

The Application of the Memory-Function Formalism to Dielectric Relaxation

P. Bordewijk

Gorlaeus Laboratories of the University, Department of Physical Chemistry, Leyden, The Netherlands

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The application of the memory-function formalism to dielectric relaxation is reconsidered. It is shown that the so-called Corresponding Micro-Macro Correlation theorem is not valid and that for a single macroscopic dielectric relaxation time, the single-molecule dipole correlation function may nevertheless be non-exponential.

The deviations from the exponential decay for the single-molecule dipole correlation function are due to spatially dependent orientational correlations, and can at least partly be interpreted in terms of dielectric friction. The unsureness about these correlations implies that it is simpler to determine the rotational diffusion coefficient from the collective orientation correlation time as determined from dielectric measurements than from the single-molecule dipole correlation function as obtained from infrared spectroscopy.

Introduction

The problem of obtaining information concerning molecular reorientation from macroscopic dielectric relaxation data has been of interest for a long time. After achievements using the model of a single molecule in a cavity in a continuous dielectric [1–8], Glarum [9] was the first to apply linear response theory to the problem. This led to a prolonged debate concerning one of the response functions to be used [11–15], but this debate has now been brought to a conclusion, leading to a wide agreement concerning the relationship between the complex permittivity and the molecular relaxation behaviour [16–18]:

$$\frac{[\hat{\epsilon}(\omega) - \epsilon_\infty][2\hat{\epsilon}(\omega) + \epsilon_\infty]\epsilon}{\hat{\epsilon}(\omega)(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)} \quad (1)$$
$$= \frac{1}{g\mu^2} \mathcal{L}_{i\omega} \langle \mu_1(0) \cdot \sum_i \mu_i(t) \rangle_0 >_0^\infty.$$

In this expression $\hat{\epsilon}(\omega)$ stands for the complex permittivity at frequency ω , ϵ for the permittivity at frequency zero, ϵ_∞ for the permittivity contribution due to induced polarization, g for the Kirkwood correlation factor [19], $\mathcal{L}_{i\omega}$ for the Laplace transform for argument $i\omega$, μ_i for the dipole moment of molecule i , and the subscript 0 for the absence of an external electric field, while the

superscript ∞ denotes that a sphere around molecule 1 embedded in an infinite medium of the same composition is concerned.

The sphere over which the summation in (1) is extended can be shrunk to such a size that it only contains the region where the two-particle distribution function deviates from the over-all density, which justifies to denote the correlation function in (1) as the microscopic correlation function. This microscopic correlation function reduces to the single-molecule dipole correlation function in the absence of short-range correlations between the dipoles, i.e. for

$$\langle \mu_i(0) \cdot \sum_{i \neq 1} \mu_i(t) \rangle_0^\infty = 0. \quad (2)$$

For $t=0$, (2) holds for those compounds where the Onsager equation applies, i.e. $g=1$. It is common to assume that for these compounds (2) also holds for $t \neq 0$, but there is no rigorous justification for this. For compounds where $g \neq 1$, the reduction from the microscopic correlation function to the single-molecule dipole correlation function is even more unsure, because there is no reason to assume that the autocorrelation function $\langle \mu_1(0) \cdot \mu_1(t) \rangle$ and the cross-correlation function $\langle \mu_1(0) \cdot \mu_2(t) \rangle$ fall off by the same rate. Still it would be highly desirable to have at one's disposal a reliable expression for the reduction of dielectric relaxation data to the single-molecule dipole correlation function, e.g. for comparison with data from Raman spectroscopy or nuclear magnetic relaxa-

Reprint requests to Dr. P. Bordewijk, Department of Physical Chemistry, Gorlaeus Laboratories, University of Leyden, NL-2300 RA Leiden, Niederlande.

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tion that also concern the reorientation of the single molecule [17, p. 176, 179], or with data from computer simulations.

In 1975, Kivelson and Madden [20] presented a new theory of dielectric relaxation based on the memory-function formalism [21], which makes it possible to calculate the single-molecule dipole correlation function from the macroscopic dielectric relaxation function. The article by Kivelson and Madden contains two remarkable conclusions:

- the single-molecule correlation function is found to be different for different macroscopic samples of the same system: “If the correlation function $\Phi_M^{(11)}(t)$ is a simple exponential for a sample with a given shape, it must be nonexponential for other shapes. Since an exponential $\Phi_M^{(11)}(t)$ implies an exponential $\Phi_S^{(11)}(t)$, we see that the single-particle correlation function is also shape-dependent” [20, p. 1759].
- For a spherical sample in vacuo with a single macroscopic relaxation time:

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + (\varepsilon - \varepsilon_\infty)/(1 + i\omega\tau) \quad (3)$$

the dipole correlation function for a molecule in an isolated sphere is found to be given by a single exponential decay, in contrast to the microscopic correlation function given in (1), which consists of two exponentials in that case:

$$\langle \mu_i(0) \cdot \sum_i \mu_i(t) \rangle_0^\infty = \frac{g\mu^2}{2\varepsilon + \varepsilon_\infty} \cdot (2\varepsilon e^{-t/\tau} + \varepsilon_\infty \exp\{-\varepsilon t/\tau\varepsilon_\infty\}). \quad (4)$$

The first conclusion is hard to accept for two reasons. First, a shape-dependence in the single-molecule dipole correlation function would imply a dependence of infra-red band shapes on the shape of the macroscopic sample that has never been observed. Furthermore, with respect to the dielectric relaxation behaviour an isolated sphere and a sphere embedded in its own medium should be considered as different macroscopic systems for which Kivelson and Madden's theory predicts different single-molecule dipole-correlation functions. This is inconsistent, however, because a given molecule simultaneously forms part of an isolated sphere and of a smaller embedded sphere.

The second conclusion implies that in cases where there is no simultaneous correlation between the dipole moment of a molecule and of its neighbours,

there is nevertheless such a correlation between these moments at different instants, and it is not clear how this correlation comes in.

For these reasons, we have reconsidered the application of the memory-function formalism to dielectric relaxation. We find that, in contrast to the macroscopic relaxation behaviour, the molecular relaxation behaviour is the same for ellipsoids with different ratios of the axes, and that it is also the same for an isolated sphere and for a sphere embedded in its own medium. This eliminates the problem of the dependence of the molecular relaxation behaviour on the sample shape. Furthermore, it is found that for a single macroscopic relaxation time, the single-molecule dipole correlation function can be more complicated due to the interaction with the surrounding molecules. In this way a new and more satisfactory treatment of the concept of dielectric friction can be given.

Introduction of the Memory-Function Formalism

With the help of the memory-function formalism for an arbitrary set of variables

$$\mathbf{A} = (A_1, A_2, \dots, A_n)$$

the derivative at any instant can be written as

$$\dot{\mathbf{A}}(t) = i\mathbf{\Omega} \cdot \mathbf{A}(t) - \int_0^t d\tau \mathbf{K}(\tau) \cdot \mathbf{A}(t - \tau) + \mathbf{F}(t). \quad (5)$$

In this equation the generalized frequency matrix $\mathbf{\Omega}$ accounts for instantaneous correlations between elements of \mathbf{A} and of $\dot{\mathbf{A}}$; if all elements of \mathbf{A} have the same symmetry in time, as will be the case throughout this article where only elements that are symmetric in time will be at issue, all elements of $\mathbf{\Omega}$ vanish. $\mathbf{F}(t)$ is known as the random force, which is defined as

$$\begin{aligned} \mathbf{F}(t) &= R_{\mathbf{A}}(t) \dot{\mathbf{A}}(0) \\ &= \exp[t(1 - P_{\mathbf{A}})iL] \dot{\mathbf{A}}(0), \end{aligned} \quad (6)$$

where L is the Liouville operator:

$$\dot{\mathbf{A}} = iL\mathbf{A} = \sum_i \left(\frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} \right) \mathbf{A}, \quad (7)$$

H standing for the Hamiltonian and the summation concerning all degrees of freedom of all molecules,

whereas P_A is a so-called projection operator defined by

$$P_A \mathbf{B} = \langle \mathbf{B} \mathbf{A} \rangle \cdot \langle \mathbf{A} \mathbf{A} \rangle^{-1} \cdot \mathbf{A}. \quad (8)$$

It follows that the random force is that part of $\dot{\mathbf{A}}(t)$ that is not correlated with $\mathbf{A}(0)$, neither by itself nor by any of its derivatives. From (8) it appears that it is essential with respect to what quantity \mathbf{F} is defined; this is made explicit in the operator $R_A(t)$.

Finally, the memory function matrix $\mathbf{K}(t)$ is related to the correlation function of $\mathbf{F}(t)$ by

$$\mathbf{K}(t) = \langle \mathbf{F}(t) \mathbf{F}(0) \rangle \cdot \langle \mathbf{A}(0) \mathbf{A}(0) \rangle^{-1}. \quad (9)$$

Equation (5) is an exact result that is known as the second fluctuation-dissipation theorem; instructive treatments of it have been given by Berne and Pecora [22] and by Hansen and McDonald [23]. Instead of containing a finite number of variables, \mathbf{A} can also be a spatially dependent function; in that case, the matrix products in the above should be changed by convolution integrals over space [24].

Using the fact that \mathbf{A} contains only variables that are symmetric in time, one obtains from (5) for the correlation matrix $\mathbf{C}(t) = \langle \mathbf{A}(0) \mathbf{A}(t) \rangle = \langle \mathbf{A}(t) \mathbf{A}(0) \rangle$:

$$\begin{aligned} \dot{\mathbf{C}}(t) &= - \int_0^t d\tau \mathbf{K}(\tau) \cdot \mathbf{C}(t - \tau) \\ &= - \frac{1}{kT} \int_0^t d\tau \langle \mathbf{F}(0) \mathbf{F}(\tau) \rangle \cdot \boldsymbol{\chi}^{-1} \cdot \mathbf{C}(t - \tau), \end{aligned} \quad (10)$$

where in the last member the equilibrium susceptibility $\boldsymbol{\chi} = \langle \mathbf{A}(0) \mathbf{A}(0) \rangle / kT = \mathbf{C}(0) / kT$ has been used. To obtain from (10) a solution for $\mathbf{C}(t)$, we take for both members the Laplace transform:

$$\begin{aligned} i\omega \mathcal{L}_{i\omega} \{ \mathbf{C}(t) \} - \mathbf{C}(0) &= \frac{1}{kT} \\ &\cdot \mathcal{L}_{i\omega} \{ \langle \mathbf{F}(0) \mathbf{F}(t) \rangle \} \cdot \boldsymbol{\chi}^{-1} \cdot \mathcal{L}_{i\omega} \{ \mathbf{C}(t) \} \end{aligned} \quad (11)$$

from which one obtains

$$\mathcal{L}_{i\omega} \{ \mathbf{C}(t) \} = kT \boldsymbol{\chi} \cdot [i\omega \boldsymbol{\chi} + \boldsymbol{\Lambda}(\omega)]^{-1} \cdot \boldsymbol{\chi} \quad (12)$$

where $\boldsymbol{\Lambda}(\omega)$ is a frequency dependent matrix of kinetic quantities, defined by

$$\boldsymbol{\Lambda}(\omega) = \frac{1}{kT} \mathcal{L}_{i\omega} \{ \langle \dot{\mathbf{A}} R_A(t) \dot{\mathbf{A}} \rangle \}. \quad (13)$$

$\boldsymbol{\Lambda}(\omega)$ itself can be expressed in terms of the complex

frequency dependent susceptibility

$$\boldsymbol{\chi}(\omega) = \frac{1}{kT} \mathcal{L}_{i\omega} \{ -\dot{\mathbf{C}}(t) \}, \quad (14)$$

by writing

$$\boldsymbol{\Lambda}(\omega) = i\omega [\boldsymbol{\chi}(\omega)^{-1} - \boldsymbol{\chi}^{-1}]^{-1}. \quad (15)$$

The above can be simplified in an interesting way, if \mathbf{A} is a set of slow variables, i.e. all components of $\mathbf{C}(t)$ fall off slowly with respect to all components of $\langle \mathbf{F}(0) \mathbf{F}(t) \rangle$. In that case on the time scale that is relevant for $\mathbf{C}(t)$, $\langle \mathbf{F}(0) \mathbf{F}(t) \rangle$ behaves as a delta function, and for values of ω that are of interest with respect to the calculation of $\mathbf{C}(t)$, the Laplace transform of $\langle \mathbf{F}(0) \mathbf{F}(t) \rangle$ and thus $\boldsymbol{\Lambda}(\omega)$ becomes independent of ω . In that case (10) can be rewritten:

$$\dot{\mathbf{C}}(t) = -\boldsymbol{\Lambda} \cdot \boldsymbol{\chi}^{-1} \cdot \mathbf{C}(t). \quad (16)$$

An Isolated Ellipsoid with Rigid Dipoles

We shall now consider an ellipsoidal system of non-polarizable dipoles with a single macroscopic dielectric relaxation time. For the electric moment of such a system along one of the axes, the susceptibility is equal to the complex, frequency dependent polarizability $\hat{\alpha}(\omega)$ along that axis, that is given by [17, p. 27]:

$$\hat{\varepsilon}(\omega) = \frac{\hat{\varepsilon}(\omega) - 1}{1 + A[\hat{\varepsilon}(\omega) - 1]} \frac{abc}{3} \quad (17)$$

where A is a factor depending on the ratio of the axes of the ellipsoid.

For dielectrics with a single relaxation time and non-polarizable molecules, the complex permittivity is given by (3) with $\varepsilon_\infty = 1$, and (17) yields

$$\hat{\varepsilon}(\omega) = \frac{\varepsilon - 1}{\tau} \frac{V}{4\pi} \frac{1}{i\omega + [1 + A(\varepsilon - 1)]/\tau}. \quad (18)$$

It follows from this expression that the correlation function for the electric moment along the axis under consideration shows a simple exponential decay with characteristic time $\tau/[1 + A(\varepsilon - 1)]$:

$$\begin{aligned} C_{M_z}(t) &= \langle M_z(0) M_z(t) \rangle = \langle M_z^2 \rangle \\ &\cdot \exp \{ -[1 + A(\varepsilon - 1)]t/\tau \}. \end{aligned} \quad (19)$$

This correlation time is different for ellipsoids with different values of A , i.e. for different ratios between the axes, confirming that the relaxation

behaviour of a macroscopic sample is shape-dependent. Because A is also different for the different axes in a given ellipsoid, it also follows that the correlation time is different for the polarization along the different axes, so that the correlation function for the polarization in an arbitrary direction is not exponential, but is built up from three parts, each with its own characteristic decay time.

If we consider the polarization along one of the axes, we obtain with (15), substituting $\hat{\alpha}(\omega)$ as given by (17) for $\chi(\omega)$:

$$\begin{aligned} A_{M_z}(\omega) &= \frac{1}{kT} \mathcal{L}_{i\omega} \{ \langle \dot{M}_z R_{M_z}(t) \dot{M}_z \rangle \} \\ &= \frac{i\omega abc/3}{\frac{1 + A[\hat{\epsilon}(\omega) - 1]}{\hat{\epsilon}(\omega) - 1} - \frac{1 + A(\epsilon - 1)}{\epsilon - 1}} \\ &= \frac{V}{4\pi} \frac{[\hat{\epsilon}(\omega) - 1](\epsilon - 1)i\omega}{\epsilon - \hat{\epsilon}(\omega)}. \end{aligned} \quad (20)$$

This is equivalent to the result by Sullivan and Deutch [24], expressed in their Eqs. (2.35) till (2.37), apart from a factor -1 , that is due to the fact that Sullivan and Deutch consider a field $E = E^0 \exp -i\omega t$ whereas we use $E = E^0 \exp i\omega t$, and apart from the projector operator used, since Sullivan and Deutch use in this operator the spatially dependent local polarization

$$\mathbf{P}(\mathbf{r}) = \sum_i \boldsymbol{\mu}_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (21)$$

whereas we use only one quantity, i.e. the total moment along the axis considered. This makes (20) a simpler result than the one by Sullivan and Deutch, while the later is more general, because its validity is not restricted to ellipsoids.

The most important aspect of (20) is that it no longer contains the shape factor A , so that the expression on the lefthand side has the same value for different axes in the same ellipsoid, and for different ellipsoids with the same composition and volume. The dependence on size can be eliminated by writing

$$\langle \dot{M}_z R_{M_z}(t) \dot{M}_z \rangle = n \langle \dot{\mu}_z R_{M_z}(t) \dot{M}_z \rangle, \quad (22)$$

n denoting the number of molecules, from which it follows:

$$\begin{aligned} &\frac{1}{kT} \mathcal{L}_{i\omega} \{ \langle \dot{\mu}_z R_{M_z}(t) \dot{M}_z \rangle \} \\ &= \frac{1}{4\pi N} \frac{[\hat{\epsilon}(\omega) - 1](\epsilon - 1)i\omega}{\epsilon - \hat{\epsilon}(\omega)}, \end{aligned} \quad (23)$$

N indicating the number density. In this way an expression concerning the kinetic properties of the molecules is derived that only depends on the local properties of the dielectric.

In the case of a single relaxation time, the right-hand sides of (20) and (23) become independent of ω . Equation (20) then changes into

$$A_{M_z} = \frac{V}{4\pi} \frac{\epsilon - 1}{\tau}, \quad (24)$$

and (23) into

$$\frac{1}{kT} \int_0^\infty dt \langle \dot{\mu}_z R_{M_z}(t) \dot{M}_z \rangle = \frac{\epsilon - 1}{4\pi N \tau}. \quad (25)$$

An Isolated Ellipsoid with Polarizable Dipoles

In the case of an ellipsoid with polarizable dipoles, the total moment can be written as [18]

$$\mathbf{M} = \sum_i \boldsymbol{\mu}_i^* = \sum_i \boldsymbol{\mu}_i \cdot \mathbf{K}_i, \quad (26)$$

where $\boldsymbol{\mu}_i^*$ is an effective moment, and \mathbf{K}_i is the local field tensor. This tensor transforms the external field \mathbf{E}_0 to the part of the local field at molecule i that is proportional with \mathbf{E}_0 . In the case of a spherical sample with isotropic polarizabilities on a cubic lattice, the local field tensor reduces to the unit tensor. If we make the same assumptions with respect to an ellipsoidal sample the local field tensor becomes a tensor with principal axes along the axes of the ellipsoid, and with principal values

$$K_\lambda = \frac{\epsilon_\infty + 2}{3[1 + (\epsilon_\infty - 1)A_\lambda]}. \quad (27)$$

The justification of the cubic-lattice approximation has been considered elsewhere [18, 25]; it implies neglect of translational fluctuations and is therefore consistent with the Clausius-Mossotti equation.

In this approximation one has

$$\begin{aligned} \hat{\alpha}_z(\omega) &= \frac{\hat{\epsilon}(\omega) - 1}{1 + A_3[\hat{\epsilon}(\omega) - 1]} \frac{abc}{3} \\ &= \frac{\epsilon_\infty - 1}{1 + A_3(\epsilon_\infty - 1)} \frac{abc}{3} - \frac{1}{kT} \\ &\quad \cdot \mathcal{L}_{i\omega} \{ \langle \dot{M}_z(0) \dot{M}_z(t) \rangle \} \\ &= \frac{\epsilon_\infty - 1}{1 + A_3(\epsilon_\infty - 1)} \frac{abc}{3} - \frac{1}{kT} \\ &\quad \cdot \frac{(\epsilon_\infty + 2)^2}{9[1 + (\epsilon_\infty - 1)A_3]^2} \\ &\quad \cdot \mathcal{L}_{i\omega} \{ \langle [\sum_i \mu_{iz}(0)] [\sum_i \dot{\mu}_{iz}(t)] \rangle \} \end{aligned} \quad (28)$$

or

$$\frac{1}{kT} \mathcal{L}_{i\omega} \{ \langle [\sum_i \mu_{iz}(0)] [-\sum_i \dot{\mu}_{iz}(t)] \rangle \} \quad (29)$$

$$= \frac{3abc[1 + (\varepsilon_\infty - 1)A_3][\hat{\varepsilon}(\omega) - \varepsilon_\infty]}{(\varepsilon_\infty + 2)^2[1 + (\hat{\varepsilon}(\omega) - 1)A_3]}.$$

This is now the expression for $\chi(\omega)$ to be used in connection with $\sum_i \mu_{iz}$ as the variable. Application of (15) gives

$$A_{\Sigma \mu_{iz}}(\omega) = \frac{V}{4\pi} \frac{9[\hat{\varepsilon}(\omega) - \varepsilon_\infty](\varepsilon - \varepsilon_\infty)i\omega}{(\varepsilon_\infty + 2)^2[\varepsilon - \hat{\varepsilon}(\omega)]}. \quad (30)$$

As was to be expected, this expression reduces to (20) for $\varepsilon_\infty = 1$. For the case of a single relaxation time, (30) yields

$$A_{\Sigma \mu_{iz}} = \frac{V}{4\pi\tau} \frac{9(\varepsilon - \varepsilon_\infty)}{(\varepsilon_\infty + 2)^2}. \quad (31)$$

A Sphere Embedded in a Medium of the Same Composition

For a sphere embedded in its own medium, the susceptibility is given by

$$\chi(\omega) = \frac{1}{kT} \mathcal{L}_{i\omega} \{ \langle [\sum_i \mu_{iz}(0)] [-\sum_i \dot{\mu}_{iz}(t)] \rangle \}$$

$$= \frac{a^3[\hat{\varepsilon}(\omega) - \varepsilon_\infty][2\hat{\varepsilon}(\omega) + \varepsilon_\infty]}{\hat{\varepsilon}(\omega)(\varepsilon_\infty + 2)^2}, \quad (32)$$

as follows from (1) on application of the Kirkwood-Fröhlich equation, which is a rigorous result for isotropic polarizabilities on a cubic lattice [18]. Apart from giving another expression for $\chi(0)$ than for an isolated sphere, (Eq.(29) with $\omega = 0$, $A_3 = \frac{1}{3}$ and $a = b = c$), (32) also gives a different correlation function. Whereas for a dielectric with a single relaxation time (29) gives an exponential correlation function, (32) gives two exponentials in that case:

$$C_{\Sigma \mu_{iz}}^\infty = \langle (\sum_i \mu_{iz})^2 \rangle^\infty \frac{1}{2\varepsilon + \varepsilon_\infty}$$

$$\cdot (2\varepsilon e^{-t/\tau} + \varepsilon_\infty \exp\{-t/\tau\varepsilon_\infty\}). \quad (33)$$

As remarked in the introduction, it seems inconsistent to conclude from this that now the single-molecule dipole correlation function also behaves different. Nevertheless (32) yields another expression for the kinetic coefficient:

$$A_{\Sigma \mu_{iz}}^\infty(\omega) \quad (34)$$

$$= \frac{i\omega a^3(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)[\hat{\varepsilon}(\omega) - \varepsilon_\infty][2\hat{\varepsilon}(\omega) + \varepsilon_\infty]}{(\varepsilon_\infty + 2)^2[2\varepsilon\hat{\varepsilon}(\omega) + \varepsilon_\infty^2][\varepsilon - \hat{\varepsilon}(\omega)]},$$

as appears from comparison with (30) for the isolated sphere. Equations (30) and (34) only differ in the low-frequency range, however, because in the high-frequency range, where $\hat{\varepsilon}(\omega) - \varepsilon_\infty$ can be neglected with respect to ε_∞ , both expressions reduce to

$$A_{\Sigma \mu_{iz}}(\omega) = A_{\Sigma \mu_{iz}}^\infty(\omega) = \frac{3a^3}{(\varepsilon_\infty + 2)^2}$$

$$\cdot i\omega[\hat{\varepsilon}(\omega) - \varepsilon_\infty], \quad \omega \rightarrow \infty. \quad (35)$$

This is illustrated by the expression for $A_{\Sigma \mu_{iz}}^\infty(\omega)$ for the case of a single relaxation time:

$$A_{\Sigma \mu_{iz}}^\infty(\omega) = \frac{3a^3(\varepsilon - \varepsilon_\infty)}{\tau(\varepsilon_\infty + 2)^2}$$

$$\cdot \left[1 - \frac{2}{3} \frac{(\varepsilon - \varepsilon_\infty)^2}{2\varepsilon^2 + \varepsilon_\infty^2 + \varepsilon_\infty(2\varepsilon + \varepsilon_\infty)i\omega\tau} \right], \quad (36)$$

which differs from the corresponding expression for the isolated sphere, (31), by the frequency dependent term within the square brackets, but reduces to the same value for $\omega \rightarrow \infty$.

It follows that the embedding of a macroscopic sphere into its own medium affects the part of the random force $R_{\Sigma \mu_{iz}}(t) \sum_i \dot{\mu}_{iz}$ that changes on the same time scale as the polarization, but not the rapidly changing part. Apparently, in an isolated sphere these slowly changing contributions to the random force for a small sphere making part of it are compensated by long-range interactions.

The most obvious reason for the change of the correlation function of the random force when a sphere is surrounded by its own medium, is in the interaction between the molecules in the sphere and the electric field due to permanent dipoles of the surrounding molecules. This field changes at the same time scale as the orientational polarization and therefore can yield a slowly changing contribution to the random force.

In the following it will be demonstrated that it is sufficient to consider the interaction between the electric moment of the sphere and the homogeneous part of the field due to the permanent moments of the surroundings, to be denoted by E_z^* . This can be done by considering $\sum_i \mu_{iz}$ and E_z^* as two interdependent variables, for which the correlation

functions of the random force with respect to both variables together are equal to the one for $\sum_i \mu_{iz}$ for an isolated sphere and the one for E_z^* in cavity without permanent dipoles, respectively. In this way, with use of the appropriate equilibrium susceptibilities, (32) for the frequency-dependent susceptibility of the embedded sphere can be re-derived, which shows that the difference between the correlation functions of the random force for the moment in an embedded and an isolated sphere is only due to the interaction between $\sum_i \mu_{iz}$ and E_z^* . To simplify the calculation, we will choose as the second variable not E_z^* itself, but the part of it that is uncorrelated with $\sum_i \mu_{iz}$. In this way in the susceptibility matrix χ only the diagonal elements remain.

To calculate the part of the field that is correlated with $\sum_i \mu_{iz}$, we first consider the average value of the total homogeneous field in the sphere due to the surroundings for given $\sum_i \mu_{iz}$, that we will indicate by $\langle E_z | \sum_i \mu_{iz} \rangle$, and that is given by [19, p. 135]

$$\langle E_z | \sum_i \mu_{iz} \rangle = \frac{2(\varepsilon - 1)(\varepsilon_\infty + 2)}{3(2\varepsilon + \varepsilon_\infty)a^3} \sum_i \mu_{iz}. \quad (37)$$

To find the contribution of the permanent dipoles in the surrounding dielectric to this field, one should subtract from it the field due to the surroundings if no permanent dipoles were present in it, which is obtained by substituting ε_∞ for ε into (37):

$$\begin{aligned} \langle E_z^* | \sum_i \mu_{iz} \rangle &= \frac{2(\varepsilon - 1)(\varepsilon_\infty + 2)}{3(2\varepsilon + \varepsilon_\infty)a^3} \sum_i \mu_{iz} \quad (38) \\ &\quad - \frac{2(\varepsilon_\infty - 1)(\varepsilon_\infty + 2)}{9\varepsilon_\infty a^3} \sum_i \mu_{iz} \\ &= \frac{2(\varepsilon - \varepsilon_\infty)(\varepsilon_\infty + 2)^2}{9\varepsilon_\infty(2\varepsilon + \varepsilon_\infty)a^3} \sum_i \mu_{iz}. \end{aligned}$$

It should be emphasized that (38) does not contain any dynamic dielectric property, although E_z^* and $\sum_i \mu_{iz}$ are time-dependent quantities, because the instantaneous correlation between these quantities is considered, which depends only on the interaction energy between the molecules, and not on the kinetic part of the Hamiltonian. Therefore $\langle E_z^* | \sum_i \mu_{iz} \rangle$ is the same as in the case of $\sum_i \mu_{iz}$ being a time-independent quantity.

We thus obtain the following set of variables:

$$A_1 = \sum_i \mu_{iz}, \quad (39)$$

$$A_2 = E_z^* - f^* \sum_i \mu_{iz}, \quad (40)$$

where f^* stands for a generalized reaction field factor:

$$f^* = \frac{2(\varepsilon - \varepsilon_\infty)(\varepsilon_\infty + 2)^2}{9\varepsilon_\infty(2\varepsilon + \varepsilon_\infty)a^3}. \quad (41)$$

The susceptibility χ_{11} can be obtained from (32):

$$\chi_{11} = \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} a^3. \quad (42)$$

Because A_2 contains only the random component of E_z^* , χ_{22} is related to the average of the square of the field due to the surroundings in the absence of permanent dipoles in the sphere:

$$\chi_{22} = \frac{1}{kT} \langle (E_z^*)^2 \rangle_0, \quad (43)$$

where the index 0 now denotes the absence of an electric moment in the sphere. This susceptibility is equal to the ratio between the average value of E_z^* in the presence of an electric moment inside the sphere, and the corresponding value of $\sum_i \mu_{iz}$.

Because this ratio is given by the generalized reaction field factor f^* , one obtains

$$\chi_{22} = \frac{2(\varepsilon - \varepsilon_\infty)(\varepsilon_\infty + 2)^2}{9\varepsilon_\infty(2\varepsilon + \varepsilon_\infty)} \frac{1}{a^3}. \quad (44)$$

The kinetic coefficients follow from the starting-point that $R_{\Sigma \mu_{iz}, E^*}(t) \sum_i \dot{\mu}_{iz}$ behaves in the same way as $R_{\Sigma \mu_{iz}}(t) \sum_i \dot{\mu}_{iz}$ for an isolated sphere, while analogously, $R_{\Sigma \mu_{iz}, E^*}(t) \dot{E}$ behaves in the same way as $R_{E^*}(t) \dot{E}(t)$ in the absence of permanent dipoles in the sphere. The kinetic coefficient $A_{\Sigma \mu_{iz}}(\omega)$ will therefore be the same as for an isolated sphere, and be given by (20), whereas $A_{E^*}(\omega)$ can be obtained with the help of (15):

$$\begin{aligned} A_{E^*}(\omega) &= i\omega \\ &\cdot \left[\frac{9\varepsilon_\infty[2\hat{\varepsilon}(\omega) + \varepsilon_\infty]a^3}{2[\hat{\varepsilon}(\omega) - \varepsilon_\infty](\varepsilon_\infty + 2)^2} - \frac{9\varepsilon_\infty(2\varepsilon + \varepsilon_\infty)a^3}{2(\varepsilon - \varepsilon_\infty)(\varepsilon_\infty + 2)^2} \right]^{-1} \\ &= \frac{2i\omega(\varepsilon - \varepsilon_\infty)[\hat{\varepsilon}(\omega) - \varepsilon_\infty](\varepsilon_\infty + 2)^2}{27a^3\varepsilon_\infty^2[\varepsilon - \hat{\varepsilon}(\omega)]}. \quad (45) \end{aligned}$$

One thus obtains for the components of $\mathbf{\Lambda}(\omega)$

$$A_{11}(\omega) = A_{\Sigma \mu_{1z}}(\omega) = \frac{3a^3 i \omega [\varepsilon(\omega) - \hat{\varepsilon}_\infty] (\varepsilon - \varepsilon_\infty)}{(\varepsilon_\infty + 2)^2 [\varepsilon - \varepsilon(\omega)]}, \quad (46)$$

$$A_{12}(\omega) = A_{21}(\omega) = \frac{1}{kT} \quad (47)$$

$$\begin{aligned} & \cdot \mathcal{L}_{i\omega} \left\{ \left\langle \sum_i \dot{\mu}_{iz} R_{\Sigma \mu_{1z}, E_z^*}(t) [\dot{E}_z^* - f^* \sum_i \dot{\mu}_{iz}] \right\rangle \right\} \\ &= -f^* A_{\Sigma \mu_{1z}}(\omega) = \frac{2i\omega(\varepsilon - \varepsilon_\infty)^2 [\hat{\varepsilon}(\omega) - \varepsilon_\infty]}{3\varepsilon_\infty(2\varepsilon + \varepsilon_\infty) [\varepsilon - \hat{\varepsilon}(\omega)]}, \\ A_{22}(\omega) &= \frac{1}{kT} \mathcal{L}_{i\omega} \left\{ \left\langle [\dot{E}_z^* - f^* \sum_i \dot{\mu}_{iz}] R_{\Sigma \mu_{1z}, E_z^*}(t) \right. \right. \\ & \quad \cdot [\dot{E}_z - f^* \sum_i \dot{\mu}_{iz}] \left. \right\rangle \left. \right\} = A_E(\omega) + f^{*2} A_{\Sigma \mu_{1z}}(\omega) \quad (48) \\ &= \frac{2i\omega(\varepsilon - \varepsilon_\infty) [\hat{\varepsilon}(\omega) - \varepsilon_\infty] (2\varepsilon^2 + \varepsilon_\infty^2) (\varepsilon_\infty + 2)^2}{9a^3 \varepsilon_\infty^2 [\varepsilon - \hat{\varepsilon}(\omega)] (2\varepsilon + \varepsilon_\infty)^2} \end{aligned}$$

where it has been assumed that there is no correlation between $R_{\Sigma \mu_{1z}, E_z^*}(t) E_z$ and $R_{\Sigma \mu_{1z}, E_z^*}(t) \sum_i \dot{\mu}_{iz}$.

Using the values for the elements of χ and $\mathbf{\Lambda}(\omega)$ as given by (42), (44), (46), (47) and (48), one obtains with (12):

$$\mathcal{L}_{i\omega} \{C_{11}(t)\} = kT \frac{a^3 [2\varepsilon \hat{\varepsilon}(\omega) + \varepsilon_\infty^2] [\varepsilon - \hat{\varepsilon}(\omega)]}{i\omega \varepsilon \hat{\varepsilon}(\omega) (\varepsilon_\infty + 2)^2}. \quad (49)$$

From this expression one reobtains (32).

The Single-Molecule Dipole Correlation Function

We will now apply the above to the calculation of the single-molecule dipole correlation function. To this end we first consider, following Berne and Pecora [22, p. 322] a system with two variables, one pertaining to the single molecule and one to the macroscopic sample, that we choose in such a way that the cross-susceptibilities are zero:

$$A_1 = \mu_{1z}, \quad (50)$$

$$A_2 = \sum_i \mu_{iz} - \mu_{1z} \langle \mu_{1z} \sum_i \mu_{iz} \rangle / \langle \mu_{1z} \mu_{1z} \rangle. \quad (51)$$

One then has for the elements of χ and $\mathbf{\Lambda}(\omega)$:

$$\chi_{11} = \frac{1}{kT} \langle \mu_{1z} \mu_{1z} \rangle, \quad (52)$$

$$\chi_{12} = \chi_{21} = 0, \quad (53)$$

$$\chi_{22} = \frac{1}{kT} [n \langle \mu_{1z} \sum_i \mu_{iz} \rangle - \langle \mu_{1z} \sum_i \mu_{iz} \rangle^2 / \langle \mu_{1z} \mu_{1z} \rangle], \quad (54)$$

$$A_{11}(\omega) = \frac{1}{kT} \mathcal{L}_{i\omega} \left\{ \left\langle \dot{\mu}_{1z} R_{\mu_{1z}, \Sigma \mu_{1z}}(t) \sum_i \dot{\mu}_{iz} \right\rangle \right\}, \quad (55)$$

$$\begin{aligned} A_{12}(\omega) = A_{21}(\omega) &= \frac{1}{kT} \mathcal{L}_{i\omega} \left\{ \left\langle \dot{\mu}_{1z} R_{\mu_{1z}, \Sigma \mu_{1z}}(t) \sum_i \dot{\mu}_{iz} \right\rangle \right. \\ & \quad \left. - \left\langle \dot{\mu}_{1z} R_{\mu_{1z}, \Sigma \mu_{1z}}(t) \dot{\mu}_{1z}(t) \right\rangle \left\langle \mu_{1z} \sum_i \mu_{iz} \right\rangle / \langle \mu_{1z} \mu_{1z} \rangle \right\}, \quad (56) \end{aligned}$$

$$\begin{aligned} A_{22}(\omega) &= \frac{1}{kT} \mathcal{L}_{i\omega} \left\{ \left[n - 2 \frac{\langle \mu_{1z} \sum_i \mu_{iz} \rangle}{\langle \mu_{1z} \mu_{1z} \rangle} \right] \right. \\ & \quad \cdot \left\langle \dot{\mu}_{1z} R_{\mu_{1z}, \Sigma \mu_{1z}}(t) \sum_i \dot{\mu}_{iz} \right\rangle + \frac{\langle \mu_{1z} \sum_i \mu_{iz} \rangle^2}{\langle \mu_{1z} \mu_{1z} \rangle^2} \\ & \quad \cdot \left. \left\langle \dot{\mu}_{iz} R_{\mu_{1z}, \Sigma \mu_{1z}}(t) \dot{\mu}_{1z} \right\rangle \right\}. \quad (57) \end{aligned}$$

In these expressions the function $\langle \mu_{1z} \sum_i \mu_{iz} \rangle$ goes to a finite limiting value for $n \rightarrow \infty$, because we consider isotropic systems, where ferroelectricity is absent. The same holds with respect to $\langle \dot{\mu}_{iz} R_{\mu_{1z}, \Sigma \mu_{1z}}(t) \sum_i \dot{\mu}_{iz} \rangle$. It follows that in the limit $n \rightarrow \infty$, i.e. for macroscopic samples, one has

$$\begin{aligned} |i\omega \chi + \mathbf{\Lambda}(\omega)| &= [i\omega \chi_{11} + A_{11}(\omega)] \\ & \quad \cdot [i\omega \chi_{22} + A_{22}(\omega)] - A_{12}^2(\omega) \\ &= [i\omega \chi_{11} + A_{11}(\omega)] \\ & \quad \cdot [i\omega \chi_{22} + A_{22}(\omega)]. \quad (58) \end{aligned}$$

With this expression for the determinant, (12) yields

$$\mathcal{L}_{i\omega} \{C_{11}(t)\} = kT \chi_{11}^2 / [i\omega \chi_{11} + A_{11}(\omega)], \quad (59)$$

$$\mathcal{L}_{i\omega} \{C_{22}(t)\} = kT \chi_{22}^2 / [i\omega \chi_{22} + A_{22}(\omega)]. \quad (60)$$

These expressions are the same as when A_1 and A_2 are considered as single variables, from which it follows:

$$\langle \dot{\mu}_{1z} R_{\mu_{1z}, \Sigma \mu_{1z}}(t) \dot{\mu}_{iz} \rangle = \langle \dot{\mu}_{1z} R_{\mu_{1z}}(t) \dot{\mu}_{1z} \rangle, \quad (61)$$

$$\langle \dot{\mu}_{1z} R_{\mu_{1z}, \Sigma \mu_{1z}}(t) \sum_i \dot{\mu}_{iz} \rangle = \langle \dot{\mu}_{1z} R_{\Sigma \mu_{1z}}(t) \sum_i \dot{\mu}_{iz} \rangle. \quad (62)$$

It follows that if in (62) the cross-correlation terms may be ignored, one easily obtains the kinetic coefficient for the moment of one molecule as a single variable from the kinetic coefficient for the sample by dividing by the number of particles. Eq. (12) then gives the single-molecule dipole correlation

function, that will contain as many exponentials as the correlation function for the macroscopic sample, in agreement with the Corresponding Micro-Macro Correlation theorem. However, it has been shown in the above that the correlation function on the righthand side of (62) is different for an isolated sphere and for an embedded sphere. This difference implies that there are long-range interactions contributing to the correlation function for the isolated sphere that do not contribute in the case of an embedded sphere, and this implies that the cross-correlation terms in (62) cannot be simply ignored. Therefore, even in the case of a single macroscopic relaxation time, where the correlation functions in (62) decay rapidly, the correlation functions in (61) may contain a slowly varying part, which is exactly compensated by the cross-correlation terms in (62). This slowly varying part in (61) is due to the interaction with the surrounding molecules, like for an embedded sphere.

If only long-range correlations are taken into account, and it is assumed that there are no short-range correlations contributing to the righthand side of (62), it follows that one should use the expression for the kinetic coefficient derived for the embedded sphere, as given by (47), and one obtains for the kinetic coefficient pertaining to the moment of one molecule as a single variable:

$$A_{\mu_z}(\omega) = i\omega \frac{3}{4\pi N} \cdot \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)[\hat{\varepsilon}(\omega) - \varepsilon_\infty][2\hat{\varepsilon}(\omega) + \varepsilon_\infty]}{(\varepsilon_\infty + 2)^2[2\varepsilon\hat{\varepsilon}(\omega) + \varepsilon_\infty^2][\varepsilon - \hat{\varepsilon}(\omega)]} \\ = i\omega \frac{g\mu^2}{3kT} \frac{\varepsilon[\hat{\varepsilon}(\omega) - \varepsilon_\infty][2\hat{\varepsilon}(\omega) + \varepsilon_\infty]}{[2\varepsilon\hat{\varepsilon}(\omega) + \varepsilon_\infty^2][\varepsilon - \hat{\varepsilon}(\omega)]} \quad (63)$$

from which one can calculate the single-molecule dipole correlation function with (12). In the case that there are also no short-range correlations between the dipole moments themselves i.e. $g=1$, one obtains

$$- \frac{1}{kT} \mathcal{L}_{i\omega} \{ \langle \mu_z(0) \dot{\mu}_z(t) \rangle \} \\ = \frac{3}{4\pi N} \frac{[\hat{\varepsilon}(\omega) - \varepsilon_\infty][2\hat{\varepsilon}(\omega) + \varepsilon_\infty]}{\hat{\varepsilon}(\omega)(\varepsilon_\infty + 2)^2}. \quad (64)$$

The normalized correlation function for the dipole moment of a single molecule is then the same as for the embedded sphere.

We will now assume that the correlation function for the electric moment of an isolated sphere consists of one or more exponentials, with deviations only for times that are small with respect to the characteristic times of these exponentials. The dielectric response of the system to an applied electric field can then be described with a number of discrete relaxation times. In that case, the correlation function of the random force can be split up into a slowly and a fastly decay part, among which the slowly decaying part is absent if there is only one exponential in the correlation function, i.e. the case of a single relaxation time. The fastly decaying part of the random force corresponds with a contribution to $A_{\Sigma\mu_{iz}}(\omega)$ that depends on frequency in the high-frequency range only, i.e. the frequency range where the description of the correlation function as a set of exponentials is not valid, and is independent of frequency in the range where this description is correct. The slowly decaying part of the random force corresponds with a contribution to $A_{\Sigma\mu_{iz}}(\omega)$ that is zero in the high-frequency range. It follows that on extrapolating the expression for $A_{\Sigma\mu_{iz}}(\omega)$ that is applicable in the low-frequency range, not accounting for deviations from dielectric relaxation behaviour at higher frequencies, one obtains a value $A_{\Sigma\mu_{iz}}(\infty)$ that is the frequency-independent value of the contribution due to the fastly decaying part of the random force in the low-frequency range.

Now it follows from (35) that although the expressions for $A_{\Sigma\mu_{iz}}(\omega)$ and $A_{\Sigma\mu_{iz}}^\infty(\omega)$ are different they do not differ in the high-frequency range. This implies that long-range correlations in eq. (62) do not contribute to $A_{\Sigma\mu_{iz}}(\omega)$ at high-frequencies, so that these long-range correlations do not exist for values of t that are small with respect to the characteristic decay times of the correlation functions. We will assume in the following that the same holds with respect to the short-range correlation terms. This assumption is certainly correct with respect to the behaviour at very short times, because it follows from fundamental statistical mechanics that all cross-correlation terms are zero for $t=0$. We in fact assume that the short-time part of the correlation function of the random force damps out before an important amount of correlation between angular velocities of different molecules has originated.

It then follows that $A_{\Sigma \mu_{iz}}(\infty)$ as defined in the above contains no cross-correlation terms, and this makes it possible to obtain from it $A_{\mu_z}(\infty)$ for the dipole moment of one molecule as a single variable by dividing by the number of molecules:

$$A_{\mu_z}(\infty) = \lim_{\omega \rightarrow \infty} \frac{9i\omega}{4\pi N} \frac{\hat{\epsilon}(\omega) - \epsilon_\infty}{(\epsilon_\infty + 2)^2}. \quad (65)$$

For a dielectric with a series of relaxation times τ_j , each with weight factor h_j , the permittivity is given by

$$\hat{\epsilon}(\omega) = \epsilon_\infty + (\epsilon - \epsilon_\infty) \sum_j \frac{h_j}{1 + i\omega\tau_j}, \quad (66)$$

if the deviations at high frequency are ignored, and (65) yields

$$A_{\mu_z}(\infty) = \frac{9}{4\pi N} \frac{\epsilon - \epsilon_\infty}{(\epsilon_\infty + 2)^2} \sum_j h_j/\tau_j. \quad (67)$$

This value can then be used to calculate the initial decrease of the single-molecule dipole-correlation function with (16) for a single variable, yielding

$$\begin{aligned} \frac{\dot{C}_1(t)}{C_1(t)} &= -\frac{9}{4\pi N} \frac{\epsilon - \epsilon_\infty}{(\epsilon_\infty + 2)^2} \frac{3kT}{\mu^2} \sum_j h_j/\tau_j \\ &= -\frac{3g\epsilon}{2\epsilon + \epsilon_\infty} \sum_j h_j/\tau_j, \end{aligned} \quad (68)$$

where in the last member the Kirkwood-Fröhlich equation was used. For a single relaxation time this reduces to

$$\dot{C}_1(0)/C_1(0) = -3g\epsilon/\tau(2\epsilon + \epsilon_\infty). \quad (69)$$

It follows that, apart from the factor g , the initial decay of the single-molecule dipole correlation function is in accordance with the microscopic relaxation time obtained by Powles [7] and by Glarum [9]. In contrast to Glarum, however, we do not find a single exponential decay with this relaxation time, due to the cross-correlation terms that make $A_{\mu_z}(\omega)$ a frequency dependent quantity, even if $A_{\Sigma \mu_{iz}}(\omega)$ is not.

It seems hard to estimate these contributions to $A_{\mu_z}(\omega)$ directly. Instead, one may try to incorporate μ_z into a complete set of slow variables. The number of variables in such a set depends in the first place on the number of macroscopic relaxation times, since the moment $\sum_i \mu_{iz}$ makes part of a set of as many slow variables as the number of relaxation times, and μ_{1z} should be coupled to

all these variables. Furthermore, we should incorporate variables that account for the interaction of the dipole with the surrounding molecules. In the case of a macroscopic sphere embedded in its own medium it was shown that only the interaction between the moment of the sphere and the homogeneous part of the electric field due to the permanent dipoles in the surroundings is relevant. When a single molecule embedded in the same medium is considered, however, also interactions with a shorter draft should be accounted for, like the field due to the quadrupole of the surrounding molecules. But even if interactions of this kind are ignored, and only the dipole-dipole interaction is considered the problem arises that one does not know the relevant susceptibilities, because there is no general expression for the reaction field that is also valid for a system with specific interactions. Only if these interactions are absent, and the Onsager model is applicable, the problem can be solved.

Then the same expressions are applicable as for an embedded macroscopic sphere, the radius a now pertaining to a sphere with volume equal to the volume available to each molecule. The normalized correlation function for the single dipole is then equal to the normalized correlation function for the embedded sphere. This is equivalent with the absence of short-range correlations in (62). The normalized correlation function is

$$C_1(t)/C_1(0) = \frac{1}{2\epsilon + \epsilon_\infty} \cdot (2\epsilon e^{-t/\tau} + \epsilon_\infty \exp\{-\epsilon t/\tau\epsilon_\infty\}). \quad (70)$$

This behaves in agreement with (69), for $g=1$. The slower decay at times $t>0$ is due to the non-instantaneous change of the field due to the surrounding molecules.

It follows that (70) gives an account of the effects of dielectric friction [26–29]. It is remarkable that from the present treatment it follows that for dielectrics with a single relaxation time, dielectric friction has only an influence on the single-dipole correlation function, and not on the correlation function of an isolated macroscopic body. This is because dielectric friction leads to a slowly varying part in the random force for the dipole of one molecule as a single variable, which is exactly compensated, in the Onsager model, by the long-range cross correlation terms in (62). It also follows that the correlation functions for the higher

Legendre polynomials are not influenced by dielectric friction, because there is no correlation between these functions and the homogeneous electric field due to the surrounding molecules. For the higher Legendre polynomials the interaction with the field gradients can play a role, of course.

It is remarkable that even for the simple case where the Onsager model is applicable, the above yields a single-molecule dipole correlation function with two exponentials, whereas Keyes and Kivelson [30] who use the equivalents of all μ_{iz} 's as separate variables, nevertheless obtain a single exponential. This is because these authors ignore that the correlation between molecular orientations depends on the position of the molecules with respect to each other. The importance of spatially dependent correlations appears from the occurrence of the reaction field, that would be absent if the dipolar correlation did not depend on the position of the molecules with respect to each other.

It follows from the above that it is not possible to obtain the single-molecule dipole correlation function from the dielectric relaxation behaviour without further assumptions concerning the molecular interactions, but it is possible to obtain the initial decay of this correlation function. This initial decay can give direct information about the reorientation process, however. For instance, if the reorientation proceeds by rotational diffusion, one has

$$\dot{C}_{11}(0)/C_{11}(0) = -2D_{\perp}^{\text{rot}}, \quad (71)$$

yielding

$$D_{\perp}^{\text{rot}} = \frac{3g\epsilon}{2\tau(2\epsilon + \epsilon_{\infty})}. \quad (72)$$

In the case the orientation proceeds by orientational jumps over an angle α with frequency k , one has

$$\dot{C}_{11}(0)/C_{11}(0) = -k(1 - \langle \cos \alpha \rangle), \quad (73)$$

and one obtains

$$k(1 - \langle \cos \alpha \rangle) = \frac{3g\epsilon}{(2\epsilon + \epsilon_{\infty})}. \quad (74)$$

Discussion

From the above, a number of remarkable conclusions can be drawn. First of all, it appears that there is nothing like a Corresponding Micro-Macro Correlation theorem, because for a dielectric with

a single relaxation time, an individual molecule can at the same time be considered as part of an isolated sphere with a single correlation time and of an embedded sphere with two relaxation times. Moreover, the single-molecule dipole correlation function does not depend on the shape of the macroscopic sample, whereas the correlation function for the moment of the macroscopic sample does.

A second important conclusion is that the occurrence of a single macroscopic relaxation time does not imply that the single-molecule dipole correlation function decays exponentially. This is mainly due to dielectric friction, but also other orientationally dependent molecular interactions may play a role. These interactions lead to a slowly varying part in the correlation function for the random force that pertains to a single molecule, which in the correlation function for the random force pertaining to a macroscopic isolated sphere is compensated by long-range cross-correlation terms. If in the rapidly decaying part of this correlation function cross-correlation terms may be ignored, it follows from our calculation that the characteristic quantity of the rotational diffusion or the jump model can be obtained from the macroscopic relaxation time by applying the Powless-Glarum ratio, corrected for the Kirkwood correlation factor. It will be hard to obtain these quantities from the single-molecule dipole correlation function as it can be determined under favourable conditions from infrared absorptions, because in this correlation function these quantities only govern the initial decay, where deviations due to the finite correlation time of the angular velocity (inertial effects) also play a role.

The calculation further shows that if dielectric friction is studied with the Onsager model, and other short-range orientational correlations between the molecules are ignored, a dipole correlation function is obtained that is equal to the correlation function for a macroscopic sphere embedded in a dielectric of the same composition, while for the higher Legendre polynomials no deviations from the single exponential decay are obtained. This deviates from results obtained before by Hubbard and Wolynes [28] and by Brito and the author [29]. Hubbard and Wolynes consider only the part of the field at the molecules that is uncorrelated with its orientation at time zero, whereas in the other publication mentioned just

the part of the field that is correlated with this orientation is taken into account. The present treatment shows that if both parts are considered, a much simpler result is obtained. Especially it is of interest that dielectric friction does not influence the correlation function for the higher Legendre polynomials, because these are not correlated with the homogeneous electric field at the molecules. In view of the correlation of the higher Legendre polynomials with other variables, however, e.g. the field gradient, this does not mean that for the higher Legendre polynomials the correlation function is purely exponential for rotational diffusion or reorientation by instantaneous jumps. It seems plausible, however, that these interactions are less important than dielectric friction.

Another problem for which the above results are relevant, is the incorporation of the reaction field in molecular-dynamics calculations [31], because they justify the splitting up of the field due to the molecules outside a sphere that is considered on a molecular basis into a part that is correlated with the moment of the latter sphere, with magnitude given by the static reaction field factor, and a random field that influences the reorientation of the dipoles in this sphere in such a way that also at later instants the correlation between the moment

of the sphere and the field due to the surroundings is in agreement with the static reaction field factor [32].

Finally, something should be said about the validity of the assumption that short-range cross-correlations do not contribute to the high-frequency part of $A_{\Sigma\mu_{iz}}(\omega)$. This assumption is not essential with respect to most of the conclusions drawn in this article, but it is essential in the derivation of the quantitative relations (72) and (74) between the macroscopic dielectric relaxation time and the molecular reorientation parameter. There is one case, in which these relations certainly do not hold, i.e. the case that the molecules form supermolecules e.g. due to association by hydrogen bonds, and these supermolecules reorient as a whole. In that case there is an important correlation between the angular velocities of the molecules within one associate, and it is not allowed to use (72) and (74). This problem can be avoided, however, by considering the reorientation of the associates as a whole, interpreting g in (72) and (74) as the correlation factor between the dipoles of these associates.

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