determine whether those conditions can be met at all it would be convenient to have a set of basic quantities in terms of which the matrix $\chi(\omega)$ is diagonal for all ω. Such a set exists, and it is given by

$$\begin{aligned}\tilde{m}_1&=m_1+m_2\\ \tilde{m}_2&=-m_1[a^3/(R^3-a^3)]+m_2-\tfrac{1}{2}m_3[R^3/(R^3-a^3)]\\ \tilde{m}_3&=-m_1[a^3/(R^3-a^3)]+m_2+m_3[R^3/(R^3-a^3)]\;.\end{aligned} \tag{6.12}$$

With respect to those new variables the matrix $\chi(\omega)$ has the form

$$\begin{gathered}\tilde{\chi}_{11}=[(\epsilon-1)/(\epsilon+2)]R^3,\quad\tilde{\chi}_{22}=[(\epsilon-1)a^3R^3/2(R^3-a^3)]\;,\\ \tilde{\chi}_{33}=[(\epsilon-1)a^3R^3/\epsilon(R^3-a^3)],\quad\tilde{\chi}_{ij}=0\ \text{ when }\ i\neq j\;.\end{gathered} \tag{6.13}$$

The nonequilibrium relaxation of the new variables $\tilde{m}_i$ will be a simple exponential when the $\tilde{\chi}_{ii}(\omega)$ have a single pole. The simple structure of these quantities makes it possible to determine which expressions for $\epsilon(\omega)$ satisfy this condition.

Up to this point our considerations have established relations between the nonequilibrium relaxation of the polarization, the frequency-dependent susceptibility, the frequency-dependent dielectric constant, and the behavior of correlation functions of the net dipole moments. Further progress cannot be realized without selection of a specific model form for one or another of these quantities. Once such a selection is made the results of Secs. II, III, and VI may be employed to determine the consequences for all the quantities of interest. We illustrate this state of affairs by examining the consequences of two celebrated choices for $\epsilon(\omega)$. It must be emphasized however that one cannot conclude anything about the form of $\epsilon(\omega)$ for actual polar liquids from considerations of the sort mentioned above and undertaken below. For example the fact that the Fatuzzo-Mason result (1.2) rather than the Glarum result (1.1) is correct for the relation between $\epsilon(\omega)$ and $\langle m_2(0)m_2(t)\rangle$ does not enable one to determine without further information the actual form of $\epsilon(\omega)$. The first choice we examine for $\epsilon(\omega)$ is the familiar

Debye expression for the dielectric constant

$$[\epsilon(\omega)-1]/[\epsilon(\omega)+2]=[(\epsilon_0-1)/(\epsilon_0+2)][1+i\omega\tau]^{-1} . \tag{6.14}$$

An alternative expression for the Debye form of $\epsilon(\omega)$ is

$$[\epsilon(\omega)-1]/[\epsilon_0-1]=[1+i\omega T]^{-1}; \quad T=[(\epsilon_0+2)/3]\,\tau . \tag{6.14a}$$

For this choice of $\epsilon(\omega)$ we see that $\tilde{\chi}_{11}$ has a pole at $\omega=i\tau^{-1}$, $\tilde{\chi}_{22}$ has a pole at $\omega=iT^{-1}=3i\tau^{-1}[\epsilon_0+2]^{-1}$ and $\tilde{\chi}_{33}$ has a pole at $\omega=i\epsilon_0 T^{-1}=3i\epsilon_0\tau^{-1}[\epsilon_0+2]^{-1}$. When we substitute the corresponding expressions for χ_{ii} in Eq. (6.9) it is seen easily that the result is compatible with the linear description of nonequilibrium behavior displayed in Eq. (6.11). Of course this remains true when we transform back to the original variables m_1, m_2, and m_3.

The procedure we just outlined cannot be applied to the "contracted" description in terms of the variables m_1 and m_2 only. For this case the required transformation of variables is

$$\begin{aligned} \hat{m}_1 &= m_1+m_2 \\ \hat{m}_2 &= -[a^3/(R^3-a^3)]m_1+m_2 . \end{aligned} \tag{6.15}$$

The matrix χ for the two-variable system on the basis (6.15) is

$$\begin{aligned} &\hat{\chi}_{11}=[(\epsilon-1)/(\epsilon+2)]R^3, \hat{\chi}_{22}=[(\epsilon-1)(2\epsilon+1)a^3R^3/9\epsilon(R^3-a^3)] \\ &\hat{\chi}_{12}=\hat{\chi}_{21}=0 . \end{aligned} \tag{6.16}$$

When we substitute Debye's expression, Eq. (6.14), we see that $\hat{\chi}_{22}$ has two poles corresponding to those of $\tilde{\chi}_{22}$ and $\tilde{\chi}_{33}$ in the more detailed description. Accordingly a description by means of a set of equations of the form (6.11) is not possible with Debye's expression for the dielectric constant. The situation is not improved when we choose instead the Onsager–Cole[23] expression

$$\frac{[\epsilon(\omega)-1][2\epsilon(\omega)+1]}{\epsilon(\omega)}=\frac{(\epsilon_0-1)(2\epsilon_0+1)}{\epsilon_0[1+i\omega\tau]} . \tag{6.17}$$

When we use this choice for $\epsilon(\omega)$, the matrix element $\hat{\chi}_{22}(\omega)$ has only a single simple pole. However, the expression for $\epsilon(\omega)$ exhibits two branchpoints at $\omega=\{i+(i\pm 2\sqrt{2})[(\epsilon_0-1)(2\epsilon_0+1)/9\epsilon_0]\}\,\tau^{-1}$. The matrix element $\hat{\chi}_{11}$ exhibits the same branchpoints in addition to a pole at $\omega=i\{1+[2(\epsilon_0-1)(2\epsilon_0+1)/9\epsilon_0]\}\,\tau^{-1}$. Accordinlgy no description of the nonequilibrium relaxation of the $\hat{m}_i$ by a simple set of equations of the type (6.11) is possible with this choice for $\epsilon(\omega)$ either. When we go the the contracted description in terms of only two variables it is no longer consistent to describe the approach to equilibrium of the quantities m_1 and m_2 by means of linear differential equations with constant coefficients for any choice of $\epsilon(\omega)$.

Of course considerations like the ones just given cannot be considered conclusive reasons to prefer an expression like (6.14) over (6.17) as an approximation to the dielectric constant for real substances. We point out for completeness' sake that the expression for $\epsilon(\omega)$ obtained by Fatuzzo and Mason,[24] Scaife,[25] and Nee and Zwanzig,[6]

$$\frac{[\epsilon(\omega)-1][2\epsilon(\omega)+1]}{\epsilon(\omega)} = \frac{(\epsilon_0-1)(2\epsilon_0+1)}{\epsilon_0}\left[1+i\omega\tau-\frac{(\epsilon_0-1)[\epsilon(\omega)-\epsilon_0]}{\epsilon_0[2\epsilon(\omega)+1]}\right]^{-1} , \tag{6.18}$$

gives rise to a single branch point in $\hat{\chi}_{11}(\omega)$, at $\omega=i\epsilon_0\tau^{-1}$, and to a pole at $i\tau^{-1}(\epsilon_0+2)^2(9\epsilon_0)^{-1}$. The function $\hat{\chi}_{22}(\omega)$ has pole at $\omega=i\tau^{-1}(\epsilon_0+1)(2\epsilon_0)^{-1}$. In addition there is a singularity of type $\alpha[\omega-\omega_0]^{-1/2}$ at the beginning of the branch cut $(\omega_0=i\epsilon_0\tau^{-1})$.

We wish to end this section with a cautionary remark about the method outlined in the preceding paragraphs. When one wants to use an expression like Eq. (6.9), it is important to make the right choice of variables. From Eq. (6.10) we see that it is necessary that all $\chi_{ij}(\omega)$ go to zero for large values of ω. In Eq. (3.18) and (6.4) this is indeed the case due to the presence of at least one factor (ϵ_i-1) in each matrix element. For the choice of variables in Eq. (6.6), m_1, m_2, and μ, it is not true however; when we construct the matrix χ associated with these variables we find for the diagonal matrix element χ_{33}^* associated with the variable μ

$$\chi_{33}^*=(2\epsilon+1)R^3a^3/2(\epsilon-1)(R^3-a^3) , \tag{6.19}$$

which approaches infinity for large ω. The variable μ will therefore not obey a relaxation equation. This' agrees with our earlier observation that μ plays the role of an external force rather than that of a response of the system. The relevance of a calculation in Ref. 9, in which the quantity μ is assumed to decay exponentially, is therefore rather questionable.

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