Molecular theory of dielectric relaxation*

D. E. Sullivan and J. M. Deutch

Department of Chemistry, Massachusetts Institute of Chemistry, Cambridge, Massachusetts 02139
(Received 7 October 1974)

A new formal relation is obtained for the frequency-dependent dielectric constant of a polar material in terms of a dipole "memory function," i.e., a modified correlation function with projected propagator. In contrast to conventional expressions for the dielectric constant in terms of dipole–dipole correlation functions, the memory function expression does not depend on sample shape. The memory function may thus be calculated either by considering the total dipole moment of a molecular sample in vacuum or the dipole moment of a smaller region embedded in the sample. It is shown that this formalism agrees with usual expressions for the dielectric constant and particular relations between the dielectric constant and dipole correlation functions of embedded regions.

I. INTRODUCTION

In the conventional linear response theory of dielectric relaxation in polar media, the polarization of a system is related to the external field acting on the system via a dipole correlation function expression. Formal relations between the dielectric constant and the dipole correlation function are derived by expressing the external field in terms of the average field in the medium by use of Maxwell's equations. As is well known, the form of these relations depends on the shape of the sample and on the nature of its surroundings, although on physical grounds we expect the dielectric constant to be a property of the material independent of sample shape or surroundings. Considerable controversy [1–6] has developed over the correct relation between the dielectric constant and the dipole correlation function of a small sphere embedded in an infinite continuum of the same material. This sample geometry has received particular attention, as in the Kirkwood[7] theory of the static dielectric constant, because it presumably eliminates the need to consider surface effects in the calculation of the dielectric constant. Furthermore, it is alleged that the embedded sphere correlation function is more directly related to relaxation processes on a molecular level than the corresponding quantity for other sample geometries, e.g., a sphere in vacuum. The controversy arises over the correct treatment of the effect of the surrounding medium on the interactions between particles in the embedded region, which is represented by a reaction field that generally depends on time and on the past history of the motion of these particles. A recent analysis by Titulaer and Deutch[8] of the conflicting proposed relations between $\epsilon(\omega)$ and the embedded sphere correlation function concludes that the Fatuzzo–Mason[1,2] expression is correct while that proposed by Glarum[3–6] is not.

In this paper we obtain a formal expression for the dielectric constant $\epsilon(\omega)$ which, in contrast to relations between $\epsilon(\omega)$ and the dipole correlation function of a sample, is independent of sample shape or surroundings. Our motivation for seeking such an expression for $\epsilon(\omega)$ is to circumvent the past controversy as well as to elucidate the long-range character of the dipole correlation function. Furthermore, such an expression should be convenient for carrying out molecular analyses. Thus we proceed with a similar motivation and approach as that recently adopted by Cole,[5] although our conclusions differ greatly from his. While the formal shape independent expression we obtain for $\epsilon(\omega)$ is new, it is quite possible to arrive at apparently different expressions by alternate derivations. If the analyses are correct, we expect these different expressions to be equivalent. In particular we remark that the result recently obtained by Fulton[9] from a different point of view is equivalent to the result presented here. Our approach, however, has the advantage of giving a formal expression for $\epsilon(\omega)$ which reveals more explicitly the dependence of $\epsilon(\omega)$ on molecular quantities.

The model of the fluid we adopt consists of molecules bearing permanent dipole moments and, in addition, interacting via arbitrary short-range anisotropic forces. The complication of molecular polarizabilities is not included here.

In Sec. II we demonstrate that $\epsilon(\omega)$ may be related to a dipole "memory function" which arises in a formal expression for the shape-dependent dipole correlation function. This expression is constructed by use of an appropriate projection operator which eliminates the shape dependence in the relation between $\epsilon(\omega)$ and the memory function, and accordingly the latter is asserted to be a short-range quantity independent of sample shape.

The analysis in Sec. II is carried out for samples of arbitrary shape in vacuum. We demonstrate that the memory function may be evaluated by considering only the dipole moment in a smaller region embedded in the sample. In Sec. III it is shown that this formalism is consistent with expressions relating $\epsilon(\omega)$ to the dipole correlation function of the embedded region. Here we treat at the outset both the immersed region and surrounding as a molecular dipolar medium and formally incorporate all interactions between dipoles in the two regions. With minor approximations, such as neglecting surface effects between the two regions, the usual relations for the dielectric constant are obtained.

Since the relation between $\epsilon(\omega)$ and the memory function is the same regardless of sample shape, the memory function is a natural quantity on which to base calculations of the dielectric constant. Such modified correlation functions have been the basis of numerous investigations of nonequilibrium phenomena,[10] and in the present case should provide a suitable starting point for in-

troducing refined relaxation models.[2,11]

II. THE DIPOLE MEMORY FUNCTION

In this section we apply the techniques of linear response theory to compute the polarization of a system of N molecules bearing permanent dipole moments, confined to a volume V of arbitrary shape in vacuum, when the dipoles interact with an external electric field $\mathbf{E}_0(\mathbf{r}, t)$. The Hamiltonian for the system is

$$H(t) = H_0 - \int_v d\mathbf{r}'\, \mu(\mathbf{r}') \cdot \mathbf{E}_0(\mathbf{r}', t), \tag{2.1}$$

where H_0 is the time-independent Hamiltonian in the absence of the external field; $\mu(\mathbf{r})$ is the dipolar density,

$$\mu(\mathbf{r}) = \sum_{i=1}^{n} \mu_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{2.2}$$

where μ_i is the dipole moment of molecule i with position $\mathbf{r}_i$, and the dependence of μ_i on orientation ω_i is not explicitly indicated. The polarization $\mathbf{P}(\mathbf{r}, t)$ of the sample is equal to the nonequilibrium expectation value of the dipolar density in the presence of the external field. From linear response theory[12] we find

$$\mathbf{P}(\mathbf{r}, t) = \int_0^\infty dt' \int_v d\mathbf{r}'\, \chi(\mathbf{r}, \mathbf{r}'; t') \cdot \mathbf{E}_0(\mathbf{r}', t - t'), \tag{2.3}$$

where the response function $\chi(\mathbf{r}, \mathbf{r}'; t)$ is given by

$$\chi(\mathbf{r}, \mathbf{r}'; t) = -\beta \frac{d}{dt} \langle \mu(\mathbf{r}) \mu(\mathbf{r}', t) \rangle. \tag{2.4}$$

In Eq. (2.4) the angular bracket denotes an equilibrium cannonical ensemble average with respect to the Hamiltonian H_0, and the time dependence

$$\mu(\mathbf{r}, t) = e^{iL_0 t} \mu(\mathbf{r}) \tag{2.5}$$

is determined by the Liouville operator L_0 of the unperturbed system governed by H_0. For an external field with time dependence

$$\mathbf{E}_0(\mathbf{r}, t) = \mathbf{E}_0(\mathbf{r}, \omega) e^{-i\omega t},$$

we find that the steady-state polarization

$$\mathbf{P}(\mathbf{r}, t) = \mathbf{P}(\mathbf{r}, \omega) e^{-i\omega t}$$

is given by

$$\mathbf{P}(\mathbf{r}, \omega) = \int_v d\mathbf{r}'\, \hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{E}_0(\mathbf{r}', \omega), \tag{2.6}$$

where

$$\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = \int_0^\infty dt\, e^{i\omega t} \chi(\mathbf{r}, \mathbf{r}'; t). \tag{2.7}$$

In the long wavelength limit, i.e., when the wavelength of the external field is large compared with the sample dimensions, the average macroscopic field in the sample $\mathbf{E}(\mathbf{r}, \omega)$ is related to the polarization by[13]

$$\mathbf{E}(\mathbf{r}, \omega) = \mathbf{E}_0(\mathbf{r}, \omega) + \int_v d\mathbf{r}'\, \mathbf{T}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}', \omega), \tag{2.8}$$

where $\mathbf{T}(\mathbf{r}, \mathbf{r}')$ is the dipole–dipole tensor

$$\mathbf{T}(\mathbf{r}, \mathbf{r}') = \nabla\nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|}.$$

We introduce the space-dependent susceptibility $\chi_0(\mathbf{r}, \mathbf{r}'; \omega)$ as the coefficient relating the polarization to the average field $\mathbf{E}(\mathbf{r}, \omega)$ as follows:

$$\mathbf{P}(\mathbf{r}, \omega) = \int_v d\mathbf{r}'\, \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{E}(\mathbf{r}', \omega). \tag{2.9}$$

From Eqs. (2.6), (2.8), and (2.9) we find that the response function $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$ and susceptibility $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$ are related by

$$\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega) + \int_v d\mathbf{r}_1\, d\mathbf{r}_2\, \hat{\chi}_0(\mathbf{r}, \mathbf{r}_1; \omega) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega). \tag{2.10}$$

In the limit of zero frequency, $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$ becomes the static dipolar density correlation function,

$$\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega = 0) = \beta \langle \mu(\mathbf{r}) \mu(\mathbf{r}') \rangle, \tag{2.11}$$

which can be analysed using the microscopic theory of Nienhuis and Deutch.[14] The microscopic expression for the static correlation function, Eq. (2.11), is

$$\langle \mu(\mathbf{r}) \mu(\mathbf{r}') \rangle = \int d\omega_1\, d\omega_2\, H_2(\mathbf{r}, \omega_1; \mathbf{r}', \omega_2) \mu(\omega_1) \mu(\omega_2), \tag{2.12}$$

where (in the notation of Ref. 14)

$$H_2(\mathbf{r}, \omega_1; \mathbf{r}', \omega_2) = (\rho/\Omega)\, \delta(\mathbf{r} - \mathbf{r}')\, \delta(\omega_1 - \omega_2) + G_2(\mathbf{r}, \omega_1; \mathbf{r}', \omega_2). \tag{2.13}$$

In these equations, ω_i denotes the orientation of dipole i, $\Omega = \int d\omega_i$, and $\rho = NV^{-1}$ is the number density; $G_2(\mathbf{r}, \omega_1; \mathbf{r}', \omega_2)$ is the reduced two-particle correlation function for positions and orientations. From the analysis of G_2 in Ref. 14 it can be shown that $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega = 0)$, Eq. (2.11), satisfies an integral equation analogous to Eq. (2.10). In this zero-frequency limit $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega = 0)$ is given by

$$\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega = 0) = \beta \int d\omega_1\, d\omega_2\, H_2^{(0)}(\mathbf{r}, \omega_1; \mathbf{r}', \omega_2)\, \mu(\omega_1)\, \mu(\omega_2), \tag{2.14}$$

where $H_2^{(0)}$ is obtained from H_2 by replacing G_2 in Eq. (2.13) by the function $G_2^{(0)}$. Nienhuis and Deutch[14] have demonstrated that $G_2^{(0)}$ is of short range, and therefore $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega = 0)$, Eq. (2.14), is a short-range function. For isotropic media, the static dielectric constant is given in Ref. 14 by

$$\frac{\epsilon(0) - 1}{4\pi} \mathbf{I} = \beta \int_v d\omega_1\, d\omega_2\, d\mathbf{r}'\, H_2^{(0)}(\mathbf{r}, \omega_1; \mathbf{r}'; \omega_2)\, \mu(\omega_1)\, \mu(\omega_2) = \int_v d\mathbf{r}'\, \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega = 0), \tag{2.15}$$

where $\mathbf{I}$ is the unit tensor.

If we tentatively *assume* that for arbitrary frequencies, $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$ is of short range and the average field $\mathbf{E}(\mathbf{r}, \omega)$ has negligible spatial variation over the range of $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$, then Eq. (2.9) may be written as

$$\mathbf{P}(\mathbf{r}, \omega) = \frac{\epsilon(\omega) - 1}{4\pi} \mathbf{E}(\mathbf{r}, \omega), \tag{2.16}$$

where

$$\frac{\epsilon(\omega) - 1}{4\pi} \mathbf{I} = \int_v d\mathbf{r}' \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega). \tag{2.17}$$

If $\hat{\chi}_0$ is indeed short-ranged, the integration in Eq. (2.17) may be extended over all space and accordingly this formal expression for $\epsilon(\omega)$ will be entirely independent of the sample shape. The expression for $\epsilon(\omega)$ in Eq. (2.17) generalizes to arbitrary frequencies the expression for the static dielectric constant in Eq. (2.15).

We seek an alternative expression for $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$ and proceed by constructing a formal relation for the shape-dependent response function $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$ in terms of a modified dipole correlation function by means of a projection operator. This procedure follows closely the projection operator theory of Zwanzig[15] and Mori[16] for evaluating time-correlation functions. With the explicit time dependence given in Eq. (2.5), the response function $\chi(\mathbf{r}, \mathbf{r}'; t)$, Eq. (2.4), may be written as

$$\chi(\mathbf{r}, \mathbf{r}'; t) = -\beta \frac{d}{dt} \langle \mu(\mathbf{r}) e^{iL_0 t} \mu(\mathbf{r}') \rangle$$
$$= -\beta \langle \mu(\mathbf{r}) e^{iL_0 t} iL_0 \mu(\mathbf{r}') \rangle. \tag{2.18}$$

We introduce the projection operator P defined by its operation on an arbitrary function $O(\mathbf{r})$:

$$PO(\mathbf{r}) = \beta \int_v d\mathbf{r}, \, d\mathbf{r}_2 \, \mu(\mathbf{r}_1) \cdot \mathbf{S}(\mathbf{r}_1, \mathbf{r}_2) \cdot \langle \mu(\mathbf{r}_2) O(\mathbf{r}) \rangle, \tag{2.19}$$

where $\mathbf{S}(\mathbf{r}_1, \mathbf{r}_2)$ is the inverse of the static correlation function $\hat{\chi}(\mathbf{r}_1, \mathbf{r}_2; \omega = 0)$, Eq. (2.11), in the sense that

$$\int_v d\mathbf{r}'' \hat{\chi}(\mathbf{r}, \mathbf{r}''; \omega = 0) \cdot \mathbf{S}(\mathbf{r}'', \mathbf{r}') = \mathbf{I} \, \delta(\mathbf{r} - \mathbf{r}'). \tag{2.20}$$

One verifies with Eqs. (2.20) and (2.11) that P defined by Eq. (2.19) is idempotent: $P^2 = P$. Next we use the operator identify

$$e^{iL_0 t} = e^{i(1-P)L_0 t} + \int_0^t ds \, e^{iL_0 s} PiL_0 e^{i(1-P)L_0(t-s)} \tag{2.21}$$

in Eq. (2.18) to obtain

$$\chi(\mathbf{r}, \mathbf{r}'; t) = -\beta \langle \mu(\mathbf{r}) e^{i(1-P)L_0 t} iL_0 \mu(\mathbf{r}') \rangle$$
$$- \beta^2 \int_0^t ds \int_v d\mathbf{r}_1 \, d\mathbf{r}_2 \, \langle \mu(\mathbf{r}) e^{iL_0 s} \mu(\mathbf{r}_1) \rangle$$
$$\cdot \mathbf{S}(\mathbf{r}_1, \mathbf{r}_2) \cdot \langle \mu(\mathbf{r}_2) iL_0 e^{i(1-P)L_0(t-s)} iL_0 \mu(\mathbf{r}') \rangle. \tag{2.22}$$

Using the relation

$$P e^{i(1-P)L_0 t} = P$$

which follows from the fact that P is idempotent, and using

$$\langle \mu(\mathbf{r}) iL_0 \mu(\mathbf{r}') \rangle = \langle \mu(\mathbf{r}) \dot{\mu}(\mathbf{r}') \rangle = 0,$$

one can show that the first term on the rhs of Eq. (2.22) vanishes. Therefore Eq. (2.22) can be written

$$\chi(\mathbf{r}, \mathbf{r}'; t) = \beta^2 \int_0^t ds \int_v d\mathbf{r}_1 \, d\mathbf{r}_2 \, \langle \mu(\mathbf{r}) e^{iL_0 s} \mu(\mathbf{r}_1) \rangle$$
$$\cdot \mathbf{S}(\mathbf{r}_1, \mathbf{r}_2) \cdot \langle \dot{\mu}(\mathbf{r}_2) e^{i(1-P)L_0(t-s)} \dot{\mu}(\mathbf{r}') \rangle. \tag{2.23}$$

The function $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$ in Eq. (2.7) is the Laplace transform with transform variable $-i\omega$ of $\chi(\mathbf{r}, \mathbf{r}'; t)$. Taking the Laplace transform of Eq. (2.23), using the definition in Eq. (2.18) and the relation between the Laplace transform of a function and the transform of its derivative, we find

$$i\omega \hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = \int_v d\mathbf{r}_1 \, d\mathbf{r}_2 [\hat{\chi}(\mathbf{r}, \mathbf{r}_1; \omega) - \hat{\chi}(\mathbf{r}, \mathbf{r}_1; \omega = 0)]$$
$$\cdot \mathbf{S}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\kappa}(\mathbf{r}_2; \mathbf{r}'; \omega) = -\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$$
$$+ \int_v d\mathbf{r}_1 \, d\mathbf{r}_2 \hat{\chi}(\mathbf{r}, \mathbf{r}_1; \omega) \cdot \mathbf{S}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\kappa}(\mathbf{r}_2, \mathbf{r}'; \omega), \tag{2.24}$$

where in obtaining the second relation we have used Eq. (2.20), and defined $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$ by

$$\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega) = \mathcal{L}[\beta \langle \dot{\mu}(\mathbf{r}) e^{i(1-P)L_0 t} \dot{\mu}(\mathbf{r}') \rangle], \tag{2.25}$$

the symbol $\mathcal{L}$ denoting Laplace transform with $z = -i\omega$.

We now seek a relation between the modified correlation function $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$ and the susceptibility $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$. We shall prove that this relation is

$$i\omega \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega) = -\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega) + \int_v d\mathbf{r}_1 \, d\mathbf{r}_2 \, \hat{\chi}_0(\mathbf{r}, \mathbf{r}_1; \omega)$$
$$\cdot \mathbf{S}_0(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\kappa}(\mathbf{r}_2, \mathbf{r}'; \omega), \tag{2.26}$$

where $\mathbf{S}_0(\mathbf{r}_1, \mathbf{r}_2)$ is the inverse of the short-range correlation function $\hat{\chi}_0(r, r'; \omega = 0)$, Eq. (2.14), in the sense that

$$\int_v d\mathbf{r}'' \mathbf{S}_0(\mathbf{r}, \mathbf{r}'') \cdot \hat{\chi}_0(\mathbf{r}'', \mathbf{r}'; \omega = 0) = \mathbf{I} \, \delta(\mathbf{r} - \mathbf{r}'). \tag{2.27}$$

To establish Eq. (2.26) it is convenient to employ a condensed operator notation. We first rewrite Eq. (2.10) as

$$\hat{\chi}(\omega) = \hat{\chi}_0(\omega) + \hat{\chi}_0(\omega) * \mathbf{T} * \hat{\chi}(\omega) \tag{2.28a}$$

or

$$\hat{\chi}_0(\omega) = \hat{\chi}(\omega) * [\mathbf{1} + \mathbf{T} * \hat{\chi}(\omega)]^{-1}, \tag{2.28b}$$

where the explicit dependence on the spatial arguments has been suppressed and $\mathbf{A} * \mathbf{B}$ symbolizes the convolution

$$\mathbf{A} * \mathbf{B} = \int_v d\mathbf{r}'' \mathbf{A}(\mathbf{r}, \mathbf{r}'') \cdot \mathbf{B}(\mathbf{r}'', \mathbf{r}'). \tag{2.29}$$

In Eq. (2.28b), 1 denotes the function $\mathbf{I} \delta(\mathbf{r} - \mathbf{r}')$. If we operate on Eq. (2.28a) in the $\omega = 0$ limit with $\mathbf{S}_0$, and if the resulting expression operates according to Eq. (2.29) on $\mathbf{S}$, we obtain using Eqs. (2.20) and (2.27)

$$\mathbf{S} = \mathbf{S}_0 - \mathbf{T}. \tag{2.30}$$

In the same notation, Eq. (2.24) may be written

$$\hat{\chi}(\omega) = \hat{\kappa}(\omega) * [\mathbf{S} * \hat{\kappa}(\omega) - i(\omega)\mathbf{1}]^{-1}. \tag{2.31}$$

Eliminating $\hat{\chi}(\omega)$ between Eqs. (2.28b) and (2.31), making use of Eq. (2.30), leads to

$$\hat{\chi}_0(\omega) = \hat{\kappa}(\omega) * [\mathbf{S}_0 * \hat{\kappa}(\omega) - i\omega \mathbf{1}]^{-1}, \tag{2.32}$$

which is equivalent to the relation Eq. (2.26) that we wish to establish.

The noteworthy feature of the relation between $\hat{\chi}_0(\omega)$ and $\hat{\kappa}(\omega)$ in Eq. (2.26) is that it involves only $\mathbf{S}_0$, the inverse of the static short-range correlation function, which is itself of short range. In contrast, the relation between $\hat{\chi}_0(\omega)$ and $\hat{\chi}(\omega)$ in Eq. (2.10) explicitly contains the long-range dipole–dipole tensor $\mathbf{T}$.

We shall *assume* that $\hat{\kappa}(\omega)$ is short-ranged. Then we may conclude from Eq. (2.26) that $\hat{\chi}_0(\omega)$ is also short-ranged and hence the dielectric constant $\epsilon(\omega)$ may be expressed by Eq. (2.16). We shall further assume that $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$ depends only on the separation $|\mathbf{r} - \mathbf{r}'|$. Then, for isotropic media

$$\int_v d\mathbf{r}' \hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega) = k(\omega) \mathbf{I}, \tag{2.33}$$

where $k(\omega)$ is a scalar quantity independent of $\mathbf{r}$. Note that because of the assumed short-range character of $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$, the region of integration in Eq. (2.33) need not be extended over the entire volume V. The integral becomes essentially independent of the region of integration once past the range of $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$. We shall use this fact shortly.

From Eqs. (2.15) and (2.27) one sees that

$$\int_v d\mathbf{r}' \mathbf{S}_0(\mathbf{r}, \mathbf{r}') = \frac{4\pi}{\epsilon(0) - 1} \mathbf{I}. \tag{2.34}$$

Integration of Eq. (2.26) over $\mathbf{r}'$ and use of Eqs. (2.17), (2.33), and (2.34) leads to the result

$$\frac{\epsilon(\omega) - 1}{\epsilon(0) - 1} = \frac{D(\omega)}{D(\omega) - i\omega}, \tag{2.35}$$

where

$$D(\omega) = \frac{4\pi k(\omega)}{\epsilon(0) - 1}. \tag{2.36}$$

The result Eq. (2.35) for the dielectric constant has been derived for arbitrary sample shape. In particular, Eq. (2.35) does not display any explicit shape-dependent terms as are obtained in relations between $\epsilon(\omega)$ and the dipole–dipole correlation function based on Eq. (2.10).[13] The molecular analysis required to justify the assumptions that $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$ is short range and translationally invariant will be formidable, but we believe, on the basis of experience with the static case, possible. We do not undertake this task here.

The function $k(\omega)$ defined by Eq. (2.33) may be written in a more explicit form by noting that

$$\int_v d\mathbf{r}' \boldsymbol{\mu}(\mathbf{r}') = \mathbf{M},$$

where $\mathbf{M}$ is the total dipole moment of the sample in V. Then from Eq. (2.33) and the expression for $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$ in Eq. (2.25) we find

$$k(\omega)\mathbf{I} = (\beta/V)\mathcal{L}[\langle \dot{\mathbf{M}} e^{i(1-P)L_0 t} \dot{\mathbf{M}} \rangle], \tag{2.37}$$

where we used the assumption that the integral in Eq. (2.33) is independent of $\mathbf{r}$ to replace the variable $\dot{\boldsymbol{\mu}}(\mathbf{r})$ by $\dot{\mathbf{M}} V^{-1}$. The function $\langle \dot{\mathbf{M}} e^{i(1-P)L_0 t} \dot{\mathbf{M}} \rangle$ is the unnormalized memory function one usually encounters in evaluating the time-correlation function $\langle \mathbf{M}\mathbf{M}(t) \rangle$ in the Zwanzig[15]–Mori[16] formalism. The expression Eq. (2.35), together with Eqs. (2.36) and (2.37), provides a formal relation for $\epsilon(\omega)$ in terms of the memory function. There are a number of techniques for approximate evaluation of these modified correlation functions, for example methods based on Mori's[17] continued fraction expansion of the memory function.[18]

Because the modified correlation function $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$ is expected to be of short range, one need not be concerned with sample shape dependence in evaluating the memory function $k(\omega)$. The short-range character of $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$ also suggests that an alternative expression for $k(\omega)$ may be obtained by considering the sample volume V to be composed of two regions, an embedded volume V_0 of arbitrary shape and a surrounding volume W. The alternative expression for $k(\omega)$ is

$$k(\omega)\mathbf{I} = \frac{\beta}{V_0} \mathcal{L}\left[\langle \dot{\mathbf{m}} e^{i(1-P)L_0 t} \dot{\mathbf{m}} \rangle\right], \tag{2.38}$$

where m refers to the dipole moment of the embedded region V_0. The definition of P, L_0, and the implicit equilibrium distribution function in Eq. (2.38) still include all molecular interactions in the composite region $(V_0 + W)$. The expression Eq. (2.38) may be established by extending the region of integration in Eq. (2.33) only over the embedded volume V_0 rather than the entire molecular volume $V = (V_0 + W)$. This step is justified due to the assumed short-range, translationally invariant character of $\hat{\kappa}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$, provided $\boldsymbol{r}$ in Eq. (2.33) denotes a position within the embedded region V_0 which is not near the boundary of V_0 and the latter includes the range of variation of $\hat{\kappa}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$.

In the following section we shall demonstrate that the formalism outlined above, in particular Eq. (2.38), is consistent with treatments relating the dielectric constant to the dipole correlation function of the embedded volume V_0.

III. CORRELATION FUNCTIONS FOR EMBEDED GEOMETRIES

Most previous theories of dielectric relaxation in polar media have considered the relation between the dielectric constant $\epsilon(\omega)$ and the dipole correlation function of a small sphere embedded in an infinite continuum of the same material Eqs. (1)–6). In this section we shall examine the more general case where the embedded sample is of arbitrary shape and the surrounding medium, is allowed to have a different dielectric constant $\epsilon_1(\omega)$.

As in the previous section, we consider the entire molecular medium to occupy a volume V, which is composed of an immersed region of volume V_0 and a surrounding region of volume W. The response function $\hat{\chi}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$ is defined by Eqs. (2.4) and (2.7), where the ensemble average and Liouville operator L_0 depend on all interactions between particles in the entire region $V = (V_0 + W)$. The expression Eq. (2.10) relating $\hat{\chi}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$ to the susceptibility $\hat{\chi}_0(\boldsymbol{r}, \boldsymbol{r}'; \omega)$ and Eq. (2.26) relating the latter to the modified correlation function $\hat{\kappa}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$ are unchanged; however, we shall rewrite these equations to explicitly indicate that V is composed of the sum of V_0 and W:

$$\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega) + \int_{(v_0+w)} d\mathbf{r}_1 d\mathbf{r}_2 \hat{\chi}_0(\mathbf{r}, \mathbf{r}_1; \omega) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega); \tag{3.1}$$

$$i\omega\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega) = -\hat{\kappa}(\mathbf{r},\mathbf{r}';\omega) + \int_{(v_0+w)} d\mathbf{r}_1\, d\mathbf{r}_2 \hat{\chi}_0(\mathbf{r},\mathbf{r}_1;\omega)\cdot \mathbf{S}_0(\mathbf{r}_1,\mathbf{r}_2) \cdot \hat{\kappa}(\mathbf{r}_2,\mathbf{r}';\omega). \quad (3.2)$$

We shall again assume that $\hat{\kappa}(\mathbf{r},\mathbf{r}';\omega)$ is of short range. It follows from Eq. (3.2) that $\chi_0(\mathbf{r},\mathbf{r}';\omega)$ is of short range and accordingly the dielectric constant at some point $\mathbf{r}$ in the medium is given by Eq. (2.17), which in the present notation can be written as

$$\frac{\epsilon(\mathbf{r};\omega)-1}{4\pi}\mathbf{I} = \int_{(v_0+w)} d\mathbf{r}'\,\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega), \quad (3.3)$$

where we have allowed the possibility that the dielectric constant depends on position in the sample. Due to the short-range character of $\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega)$, the integration in Eq. (3.3) gives a non-negligible contribution only when $\mathbf{r}'$ is within a microscopic region surrounding point $\mathbf{r}$. We shall consider the case where

$$\epsilon(\mathbf{r};\omega) = \begin{cases} \epsilon(\omega) & \mathbf{r} \text{ in } V_0 \\ \epsilon_1(\omega) & \mathbf{r} \text{ in } W \end{cases}. \quad (3.4)$$

If the arguments $\mathbf{r}$ and $\mathbf{r}'$ are positions in the embedded volume V_0 but are not within a nicroscopic region at the boundary of V_0, the region W gives a negligible contribution to the integral in Eq. (3.2). In this case Eq. (3.2) may be written

$$i\omega\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega) = -\hat{\kappa}(\mathbf{r},\mathbf{r}';\omega) + \int_{v_0} d\mathbf{r}_1 d\mathbf{r}_2 \hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega)\cdot \mathbf{S}_0(\mathbf{r}_1,\mathbf{r}_2) \cdot \hat{\kappa}(\mathbf{r}_2,\mathbf{r}';\omega). \quad (3.5)$$

Neglecting surface contributions which arise when $\mathbf{r}$ or $\mathbf{r}'$ are near the boundary of V_0, we can obtain from Eq. (3.5), by integrating $\mathbf{r}'$ over V_0, the result for the dielectric constant $\epsilon(\omega)$ of the embedded volume given in Eq. (2.35). This procedure also results directly in the expression Eq. (2.38) for $k(\omega)$ in terms of the memory function of the embedded region.

Next we investigate the relation between $\epsilon(\omega)$ and the time-dependent dipole–dipole correlation function $\chi_{v_0}(\omega)$ of the embedded region V_0, which is given by

$$\chi_{v_0}(\omega) = -\frac{\beta}{V_0}\mathfrak{L}\left[\frac{d}{dt}\langle \mathbf{m}\,\mathbf{m}(t)\rangle\right] = \int_{V_0} d\mathbf{r}'\,\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)\,, \quad (3.6)$$

where the argument $\mathbf{r}$ in $\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)$ is a point in V_0 which is not near the boundary. In Eq. (3.6) one integrates only over the embedded volume V_0, while the relation between $\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)$ and the susceptibility $\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega)$ in Eq. (3.1) involves integrations extending over the entire region $V=(V_0+W)$. We shall demonstrate by eliminating the integrations over the external region W that Eq. (3.1) can, with minor restrictions, be written as

$$\hat{\chi}(\mathbf{r},\mathbf{r}';\omega) = \hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega) + \int_{V_0} d\mathbf{r}_1\, d\mathbf{r}_2 \hat{\chi}_0(\mathbf{r},\mathbf{r}_1;\omega) \cdot [\mathbf{T}(\mathbf{r}_1,\mathbf{r}_2) + \mathbf{R}_W(\mathbf{r}_1,\mathbf{r}_2;\epsilon_1(\omega))] \cdot \hat{\chi}(\mathbf{r}_2,\mathbf{r}';\omega)\,. \quad (3.7)$$

In Eq. (3.7), $\mathbf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_1(\omega))$ has the physical interpretation of a "reaction field" tensor; $\mathbf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_1(\omega))\cdot\mathbf{P}$ is the field at $\mathbf{r}$ in V_0 due to polarization of the region W caused by a dipole $\mathbf{P}$ oscillating with frequency ω at point $\mathbf{r}'$ in V_0, when V_0 is empty and W is filled with a continuum of dielectric constant $\epsilon_1(\omega)$.

This equation may be understood in the following way. In the presence of an external field $\mathbf{E}_0(\mathbf{r},\omega)$ which interacts only with the dipoles in the embedded region V_0, the polarization at a point $\mathbf{r}$ in V_0 is given in linear response theory by

$$\mathbf{P}(\mathbf{r},\omega) = \int_{V_0} d\mathbf{r}'\,\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)\cdot\mathbf{E}_0(\mathbf{r},\omega)\,. \quad (3.8)$$

When the external region W is a macroscopic continuum of dielectric constant $\epsilon_1(\omega)$ the relation that holds between $\mathbf{E}_0(\mathbf{r},\omega)$ and the average field $\mathbf{E}_m(\mathbf{r}',\omega)$ in the long wavelength limit is[14]

$$\mathbf{E}_m(\mathbf{r},\omega) = \mathbf{E}_0(\mathbf{r},\omega) + \int_{V_0} d\mathbf{r}'\,[\mathbf{T}(\mathbf{r},\mathbf{r}') + \mathbf{R}_w(\mathbf{r},\mathbf{r}';\epsilon_1(\omega))]\cdot\mathbf{P}(\mathbf{r}';\omega)\,. \quad (3.9)$$

The subscript m on $\mathbf{E}_m(\mathbf{r},\omega)$ denotes the fact that this is the average field inside V_0 when W is a *macroscopic continuum*. We seek a relation between the polarization and $\mathbf{E}_m(\mathbf{r},\omega)$ of the form

$$\mathbf{P}(\mathbf{r},\omega) = \int_{V_0} d\mathbf{r}'\,\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega)\cdot\mathbf{E}_m(\mathbf{r}',\omega)\,. \quad (3.10)$$

From Eqs. (2.8), (3.9), and (3.10), the relation between $\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)$ and $\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega)$ is found to be that given in Eq. (3.7). Therefore, Eq. (3.7) is the appropriate relation between $\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)$ and $\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega)$ when the volume V_0 is embedded in a macroscopic continuum W of dielectric constant $\epsilon_1(\omega)$. We shall demonstrate later that Eqs. (3.6) and (3.7) lead to well-known relations between $\epsilon(\omega)$ and $\chi_{V_0}(\omega)$. For the present, we wish to show that, with minor restrictions, Eq. (3.7) for $\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)$ is equivalent to Eq. (3.1). We emphasize the fact that Eq. (3.1) is exact and that the functions $\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)$ and $\hat{\chi}_0(\mathbf{r},\mathbf{r}';\omega)$ depend on all interactions between dipoles in the entire region $V=(V_0+W)$.

One notes that the equivalence of Eqs. (3.7) and (3.1) for the relationship between $\hat{\chi}$ and $\hat{\chi}_0$ is analogous to the equivalence of Eqs. (3.9) and (2.8) for the relation between $\mathbf{E}$ and $\mathbf{E}_0$. Neither Eq. (3.9) nor Eq. (2.8) requires a constitutive relation to hold between $\mathbf{P}$ and $\mathbf{E}$. *If* we assume that W is a dielectric continuum where for $\mathbf{r}'$ in W,

$$\mathbf{P}(\mathbf{r}',\omega) = \frac{\epsilon_1(\omega)-1}{4\pi}\mathbf{E}(\mathbf{r}',\omega)\,,$$

and that $\mathbf{E}_0$ vanishes in W, then it can be shown by macroscopic electrostatic arguments that Eqs. (2.8) and (3.9) are equivalent. This demonstration is based on relations satisfied by the reaction field tensor $\mathbf{R}_W$ derived previously[14] and summarized in the Appendix. A similar procedure will now be employed in the microscopic analysis to show that Eqs. (3.1) and (3.7) for $\hat{\chi}(\mathbf{r},\mathbf{r}';\omega)$ are equivalent when both $\mathbf{r}$ and $\mathbf{r}'$ are points in the embedded region V_0.

If $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$ is of short range and $\mathbf{r}$ is in V_0 (however not in a microscopic region near the boundary of V_0) the integration in Eq. (3.1) over $\mathbf{r}_1$ will give a negligible contribution unless $\mathbf{r}_1$ is in V_0. We then write the integral in Eq. (3.1) as the sum of two terms, depending on whether $\mathbf{r}_2$ is integrated over V_0 or W:

$$\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega) + \int_{V_0} d\mathbf{r}_1\, d\mathbf{r}_2 \hat{\chi}_0(\mathbf{r}, \mathbf{r}_1; \omega) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega) + \int_{V_0} d\mathbf{r}_1\, \hat{\chi}_0(\mathbf{r}, \mathbf{r}_1; \omega) \cdot \mathbf{A}(\mathbf{r}_1, \mathbf{r}'; \omega)\,, \tag{3.11}$$

where we have defined

$$\mathbf{A}(\mathbf{r}, \mathbf{r}'; \omega) = \int_W d\mathbf{r}''\, \mathbf{T}(\mathbf{r}, \mathbf{r}'') \cdot \hat{\chi}(\mathbf{r}'', \mathbf{r}'; \omega)\,. \tag{3.12}$$

The arguments $\mathbf{r}$ and $\mathbf{r}'$ in $\mathbf{A}(\mathbf{r}, \mathbf{r}'; \omega)$ are points in the embedded region. The function $\mathbf{A}(\mathbf{r}, \mathbf{r}'; \omega)$ can be evaluated by substituting for $\hat{\chi}(\mathbf{r}'', \mathbf{r}'; \omega)$ in Eq. (3.12) the relation Eq. (3.1). At this stage we introduce two approximations. The arguments $\mathbf{r}''$ and $\mathbf{r}'$ of $\hat{\chi}(\mathbf{r}'', \mathbf{r}'; \omega)$ in Eq. (3.12) denote postions in the regions W and V_0, respectively. Then, except for a microscopic region at the boundary between V_0 and W, the short-range function $\hat{\chi}_0(\mathbf{r}'', \mathbf{r}'; \omega)$ is essentially zero. Thus our first approximation is to neglect entirely the boundary effects between V_0 and W. In this case Eq. (3.1) can be written ($\mathbf{r}''$ in W, $\mathbf{r}'$ in V_0)

$$\hat{\chi}(\mathbf{r}'', \mathbf{r}'; \omega) = \int_W d\mathbf{r}_1 \int_{(v_0+w)} d\mathbf{r}_2\, \hat{\chi}_0(\mathbf{r}'', \mathbf{r}_1; \omega) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega)\,. \tag{3.13}$$

The second approximation is to replace the short-range function $\hat{\chi}_0(\mathbf{r}'', \mathbf{r}_1; \omega)$ in Eq. (3.13), where both arguments denote points in the region W, by the local function

$$\hat{\chi}_0(\mathbf{r}'', \mathbf{r}_1; \omega) = \frac{\epsilon_1(\omega) - 1}{4\pi} \mathbf{I}\, \delta(\mathbf{r}'' - \mathbf{r}_1)\,, \tag{3.14}$$

which is consistent with the definition of the dielectric constant of W in Eqs. (3.3) and (3.4). Thus Eq. (3.12) for $\mathbf{A}$ with use of Eqs. (3.13) and (3.14) becomes

$$\mathbf{A}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{\epsilon_1(\omega) - 1}{4\pi} \int_W d\mathbf{r}_1 \int_{(v_0+w)} d\mathbf{r}_2\, \mathbf{T}(\mathbf{r}, \mathbf{r}_1) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega), \tag{3.15}$$

which can be rewritten as an integral equation for $\mathbf{A}$:

$$\mathbf{A}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{\epsilon_1(\omega) - 1}{4\pi} \left[\int_{(v_0+w)} d\mathbf{r}_1\, d\mathbf{r}_2\, \mathbf{T}(\mathbf{r}, \mathbf{r}_1) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega) - \int_{v_0} d\mathbf{r}_1\, d\mathbf{r}_2 \mathbf{T}(\mathbf{r}, \mathbf{r}_1) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega) - \int_{v_0} d\mathbf{r}_1 \mathbf{T}(\mathbf{r}, \mathbf{r}_1) \cdot \mathbf{A}(\mathbf{r}_1, \mathbf{r}'; \omega) \right], \tag{3.16}$$

where the definition of $\mathbf{A}$ in Eq. (3.12) has been employed. From the Appendix, Eq. (A2), we have the following relationship:

$$\int_{(V_0+W)} d\mathbf{r}_1\, \mathbf{T}(\mathbf{r}, \mathbf{r}_1) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) = -4\pi \mathbf{T}(\mathbf{r}, \mathbf{r}_2) + \frac{4\pi}{\epsilon_1(\omega) - 1} \mathbf{R}^*_{(V_0+W)}(\mathbf{r}, \mathbf{r}_2; \epsilon_1^{-1}(\omega)) - \int_{(V_0+W)} d\mathbf{r}_1\, \mathbf{R}^*_{(V_0+W)}(\mathbf{r}, \mathbf{r}_1; \epsilon_1^{-1}(\omega)) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2). \tag{3.17}$$

This is an exact mathematical relationship despite the appearance of the parameter $\epsilon_1(\omega)$ on the rhs of Eq. (3.17). The mathematical integrity of Eq. (3.17) is assured by regarding it as the definition of the quantity $\mathbf{R}^*_{(V_0+W)}$. However, it turns out that $\mathbf{R}^*_{(V_0+W)}$ can be given a simple physical interpretation in terms of macroscopic electrostatics. Rather than pursue the mathematics we adopt the physical picture herewith. Thus $\mathbf{R}^*_{(V_0+W)}$ is interpreted such that $\mathbf{R}^*_{(V_0+W)}(\mathbf{r}, \mathbf{r}'; \epsilon_1^{-1}(\omega)) \cdot \mathbf{p}$ is the reaction field at $\mathbf{r}$ due to a dipole $\mathbf{p}$ at $\mathbf{r}'$ when the total volume $(V_0 + W)$ is empty and the infinite space outside $(V_0 + W)$ is filled with a continuum of dielectric constant $\epsilon_1^{-1}(\omega)$.

When Eq. (3.17) is substituted into the first integral on the rhs of Eq. (3.16), use is made of the result ($\mathbf{r}, \mathbf{r}'$ in V_0)

$$\int_W d\mathbf{r}_2\, \mathbf{R}^*_{(V+W)}(\mathbf{r}, \mathbf{r}_2; \epsilon_1^{-1}(\omega)) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega) = \frac{\epsilon_1(\omega) - 1}{4\pi} \int_W d\mathbf{r}_1 \int_{(V_0+W)} d\mathbf{r}_2\, \mathbf{R}^*_{(V_0+W)}(\mathbf{r}, \mathbf{r}_1; \epsilon_1^{-1}(\omega)) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega),$$

which follows in the same way that Eq. (3.15) is derived from (3.12), and using again the definition of $\mathbf{A}$ in Eq. (3.12), we find that Eq. (3.16) becomes

$$\epsilon_1(\omega) \mathbf{A}(\mathbf{r}, \mathbf{r}'; \omega) = \int_{v_0} d\mathbf{r}_1 [\mathbf{R}^*_{(v_0+w)}(\mathbf{r}, \mathbf{r}_1; \epsilon_1^{-1}(\omega)) + (1 - \epsilon_1(\omega)) \mathbf{T}(\mathbf{r}, \mathbf{r}_1)] \cdot \hat{\chi}(\mathbf{r}_1, \mathbf{r}'; \omega) - \left(\frac{\epsilon_1(\omega) - 1}{4\pi} \right) \int_{v_0} d\mathbf{r}_1 [\mathbf{T}(\mathbf{r}, \mathbf{r}_1) + \mathbf{R}^*_{(v_0+w)}(\mathbf{r}, \mathbf{r}_1; \epsilon_1^{-1}(\omega))] \cdot \left[\mathbf{A}(\mathbf{r}_1, \mathbf{r}'; \omega) + \int_{v_0} d\mathbf{r}_2\, \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega) \right]. \tag{3.18}$$

The solution to this equation is

$$\mathbf{A}(\mathbf{r}, \mathbf{r}'; \omega) = \int_{V_0} d\mathbf{r}_2 \mathbf{R}_w(\mathbf{r}, \mathbf{r}_2; \epsilon_1(\omega)) \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega), \tag{3.19}$$

where $\mathbf{R}_w$ is the reaction field tensor for the reaction inside V_0 when the latter is empty and the region W is filled with a continuum of dielectric constant $\epsilon_1(\omega)$. This result can be verified by substituting Eq. (3.19) into (3.18) and noting that the resulting integral equation for $\mathbf{R}_w$ is identical to Eq. (A1).

With the result Eq. (3.19) for $\mathbf{A}$ we find that Eq. (3.11) becomes

$$\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega) + \int_{V_0} d\mathbf{r}_1 d\mathbf{r}_2 \hat{\chi}_0(\mathbf{r}, \mathbf{r}_1; \omega) \cdot [\mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) + \mathbf{R}_w(\mathbf{r}_1, \mathbf{r}_2; \epsilon_1(\omega))] \cdot \hat{\chi}(\mathbf{r}_2, \mathbf{r}'; \omega),$$

which is the desired result, Eq. (3.7), for the response function.

To summarize, we have shown that the exact integral equation Eq. (3.1) for $\hat{\chi}(\omega)$ reduces to Eq. (3.7), which is the form appropriate for the response function of the embedded region V_0 when the surrounding W is treated as a macroscopic continuum. This result has been obtained under the approximations that boundary effects may be neglected and that $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$ is a local function of the form Eq. (3.14) when its arguments denote points in the external region W. Formally, however, interactions between the two regions are still to be included in evaluating the susceptibility $\hat{\chi}_0(\omega)$ of the embedded volume. Although it is beyond the scope of this paper, we expect that a detailed microscopic analysis of $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$, or equivalently the modified correlation function $\hat{\kappa}(\mathbf{r}, \mathbf{r}'; \omega)$, would reveal that interactions between dipoles in V_0 and those in W give negligible contributions to these short-ranged correlation functions. This is in keeping with the physical expectation that the dielectric constant of the embedded region is independent of the nature of the surrounding medium.

We shall conclude this section by verifying explicitly that Eq. (3.7) for the response function of the embedded region, when used to compute the correlation function $\chi_{V_0}(\omega)$ in Eq. (3.6), leads to expressions for the dielectric constant which agree with previously derived results. We shall restrict ourselves to consideration of uniform polarization geometries, that is sample shapes for which the integral ($\mathbf{r}$ in V_0)

$$\mathbf{F}(\omega) \equiv \int_{V_0} d\mathbf{r}' [\mathbf{T}(\mathbf{r}, \mathbf{r}') + \mathbf{R}_w(\mathbf{r}, \mathbf{r}'; \epsilon_1(\omega))]$$

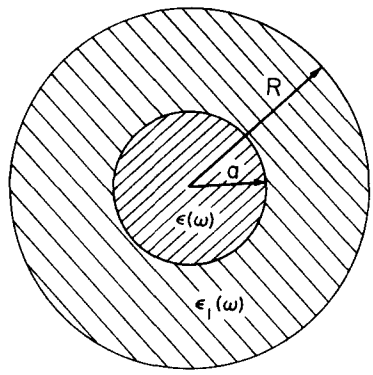

FIG. 1. An example of the system considered in Sec. III. A sphere of radius a and dielectric constant $\epsilon(\omega)$ is embedded in a larger sphere of radius R and dielectric constant $\epsilon_1(\omega)$.

is independent of $\mathbf{r}$. In particular, we shall consider the geometry illustrated in Fig. 1: V_0 is a sphere of radius a and W is a concentric spherical shell of outer radius R.

By integrating both sides of Eq. (3.7) over $\mathbf{r}'$, we obtain using Eq. (3.3), (3.4), and (3.6)

$$\hat{\chi}_{V_0}(\omega) = \frac{\epsilon(\omega) - 1}{4\pi} \left[\mathbf{I} - \left(\frac{\epsilon(\omega) - 1}{4\pi} \right) \mathbf{F}(\omega) \right]^{-1}. \tag{3.20}$$

From Eq. (A1), one can show that

$$\mathbf{F}(\omega) = \frac{1}{\epsilon_1(\omega)} \left[\mathbf{I} + \left(\frac{\epsilon_1(\omega) - 1}{4\pi} \right) \mathbf{G}(\omega) \right]^{-1} \cdot \mathbf{G}(\omega), \tag{3.21}$$

where ($\mathbf{r}$ in V_0)

$$\mathbf{G}(\omega) = \int_{V_0} d\mathbf{r}' [\mathbf{T}(\mathbf{r}, \mathbf{r}') + \mathbf{R}^*_{(V_0+W)}(\mathbf{r}, \mathbf{r}'; \epsilon_1^{-1}(\omega))].$$

When the outer surface of W is a sphere of radius R, Eq. (A3) gives an explicit expression for the reaction field tensor $\mathbf{R}^*_{(V_0+W)}$. From this one finds for the case where V_0 is a concentric sphere of radius a

$$\int_{V_0} d\mathbf{r}' \mathbf{R}^*_{(V_0+W)}(\mathbf{r}, \mathbf{r}'; \epsilon_1^{-1}(\omega)) = \frac{-8\pi}{3} \left(\frac{\epsilon_1(\omega) - 1}{\epsilon_1(\omega) + 2} \right) \frac{a^3}{R^3} \mathbf{I}. \tag{3.22}$$

This equation, together with the result for a sphere

$$\int_{V_0} d\mathbf{r}' \mathbf{T}(\mathbf{r}, \mathbf{r}') = \frac{-4\pi}{3} \mathbf{I},$$

gives

$$\mathbf{G}(\omega) = \frac{-4\pi}{3} \left[\frac{(\epsilon_1(\omega) + 2) R^3 + 2(\epsilon_1(\omega) - 1) a^3}{(\epsilon_1(\omega) + 2) R^3} \right] \mathbf{I}. \tag{3.23}$$

This result for $\mathbf{G}(\omega)$ is substituted into Eq. (3.21) for $F(\omega)$, which in turn leads to the expression for $\chi_{V_0}(\omega)$,

$$\chi_{V_0}(\omega) = \frac{\epsilon(\omega) - 1}{4\pi} \left[\frac{(2\epsilon_1(\omega) + 1)(\epsilon_1(\omega) + 2) R^3 - 2(\epsilon_1(\omega) - 1)^2 a^3}{(\epsilon_1(\omega) + 2)(2\epsilon_1(\omega) + \epsilon(\omega)) R^3 + 2(\epsilon_2(\omega) - 1)(\epsilon(\omega) - \epsilon_1(\omega)) a^3} \right] \mathbf{I}. \tag{3.24}$$

The expression Eq. (3.24) relates the dielectric constant $\epsilon(\omega)$ of a sphere of radius a embedded in a larger sphere of radius R and dielectric constant $\epsilon_1(\omega)$ to the Laplace transform of the dipole-dipole correlation function of the embedded sphere. This result agrees with Eq. (2.1) of Ref. 19 when the latter is specialized to

this case. In the case $a = R$, Eq. (3.24) becomes

$$\chi_{V_0}(\omega) = \frac{3}{4\pi}\left(\frac{\epsilon(\omega)-1}{\epsilon(\omega)+2}\right)\mathbf{I}, \tag{3.25}$$

which is the well-known relation between $\epsilon(\omega)$ and the correlation function of a sphere in vacuum. On the other hand, when $R \gg a$ and $\epsilon_1(\omega) = \epsilon(\omega)$, we obtain from Eq. (3.24)

$$\chi_{V_0}(\omega) = \frac{(\epsilon(\omega)-1)(2\epsilon(\omega)+1)}{12\pi\epsilon(\omega)}\mathbf{I} \tag{3.26}$$

which is the relation, first derived by Fatuzzo and Mason,[1] for a sphere embedded in an infinite continuum of the same dielectric constant.

The long-range part of the polarization fluctuations in the embedded sample V_0 may be determined from the expression Eq. (3.7) for $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$. From Eqs. (2.4) and (2.7) the polarization fluctuations are related to $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega)$ by

$$\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = -\beta\mathcal{L}\left[\frac{d}{dt}\langle\mu(\mathbf{r})\mu(\mathbf{r}', t)\rangle\right].$$

The long-range part of these fluctuations is defined by

$$\hat{\chi}_L(\mathbf{r}, \mathbf{r}'; \omega) = \hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) - \hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega). \tag{3.27}$$

Thus we may write Eq. (3.7) as

$$\hat{\chi}_L(\mathbf{r}, \mathbf{r}'; \omega) = \int_{V_0} d\mathbf{r}_1\, d\mathbf{r}_2 \hat{\chi}_0(\mathbf{r}, \mathbf{r}_1; \omega) \cdot [\mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) + \mathbf{R}_W(\mathbf{r}_1, \mathbf{r}_2; \epsilon_1(\omega))] \cdot [\hat{\chi}_0(\mathbf{r}_2, \mathbf{r}'; \omega) + \hat{\chi}_L(\mathbf{r}_2, \mathbf{r}'; \omega)]. \tag{3.28}$$

When $\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega)$ is approximated by ($\mathbf{r}, \mathbf{r}'$ in V_0)

$$\hat{\chi}_0(\mathbf{r}, \mathbf{r}'; \omega) = \frac{\epsilon(\omega)-1}{4\pi}\mathbf{I}\,\delta(\mathbf{r}-\mathbf{r}'), \tag{3.29}$$

Eq. (3.28) becomes

$$\hat{\chi}_L(\mathbf{r}, \mathbf{r}'; \omega) = \left(\frac{\epsilon(\omega)-1}{4\pi}\right)^2 [\mathbf{T}(\mathbf{r}, \mathbf{r}'; \omega) + \mathbf{R}_W(\mathbf{r}, \mathbf{r}'; \epsilon_1(\omega))] + \left(\frac{\epsilon(\omega)-1}{4\pi}\right)\int_{V_0} d\mathbf{r}''[\mathbf{T}(\mathbf{r}, \mathbf{r}'') + \mathbf{R}_W(\mathbf{r}, \mathbf{r}''; \epsilon_1(\omega))] \cdot \hat{\chi}_L(\mathbf{r}'', \mathbf{r}'; \omega). \tag{3.30}$$

This equation involves both parameters $\epsilon(\omega)$, $\epsilon_1(\omega)$. Using techniques similar to those described by Nienhuis and Deutch[14] (see also the discussion in Ref. 19, Sec. IV), we can show that the solution to Eq. (3.30) is

$$\hat{\chi}_L(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{\epsilon(\omega)}\left(\frac{\epsilon(\omega)-1}{4\pi}\right)^2 \times [\mathbf{T}(\mathbf{r}, \mathbf{r}') + \mathbf{R}_{V_0}(\mathbf{r}, \mathbf{r}'; \epsilon(\omega), \epsilon_1(\omega))]. \tag{3.31}$$

The tensor $\mathbf{R}_{V_0}$ in Eq. (3.31) describes the reaction field inside V_0 due to polarization of the region W with dielectric constant $\epsilon_1(\omega)$ when V_0 is characterized by dielectric constant $\epsilon(\omega)$. This result is equivalent to that obtained by Titulaer and Deutch[19] on the basis of macroscopic fluctuation theory, in the limit where retardation effects are neglected.

The approximation in Eq. (3.29) is equivalent to an approximation made by Nienhuis and Deutch[14] [in passing from Eq. (3.28) to (3.29) in Ref. 14] in order to obtain an explicit expression for the long-range part of the static polarization fluctuations. One notes that this approximation need *not* be invoked to obtain results for the dielectric constant.

IV. CONCLUSION

The principal aim of this paper has been to justify Eq. (2.35) as an alternative formal relation for the frequency-dependent dielectric constant of polar media. In contrast to expressions for $\epsilon(\omega)$ in terms of dipole–dipole correlation functions, Eq. (2.35) contains no explicit shape-dependent terms and therefore reveals more directly the dependence of $\epsilon(\omega)$ on short-ranged molecular quantities. In the present theory, the fundamental quantity determining $\epsilon(\omega)$ is the dipolar memory function $k(\omega)$, which as indicated in Eqs. (2.37) and (2.38) can be evaluated either by considering the total dipole moment of a molecular sample in vacuum or the dipole moment of a smaller region within the sample. Since the time dependence of the memory function is governed by a projected Liouville operator, one might say that the projection operator "projects out" the long-range behavior from the full dipole correlation function, although as is generally the case it is difficult to attach any physical meaning to the use of projection operators.

A second result of this work is the analysis in Sec. III of the relation between correlation functions of a sample in vacuum and of a smaller region embedded in the sample. The analysis reveals clearly the origin of the *frequency-dependent* reaction field term in Eq. (3.7) which represents the long-range correlations between dipoles in the embedded region and those in the surroundings. One notes that the approximations necessary to obtain Eq. (3.7) from Eq. (3.1), i.e., neglecting surface effects and replacing the susceptibility of the external region by a local function, are in analogy with the procedure of reducing Eq. (3.8) for the Maxwell field to Eq. (3.9) by specifying the constitutive relations of the surrounding medium. Therefore the connection between response functions of distinct spatial regions, in the approximations of Sec. III, is already contained in the solution to Maxwell's equations together with the constitutive relations.[20]

An analysis of the relation between short- and long-range time-dependent correlations in dipolar media from a somewhat different standpoint has recently been presented by Fulton.[9] His discussion is equivalent to that presented here in that both are based on Eq. (3.1) as the relation between the shape-dependent response function and the short-range susceptibility. However, Fulton eliminates surface effects at the outset by considering only media which are infinite in extent. In relating the susceptibility to a memory function, the present work also has the advantage of indicating a method, albeit formal, for directly calculating the susceptibility in a sample of arbitrary shape. The use of this theory in practical calculations of the frequency-dependent dielectric constant will be investigated in subsequent work.

Finally we note that the formalism we have developed holds for all models of isotropic materials consisting of rigid dipoles. The particular model is not specified until the form of the Liouville operator L_0 is specified. While we have adopted the language of a polar fluid, our analysis applies with minor modification to polar lattices, for example the lattice diffusion model investigated by Zwanzig[21] and Cole.[6]

APPENDIX: REACTION FIELD TENSORS

In Ref. 14, Nienhuis and Deutch derived an integral equation relating the reaction field tensors $\mathbf{R}_W$ and $\mathbf{R}^*_{(V_0+W)}$ (these have been defined in the text). This relation may be employed for the case where $\epsilon_1(\omega)$ depends on frequency, provided the wavelength associated with frequency ω is large compared with the dimensions of the volume V_0. The relevant equation, Eq. (2.23) of Ref. 14, generalized to the frequency-dependent case is

$$\epsilon_1^{-1}(\omega)[\mathbf{T}(\mathbf{r},\mathbf{r}')+\mathbf{R}^*_{(V_0+W)}(\mathbf{r},\mathbf{r}';\epsilon_1^{-1}(\omega))]$$
$$=\mathbf{T}(\mathbf{r},\mathbf{r}')+\mathbf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_1(\omega))+\left(\frac{\epsilon_1(\omega)-1}{4\pi\epsilon_1(\omega)}\right)\int_{V_0}d\mathbf{r}''[\mathbf{T}(\mathbf{r},\mathbf{r}'')$$
$$+\mathbf{R}_{(V_0+W)}(\mathbf{r},\mathbf{r}'';\epsilon_1^{-1}(\omega))]\cdot[\mathbf{T}(\mathbf{r}'',\mathbf{r}')+\mathbf{R}_W(\mathbf{r}'',\mathbf{r}';\epsilon_1(\omega))]\,. \tag{A1}$$

If the region W is not present, then $\mathbf{R}_W=0$ and Eq. (A1) becomes an integral equation for the reaction field tensor $\mathbf{R}^*_{V_0}(\mathbf{r},\mathbf{r}';\epsilon_1^{-1}(\omega))$ describing the reaction field inside V_0 when the latter is empty and the infinite space outside V_0 has dielectric constant $\epsilon_1^{-1}(\omega)$. By replacing V_0 by (V_0+W), we then can obtain an equation for $\mathbf{R}^*_{(V_0+W)}$ since the latter depends only on the total volume (V_0+W) and not on the two volumes separately. Thus we have

$$\epsilon_1^{-1}(\omega)[\mathbf{T}(\mathbf{r},\mathbf{r}')+\mathbf{R}^*_{(V_0+W)}(\mathbf{r},\mathbf{r}';\epsilon_1^{-1}(\omega))]$$
$$=\mathbf{T}(\mathbf{r},\mathbf{r}')+\left(\frac{\epsilon_1(\omega)-1}{4\pi\epsilon_1(\omega)}\right)\int_{(V_0+W)}d\mathbf{r}''[\mathbf{T}(\mathbf{r},\mathbf{r}'')$$
$$+\mathbf{R}^*_{(V_0+W)}(\mathbf{r},\mathbf{r}'';\epsilon_1^{-1}(\omega))]\cdot\mathbf{T}(\mathbf{r}'',\mathbf{r}')\,. \tag{A2}$$

One notes that the integration in Eq. (A2) is over the total volume (V_0+W).

In general, explicit expressions for the reaction field tensors $\mathbf{R}_W$ and $\mathbf{R}^*_{(V_0+W)}$ are difficult to compute. However, when (V_0+W) is a sphere of radius R an expression for $\mathbf{R}^*_{(V_0+W)}$ has been given by Nienhuis and Deutch.[14] From Eq. (58) of Ref. 14 we have

$$\mathbf{R}^*_{(V_0+W)}(\mathbf{r}_1,\mathbf{r}_2;\epsilon_1^{-1}(\omega))$$
$$=\nabla_{r_1}\nabla_{r_2}\sum_{l=0}^{\infty}\frac{(1-\epsilon_1(\omega))(l+1)}{\epsilon_1(\omega)l+(l+1)}\frac{(r_1r_2)^l}{R^{2l+1}}P_l(\cos\Theta_{12}), \tag{A3}$$

where P_l are the legendre polynomials and θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$.

*Supported in part by the National Science Foundation.

[1]E. Fatuzzo and P. R. Mason, Proc. Phys. Soc. Lond. 90, 741 (1967).
[2]T. W. Nee and R. W. Zwanzig, J. Chem. Phys. 52, 6353 (1970).
[3]S. H. Glarum, J. Chem. Phys. 33, 1371 (1960).
[4]S. H. Glarum, Mol. Phys. 24, 1327 (1972).
[5]R. H. Cole, Mol. Phys. 26, 969 (1974).
[6]R. H. Cole, Mol. Phys. 27, 1 (1974).
[7]J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).
[8]U. M. Titulaer and J. M. Deutch, J. Chem. Phys. 60, 1502 (1974).
[9]R. L. Fulton, Mol. Phys. (to be published).
[10]See, e.g., B. J. Berne in *Physical Chemistry, An Advanced Treatise*, edited by D. Henderson (Academic, New York, 1971), Vol. 8B, p. 540.
[11]D. Kivelson and P. Madden, J. Chem. Phys. (to be published).
[12]See, e.g., R. Kubo in *Statistical Mechanics of Equilibrium and Non-Equilibrium*, edited by J. Meixner (North-Holland, Amsterdam, 1965), p. 81.
[13]P. Mazur in *Cargèse Lectures in Theoretical Physics*, 1964, *Statistical Mechanics*, edited by B. Jancovici (Gordon and Breach, New York, 1966), p. 215.
[14]G. Nienhuis and J. M. Deutch, J. Chem. Phys. 55, 4213 (1971).
[15]R. W. Zwanzig in *Lectures in Theoretical Physics* (Interscience, New York, 1961), Vol. 3, p. 106.
[16]H. Mori, Prog. Theor. Phys. (Kyoto) 33, 423 (1969).
[17]H. Mori, Prog. Theor. Phys. (Kyoto) 34, 399 (1965).
[18]The use of Mori's formalism in connection with the theory of dielectric relaxation is investigated by Kivelson and Madden in Ref. 10.
[19]U. M. Titulaer and J. M. Deutch, J. Chem. Phys. 60, 2703 (1974).
[20]This is similar to the occurrence of "extinction theorems" in both microscopic and macroscopic theories of the refractive index. See J. de Goede and P. Mazur, Physica 58, 568 (1972); J. de Goede, *ibid.* 70, 125 (1973).
[21]R. W. Zwanzig, J. Chem. Phys. 38, 2776 (1963).