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THE RELATIONSHIP BETWEEN THE DIELECTRIC RELAXATION TIME AND SINGLE PARTICLE CORRELATION TIME IN A LIQUID*

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Using Frohlich's model of dielectric and Mori formalism the relationship between the dielectric relaxation time and single particle correlation time for molecules with a symmetry of C_{2v} or higher was established. The main assumptions in this paper differ substantially from those used in Kivelson and Madden's theory. The relationship depends on long-range electric interactions which are introduced via local field and short-range interactions. These are represented by Kirkwood's coefficient. Moreover, in spite of symmetry this depends on the dynamic correlation coefficient which appears in Kivelson and Madden's relation, but in a slightly different way.

1. Introduction

Dielectric relaxation measurements are still a valuable source of information on the molecular reorientation in a liquid. This is especially clear since a number of difficulties with infrared absorption, Raman and Rayleigh scattering of light are revealed. The main disadvantage of dielectric relaxation is the relation between single particle correlation time (SPCT) and macroscopic correlation time (MCT) which is measured.

The most advanced theories of the dielectric relaxation phenomenon based on linear response formalism [1, 2] automatically involve the multiparticle microscopic correlation time (MMCT). MMCT bridges MCT and SPCT. Before the papers of Kivelson et al. [3, 4] the influence of short range dipole-dipole correlations concerning the relation between MCT and SPCT were neglected and the role of local fields was intensively investigated ([1–11] in [4]). In Kivelson and Madden [4] the Mori formalism [5] was successfully used to overcome the problems mentioned above. In addition, there is the claim that the problem of the local field, using the Mazur and Mandel's macroscopic treatment of dielectrics [6], is avoided. This seems hardly possible because even in the static case an effective expression

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for electric polarisation requires a model for the local field [7]. Here MCT is related to MMCT using Fröhlich's model of dielectrics [8], whereas, MMCT is related to the SPCT due to application of Mori formalism with a choice of dynamical variables proposed by Gierke [9]. For molecules with a C_{2v} or higher symmetry it gives a workable relation between MCT and SPCT which is slightly different than previously proposed [4].

2. *The relationship between MCT and MMCT*

This section is to establish the relation between MCT usually called the dielectric relaxation time and the MMCT of dipole moments. For this purpose we found it useful to apply Fröhlich's model of liquid dielectrics [8] first used to describe static dielectric properties. Therefore, a semi-macroscopical sphere filled with a continuous "dielectric" substance having the susceptibility $x(\infty)$, and immersed in a real dielectric having the susceptibility $\chi(\omega)$, is taken into consideration. Inside the sphere discussed we assume to have N identical "permanent" dipoles with co-ordinates μ_α^n where n and α denote the molecule and co-ordinates. Obviously these "permanent" dipole moments differ from the gaseous dipole moments because of intermolecular interactions. When inside the sphere there is an average time-dependent electric field, $\boldsymbol{F}(t)$, with co-ordinates $F_\alpha(t)$, then the dipole moments interaction with such a field takes the form of:

$$\mathscr{H}_{\mathrm{IN}}(t) = - \sum_{n=1}^{N} \mu_\alpha^n F_\alpha(t) = -\boldsymbol{M} \cdot \boldsymbol{F}(t). \tag{2.1}$$

We assume that $\boldsymbol{F}(t)$ is parallel to an external field characterised by the strength $E(t)$ and the unit vector, $\boldsymbol{e}$. The electric polarisation for the model described above is given by:

$$P(t) = P_\infty(t) + \frac{1}{V} \langle \boldsymbol{M} \cdot \boldsymbol{e} \rangle_{\mathrm{ne}}, \tag{2.2}$$

where $P_\infty(t)$ denotes the polarisation due to susceptibility $\chi(\infty)$, V is the volume of the sphere and the angular brackets with an index "ne" denote the non-equilibrium averaging. The final results of such averaging depend on the shape of the total Hamiltonian. For our purposes it is enough to assume that the total Hamiltonian consists of two terms. That is, one term which is independent on $\boldsymbol{F}(t)$ and the other which is given by (2.1). According to [2, 3] and using the linear respons theory [5] we find that:

$$P(t) = \chi(\infty)F(t) - \frac{\langle M^2 \rangle}{3VkT} (\dot{G}_{\mathrm{M}} * F)(t), \tag{2.3}$$

where the microscopic multiparticle correlation function (MMCF)

$$G_{\mathrm{M}}(t) = \begin{cases} \dfrac{\langle \boldsymbol{M}(t) \cdot \boldsymbol{M}(0) \rangle}{\langle \boldsymbol{M}^2 \rangle} & \text{for } t \geqslant 0 \\ 0 & \text{for } t < 0, \end{cases} \tag{2.4}$$

* denotes a convolution and all averages marked by angular brackets are taken for an equilibrium state.

Generally, a frequency dependent electric susceptibility can be defined using the Fourier transformations, $\mathscr{F}$, of $P(t)$ and $E(t)$ as follows:

$$\chi(\omega) = \frac{\partial\mathscr{F}[P](\omega)}{\partial\mathscr{F}[E](\omega)}. \tag{2.5}$$

This definition when applied to (2.3) leads to:

$$\eta_\xi(\omega) \equiv \frac{\dfrac{\chi(\omega)}{\xi(\omega)} - \dfrac{\chi(\infty)}{\xi(\infty)}}{\dfrac{\chi(0)}{\xi(0)} - \dfrac{\chi(\infty)}{\xi(\infty)}} = -\mathscr{F}[\dot{G}_\mathrm{M}](\omega), \tag{2.6}$$

where

$$\xi(\omega) = \frac{\partial\mathscr{F}[F](\omega)}{\partial\mathscr{F}[E](\omega)}. \tag{2.7}$$

This characterises the dispersion of field $F(t)$. If $F(t)$ depends linearly on $E(t)$ then,

$$F(t) = \mathscr{F}^{-1}[\xi](t) * E(t) \tag{2.8}$$

and the inverse Fourier transformation, $\mathscr{F}^{-1}[\xi](t)$, characterizes the memory function for a field of $F(t)$. If this field did not have a memory, the function, $\xi(\omega)$, would be independent of the frequency and therefore $G_\mathrm{M}(t)$ would be identical with the macroscopic relaxation function, MRF. It was shown [10] however that for an electromagnetic wave having a frequency of ω

$$\xi(\omega) = \frac{3\varepsilon(\omega)}{2\varepsilon(\omega)+\varepsilon(\infty)}. \tag{2.9}$$

This is a generalisation of the formula for the static case. This shows the difference between MMCF $G_\mathrm{M}(t)$ and MRF $G_\mathrm{D}(t)$.

Now the relationship between MMCT τ_M which corresponds to MMCF and the dielectric relaxation time, (DRT) τ_D, which corresponds to MRF will be established. The partial integration of RHS of (2.6) leads to:

$$\eta_\xi(\omega) = 1 - i\omega \int_0^\infty e^{-i\omega t} G_\mathrm{M}(t)dt. \tag{2.10}$$

Using this formula we obtain the following for MMCT τ_M:

$$\tau_\mathrm{M} \equiv \int_0^\infty G_\mathrm{M}(t)dt = \lim_{\omega\to 0} \frac{1-\eta_\xi(\omega)}{i\omega}. \tag{2.11}$$

This is almost identical with the expression introduced by Nee and Zwanzig [11] for τ_D. The only difference will be the change if $\eta_\xi(\omega)$ is replaced by:

$$\chi(\omega) = \frac{\chi(\omega)-\chi(\infty)}{\chi(0)-\chi(\infty)}. \tag{2.12}$$

Therefore, the mentioned above relationship has the form:

$$\tau_M = \left\{ \lim_{\omega\to 0} \frac{1-\eta_\xi(\omega)}{1-\eta(\omega)} \right\} \tau_D, \tag{2.13}$$

which for $\eta_\xi(\omega)$ given by (2.9) is reduced to:

$$\tau_M = \frac{1+\dfrac{\varepsilon(\infty)}{2\varepsilon^2(0)}}{1+\dfrac{1}{2\varepsilon(0)}}\tau_D \equiv f[\varepsilon(0), \varepsilon(\infty)]\tau_D. \tag{2.14}$$

This relationship differs greatly from the most frequently used expression proposed by Powles [12] as well as from the others [13, 14]. The derivation of (2.14) has great advantages over derivation of the other, mentioned above, relationships between τ_M and τ_D. These advantages are simplicity and clearness. In addition if the Lorentz type of local field applies to (2.13) the results obtained by Cole [2] are recovered.

It is worthwhile to find a value for the ratio of τ_M/τ_D in (2.14) when typical values of $\varepsilon(0)$ and $\varepsilon(\infty)$ are taken into consideration. Assuming that $\varepsilon(0) = 5$ and $\varepsilon(\infty) = 2.25$ we find that this ratio is 0.95. This suggests that τ_M differs only by a few per cent from τ_D. This agrees with the suggestions of Hill [15] that $\tau_D = \tau_M$.

3. *Relation between MMCT and SMCT*

In this section relationship between τ_M and SMCT is discussed. Our discussion is limited, however, to the molecules with a symmetry not lower than C_{2v}. Following Kivelson and Madden [4] we use the Mori formalism [5] to achieve the above relationship. On the other hand, our choice of the dynamical variables is based on Gierke's paper [9].

Let us remember the basic equations which are important in this case. Since we have chosen the set of primary dynamical variables, $\{f_0^{(m)}\}$, denoted by indices, m, and the proper scalar product is known, then we can construct the square matrix of the normalised correlation functions, $R_1(t)$, that contain the elements:

$$\frac{(f_1^{(j)}(t), f_1^{(m)}(0))}{(f_1^{(m)}(0), f_1^{(m)}(0))}. \tag{3.1}$$

Under the assumption that the primary variables, $\{f_1^{(m)}\}$, are slowly variable compared with the secondary variables, $\{f_2^{(m)}\}$, obtained by the projection technique [5] the matrix,

$R_1(t)$, satisfies equation [16, 17]:

$$\frac{dR_1(t)}{dt} = R_1(t)\left\{i\gamma - \int_0^\infty \theta(t')dt\right\}, \tag{3.2}$$

where the square matrices, $i\gamma$, and $\theta(t)$, are defined by their elements as:

$$(i\gamma)_{km} = \frac{(\dot{f}_1^{(k)}(0), f_1^{(m)}(0))}{(f_1^{(m)}(0), f_1^{(m)}(0))} \quad \text{and} \quad \theta_{nm}(t) = \frac{(f_2^{(n)}(t), f_2^{(m)}(0))}{(f_1^{(m)}(0), f_1^{(m)}(0))}. \tag{3.3}$$

It is known that such molecular properties as the dipole moment and polarisability can be expressed in a molecular frame using spherical tensors. The co-ordinates of the spherical tensor of the rank, l, are simply the spherical harmonics, $Y^l_m(\Omega)(m = -l, \ldots, l)$, and the spherical angles, $\Omega = (\varphi, \vartheta)$, depend on the particular tensorial property of the molecule. Under rotation the spherical tensors are transformed using irreducible representations of the rotational group, O_3^+. As the results in laboratory frame molecular properties of interest are expressed by the spherical harmonics, $Y^l_m[\Omega(t)]$. However, now the spherical angles, $\Omega(t)$, depend on the orientation of a given molecule. Therefore, $\Omega(t)$ changes with time. Such arguments suggest the following primary dynamical variables:

$$f_1^{(m)}(t) = \sum_{k=1}^{N} Y^l_m[\Omega_k(t)] \equiv \sum_{k=1}^{N} e^{im\varphi_k(t)} d^l_m[\vartheta_k(t)], \tag{3.4}$$

where summation occurs over all the molecules.

It was shown [8] that the time development of $Y^l_m(t)$ can be expressed by co-ordinates of angular velocity $\omega_\alpha(t)$ ($\alpha = x, y, z$) taken in the molecular frame at $t = 0$ usingan equation containing the infinitesimal operators, I^l_α, of certain irreducible representation of O_3^+

$$\frac{dY^l_m(t)}{dt} = \omega_\alpha(t)\,[I^l_\alpha]_{m,n} Y^l_n(t). \tag{3.5}$$

Consequently this type of equation describes the time development of molecular tensors $Y^l_m(t)$ in every possible nonrotating frame. Especially it is valid for a laboratory frame.

Using the projection procedure to obtain variables of rank s [5] we find that in the case of thermodynamical equilibrium

$$f_s^{(m)}(t) = \frac{d^{s-1}}{dt^{s-1}} f_1^{(m)}(t). \tag{3.6}$$

Since these variables are transformed from one (1) to the other laboratory frame (2) according to an irreducible representation of $O_3^+ (g \in O_3^+)$, then their correlation functions hold the following relation

$$(f_s^{(m)}(t), f_s^{(n)}(0))_{(2)} = [D^l(g)]_{mm'}\,[D_{l*}(g)]_{n'n}(f_s^{(m')}(t), f_s^{(n')}(0))_{(1)}, \tag{3.7}$$

where the star denotes a hermitian conjugate. On the other hand for an isotropic liquid such correlation functions should not depend on a choice of laboratory frame. If so, the relation (3.6) gives

$$(f_s^{(m)}(t), f^{(n)}(0)) \sim \delta_{mn}. \tag{3.8}$$

Applying (3.6) and (3.5) we have

$$f_2^{(m)}(t) = \sum_{k=1} \omega_\alpha^{(n)}(t)\,[I_\alpha^l]_{mn} Y_n^l[\Omega_k(t)]. \tag{3.9}$$

It shows that the matrix, γ, in equation (3.2) is a zero matrix. This is because the scalar product in the numerator of $(i\gamma)_{km}$ (3.3) contains $\omega_\alpha(t)$ linearly. Moreover, due to relation (3.8) the matrices $R_1(t)$ and $\theta(t)$ in equation (3.2) are diagonal and the multiparticle microscopic correlation function, R_1^{00}, connected with molecular dipole moments fulfils the following equation

$$\frac{dR_1^{00}(t)}{dt} = -\left\{\int_1^\infty \theta_{00}(t')dt'\right\} R_1^{00}(t) \equiv -\frac{1}{\tau_M} R_1^{00}(t). \tag{3.10}$$

The numerator and denominator of (3.3) contain one-particle and two-particle correlation functions taken in a laboratory frame. Therefore, *we cannot apply arguments on molecular symmetry unless mentioned above correlation functions are replaced by correlation functions taken in molecular frame* of molecule which is involved in a given correlation function. Such replacement is omitted in Gierke's paper [9] and in result some dynamical correlation factors do not appear.

Using transformational properties, statistical equivalency of molecules as well as molecular pairs and taking into account isotropy of liquid, we find

$$\theta_{00} = [I_\alpha^1]_{mn}[I_\beta^1]_{mn'} \left\{ \frac{(\omega_\alpha^{(1)}(t)Y_n^1(1, t), \omega_\beta^{(1)}(0)Y_{n'}^1(1, 0))}{(Y_n^1(1, 0), Y_n^1(1, 0)) + (N-1)\,(Y_n^1(2, 0), Y_n^1(1, 0))}, \right.$$
$$\left. +(N-1)\frac{(\omega_\alpha^{(2)}(t)Y_n^1(2, t), \omega_\beta^{(1)}(0)Y_{n'}^1(1, 0))}{(Y_n^1(1, 0), Y_n^1(1, 0) + (N-1)\,(Y_n^1(2, 0), Y_n^1(1, 0))} \right\}, \tag{3.11}$$

where ω_α and Y_{M}^1 are additionally labelled with molecular numbers 1 or 2. Assuming that Y_n^1 is a slow variable in comparison with ω_α and that molecular dipole moment is situated along molecular z-axis $(Y_n'(1, 0) = \delta_{\mathrm{n}0})$, we obtain

$$\tau_{\mathrm{M}}^{-1} = K^{-1}\{(\tau_0^1)^{-1} + (1-K^{-1})\int_0^\infty (\omega_\perp^{(2)}(t), \omega_\perp^{(1)}(0))dt\}, \tag{3.12}$$

where τ_0^1 is the SPCT of the dipole moment related to an angular velocity correlation time by Hubbard's relation, $\omega_\perp$ denotes the angular velocity coordinate which is perpendicular to z-axis of molecule (1) and

$$K = 1 + (N-1)\,(Y_0^1(2, 0), 1) \tag{3.13}$$

represents Kirkwood's coefficient.

The result (3.12) differs only slightly (due to preintegral coefficient in the second term) from Kivelson and Madden's result [4]. This is because in their choice of dynamical variables nonabelian character of O_3^+ has not been taken into account. This is not very important because usually $K \gg K-1$ and we expect that the integral in the second term is much smaller than $(\tau_0^1)^{-1}$. If so, this term may be neglected.

4. *Kirkwood's coefficient*

In this section Kirkwood's coefficient, K, for the model of the dielectric introduced in Section 2 is discussed. Assuming an ellipsoidal shape of the molecule the Kirkwood coefficient has the form [19]:

$$K = \frac{VkT}{N\mu_g^2} \frac{(\varepsilon(0)-\varepsilon(\infty))(2\varepsilon(0)+\varepsilon(\infty))}{[1+D(\varepsilon(\infty)-1)]^2\varepsilon(0)}, \tag{4.1}$$

where D denoted the depolarisation coefficient along the principal axis of ellipsoid which is parallel to the dipole moment. The molecule has at least the symmetry of C_{2v}, and μ_g represents the length of the gaseous dipole moment.

Two of these assumptions which restrict Kirkwood's coefficient (4.1), need special clarification. These are:

(1) a molecular dipole is placed exactly in the centre of mentioned above ellipsoid,
(2) an effective dipole moment, μ, introduced in Section 2 depends only on instant polarisation which is characterised by $\varepsilon(\infty)$.

A localization of the dipole moment within the molecule is usually uncertain. However, when we have an electrically neutral molecule its dipole moment is translationally invariant. Therefore, it is always possible to put such a moment in the centre of a chosen ellipsoid simultaneously changing the higher electric moments. Dielectric relaxation does not depend directly on higher moments because the electromagnetic wave length is many orders higher than the linear dimension of the molecule. Obviously an indirect influence via the reaction field is possible if the total polarizability of the molecule is treated as a point property and usually placed in the centre of the ellipsoid is moved from the centre. Such an effect might play an important role if only the replacement of total polarizability would be significant compared to the size of the ellipsoid [20]. There is no physical justification for such a significant replacement so that (4.1) holds possibly even for dipole moments out of the centre of the ellipsoid.

With the second restriction we must remember that the dipole of interest rotates fast enough to cause a significant delay in the response of the other dipole moments [10]. This response is mainly due to short range interactions.

Taking the above into account we may expect that the final relation

$$\tau = f[\varepsilon(0), \varepsilon(\infty)]K^{-1}\tau_D \tag{4.2}$$

represents a very reasonable approximation. The coefficient, f, is defined by (2.14).

5. Conclusions

1) Relation (4.2) between the SPCT (τ) and MCT (τ_D) depends on:
    (a) long-range electrical interactions characterised by the coefficient $f[\varepsilon(0), \varepsilon(\infty)]$ which was introduced because of the local field
    (b) short-range interactions which are in Kirkwood's coefficient K.
2) Long-range electrical interactions via local field are almost negligible (Section 2).
3) The non-spherical shape of the molecule must be taken into consideration it formula (4.1) for K is used.
4) Relation (4.2) is valid if the second term in (3.12) can be neglected.

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