THE USE OF THE DIPOLE CORRELATION FUNCTION IN DIELECTRIC RELAXATION

GRAHAM WILLIAMS

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, England

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I. Introduction

In recent years there has been an increasing interest in applying time correlation functions to different types of molecular motion. This approach has been of value for such diverse subjects as infrared vibration–rotation spectroscopy, dielectric (dipole) relaxation, nuclear magnetic resonance relaxation, light scattering, neutron scattering, depolarization of fluorescence, microwave double resonance, sound absorption, shear and bulk viscosity, thermal conductivity, chemical relaxation, and electrical conductivity. The basic concepts of correlation functions and their application have been outlined by Kubo,[1,2] Zwanzig,[3] Gordon,[4] Mountain,[5] Berne and Harp,[6] Harp and Berne,[7] and Deutch and Oppenheim.[8] The essential feature with regard to models for molecular motion is that they are most conveniently expressed in terms of time correlation functions. The experiments which detect molecular motions may be made in the time domain or the frequency domain. It will be shown below that these are connected by a Fourier transformation. If an experiment is made in the frequency domain (complex dielectric permittivity, say), then in principle the frequency-dependent macroscopic quantity should be measured over a very wide frequency range, and then be transformed into the appropriate molecular time correlation function. There are two problems associated with such a procedure. (i) There are local field problems involved in relating macroscopic and molecular quantities. (ii) The information must be obtained over a wide range of frequency in order to carry out the Fourier transformation. These difficulties are not easily overcome in practice. Another procedure is to take an analytical or numerical form for the time correlation function and then to transform (with the associated local field problems) into the frequency domain in order to compare the theory with experimental data obtained over a limited frequency range.

In this article a brief account will be given of the application of time correlation functions to dielectric relaxation processes. The interest in this subject has developed rapidly since Glarum[9] in 1960 considered the complex dielectric permittivity in terms of the time correlation function approach of Kubo.[1,2] In section II, the macroscopic relations between time-dependent and frequency-dependent quantities will be briefly outlined. In section III, the molecular theory relating the dipole moment–time correlation function to the macroscopic complex dielectric permittivity is outlined, and the local field problems are discussed. The remaining sections are concerned with the applications that have been made of dielectric correlation functions to molecular relaxation processes. Since much of this work relates experimental dielectric relaxation behavior to mechanisms of molecular motion—as expressed by the correlation function—it is hoped that the present review will indicate the degree of understanding which has been recently achieved in certain aspects of dipole relaxation phenomena.

II. Macroscopic Theory

For comprehensive accounts of the macroscopic theory of dielectric relaxation, the reader is referred to the text of Fröhlich[10] and the articles of Scaife[11] and O'Dwyer and Harting.[12] Further references are Glarum,[9] Macdonald and Brachman,[13] Macdonald and Barlow,[14] Schwarz,[15] Manning and Bell,[16] and McCrum, Read, and Williams.[17]

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The complex dielectric permittivity $\epsilon^*(i\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, where $\omega = 2\pi\nu$ (Hz), of a dielectric medium is given by the superposition relation[10,12,16,17]

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \mathrm{d}t\,[\exp(-i\omega t)]\left[-\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}\right] = 1 - i\omega\int_0^\infty \mathrm{d}t\,[\exp(-i\omega t)]\phi(t) \quad (1)$$

ϵ_0 and ϵ_∞ are the limiting low- and high-frequency permittivities, respectively. $\phi(t)$ is the normalized decay function of the polarization when a steady macroscopic electric field is removed from the medium. $\phi(t)$ contains contributions from relaxation processes only. $[\mathrm{d}\phi(t)/\mathrm{d}t]$ may be regarded as the normalized transient current which flows when the steady field is removed from the medium. This forms the basis of transient experiments which are made[16-20] in order to obtain dielectric data in the low frequency range 10^{-1} to 10^{-4} Hz.

Equation 1 states that the normalized complex permittivity is given by the one-sided Fourier transform[21] of the quantity $[-\mathrm{d}\phi(t)/\mathrm{d}t]$. It is a property of Fourier transforms that they may be inverted, and it follows from eq 1 that[11,22,23]

$$\frac{\epsilon'(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \mathrm{d}t\left[\frac{-\mathrm{d}\phi(t)}{\mathrm{d}t}\right]\cos\omega t \quad (2a)$$

$$\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \mathrm{d}t\left[\frac{-\mathrm{d}\phi(t)}{\mathrm{d}t}\right]\sin\omega t \quad (2b)$$

$$\left[\frac{-\mathrm{d}\phi(t)}{\mathrm{d}t}\right] = \frac{2}{\pi}\int_0^\infty \mathrm{d}\omega\left[\frac{\epsilon'(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}\right]\cos\omega t = \frac{2}{\pi}\int_0^\infty \mathrm{d}\omega\left[\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty}\right]\sin\omega t \quad (3)$$

$$\omega > 0$$

$$\phi(t) = \frac{2}{\pi}\int_0^\infty \frac{\mathrm{d}\omega}{\omega}\left[\frac{\epsilon_0 - \epsilon'(\omega)}{\epsilon_0 - \epsilon_\infty}\right]\sin\omega t = \frac{2}{\pi}\int_0^\infty \frac{\mathrm{d}\omega}{\omega}\left[\frac{\epsilon''(\omega)}{\epsilon_0 - \infty}\right]\cos\omega t \quad (4)$$

$$\omega > 0$$

Equations 3 and 4 show that if one of the parts of the normalized complex permittivity is known over the entire relaxation range, then $[-\mathrm{d}\phi(t)/\mathrm{d}t]$ and $\phi(t)$ are also known over the entire relaxation range. It is clear from eq 1 that a simple exponential decay function $\phi(t) = \exp(-t/\tau)$, $t > 0$, where τ is a time constant, gives the single relaxation time expression

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau} \quad (5)$$

If $\phi(t)$ is given by a weighted sum of exponential decay functions $\phi(t) = \sum_i w_i \exp(-t/\tau_i)$, where $\sum_i w_i = 1$, then eq 1 becomes

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_i \frac{w_i}{1 + i\omega\tau_i} \quad (6)$$

Equation 6 corresponds to a discrete set of relaxation times, and its integral analog[17] involves the continuous distribution of relaxation times. It should be emphasized that if $\phi(t)$ is not a single exponential decay in linear time, then the numerical fitting of $\phi(t)$ to a weighted sum of exponential decay terms does not necessarily mean that a distribution of relaxation times is present. It is possible that $\phi(t)$ has a natural "nonexponential" form in linear time, as will be seen in section IV.C.1.b below.

There has been some success in fitting experimental data to empirical representations for $[(\epsilon^*(i\omega) - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)]$. These representations have involved an empirical modification of the single relaxation time expression, eq 5. The expressions of Cole and Cole,[24] Fuoss and Kirkwood,[25] Davidson and Cole,[26,27] and Havriliak and Negami[28-30] have had success in representing broad loss curves in a variety of systems. Recently Williams and Watts[31] and Williams, Watts, Dev, and North[32] have shown the empirical decay function $\phi(t) = \exp[-(t/\tau_0)^{\bar{\beta}}]$, $0 < \bar{\beta} \leqslant 1$, leads to nonsymmetrical dielectric relaxation curves which give a reasonable representation of the observed α relaxation processes for a wide range of solid amorphous polymers. The effect of temperature on the distribution function of relaxation times has been considered by Read and Williams[33] and by Adam and Müller,[34] where it has been shown, for example, that the area under the plot of the dielectric loss factor ϵ'' against $[1/T(°\mathrm{K})]$ at a fixed frequency may yield an average activation energy for the dielectric relaxation process. Further considerations of the effect of temperature on distributions of relaxation times have been given by Macdonald.[35,36]

III. Molecular Theory

A. DIPOLE MOMENT CORRELATION FUNCTION

First it is appropriate to discuss the general features of the time correlation function, and then to outline the nature of the dipole moment correlation function. The detailed consideration of the mathematical criteria for correlation functions is given by Kubo,[1,2] Zwanzig,[3] Gordon,[4] Mountain,[5] Berne and Harp,[6] Harp and Berne,[7] and Keller, Ebersold, and Kneubühl,[37] so only a brief account will be given here. Following Gordon we write the autocorrelation function C(t) of a quantity A as

$$C(t) = \langle A(0)A(t)\rangle_0 \quad (7)$$

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A is a dynamic function of the variables of a given system. In the dielectric case we might have $A = \boldsymbol{\mu}$, the dipole moment of a molecule. The average is taken over an ensemble of systems at the reference time $t = 0$. In quantum mechanics $A(0)$ and $A(t)$ usually do not commute so that a quantum mechanical correlation function is a complex quantity,[4] where its real part $\mathrm{Re}[\mathrm{C}(t)]$ is an even function of time and its imaginary part $\mathrm{Im}[\mathrm{C}(t)]$ is an odd function of time. Gordon[4] has shown that

$$\mathrm{Im}[\mathrm{C}(t)] \approx -\tan\left[\left(\frac{\hbar}{2kT}\right)\frac{\partial}{\partial t}\right]\mathrm{Re}[\mathrm{C}(t)] \tag{8}$$

Thus $\mathrm{Im}[\mathrm{C}(t)]$ is only a small quantum mechanical term which for high temperatures may be extremely small. For the classical limit the correlation function becomes a real and even function of time. For a random stationary process the classical correlation function has the following properties[37]

$$\left[\frac{\mathrm{d}[\mathrm{C}_\mathrm{c}(t)]}{\mathrm{d}t}\right]_{t=0} = 0 \tag{9a}$$

$$\lim_{t\to\infty} \mathrm{C}_\mathrm{c}(t) = 0 \tag{9b}$$

Since the classical $\mathrm{C}(t)$ is a real even function of time it follows that it may be expanded as an even power series[7]

$$\mathrm{C}_\mathrm{c}(t) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!}\gamma_{2n}t^{2n} \tag{10}$$

The coefficients γ_{2n} are determined by the equilibrium properties of the system. For example in the case of the dipole moment correlation function for a linear rotator[4] $\gamma_2 = 2kT/I$ and $\gamma_4 = \{8(kT)^2 + \langle(\mathbf{O}V)^2\rangle\}/I^2$, where I is the moment of inertia and $-\mathbf{O}V$ is the torque on a molecule due to its neighbors. Harp and Berne[7] give a table indicating the γ_{2n}'s for different time correlation functions.

Following Gordon[4,38] the complete autocorrelation function may be written as a series

$$\mathrm{C}(t) = \sum_{k=0}^{\infty} \frac{(it)^k}{k!}M(k) \tag{11}$$

where $i = \sqrt{-1}$ and the $M(k)$'s are the moments defined by

$$M(k) = \int_{-\infty}^{\infty} \mathrm{d}\omega\ \omega^k I(\omega) \tag{12}$$

where the spectral density $I(\omega)$ is defined by the relation

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\ \mathrm{C}(t)\exp(-i\omega t) \tag{13}$$

Note that eq 13 is a Fourier transform which may be inverted. In dielectric relaxation $I(\omega)$ is related to (ϵ''/ω), and this is considered below in section III.B. It is readily shown[4,38] from eq 11 and 12 that

$$M(k) = (-i)^k\left[\frac{\mathrm{d}^k\mathrm{C}(t)}{\mathrm{d}t^k}\right]_{t=0} \tag{14}$$

For the classical case only the even values of k are considered (see ref 74), and the $M(k)$'s are the coefficients of the power series expansion of the even function $\mathrm{C}_\mathrm{c}(t)$. For example, for the classical linear rotator quoted above[4,39]

$$M(2) = \gamma_2 = \{-\mathrm{d}^2[\mathrm{C}_\mathrm{c}(t)]/\mathrm{d}t^2\}_{t=0} = \frac{2kT}{I} \tag{15}$$

Thus the moments $M(k)$ from eq 12 immediately lead to the coefficients in the power series of $\mathrm{C}(t)$, and in the classical case $[\mathrm{C}_\mathrm{c}(t)]$ to the coefficients of t^{2n}, $n = 1, 2, \ldots$.

We now consider the dipole moment correlation function. Consider a unit macroscopic volume containing N dipoles. We define $\mathbf{M}(t)$ as the dipole moment of this volume at time t arising from the elementary dipoles $\boldsymbol{\mu}_i(t)$. $\mathbf{M}(t)$ is the vector sum of $\boldsymbol{\mu}_i(t)$ so the dipole correlation function $\Lambda(t)$ may be written as[4,22,40–45]

$$\Lambda(t) = \frac{\langle\mathbf{M}(0)\cdot\mathbf{M}(t)\rangle}{\langle\mathbf{M}(0)\cdot\mathbf{M}(0)\rangle} = \frac{\sum_{i'}^{N}\sum_{i}^{N}\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_{i'}(t)\rangle}{\sum_{i'}^{N}\sum_{i}^{N}\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_{i'}(0)\rangle} \tag{16}$$

The terms $\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_{i'}(0)\rangle$ express the equilibrium orientation correlation between dipoles i and i' in the medium, and the denominator in eq 16 may be written as $Ng(0)\mu^2$ for a phase containing only one type of dipole (*e.g.*, liquid chlorobenzene). Here $g(0)$ is the Kirkwood equilibrium correlation factor, and $g(0) = 1$ for no orientation correlations between dipoles.

Equation 16 on expansion gives[22,41,42]

$$\Lambda(t) = \frac{\sum_{i=1}^{N}\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle + 2\sum_{i=2}^{N}\sum_{i'=1}^{i-1}\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_{i'}(t)\rangle}{\sum_{i=1}^{N}\mu_i^2 + 2\sum_{i=2}^{N}\sum_{i'=1}^{i-1}\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_{i'}(0)\rangle} \tag{17}$$

Equation 17 is general for a medium containing more than one type of dipole, *e.g.*, a mixture of polar molecules. Consider the term $\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle = \mu_i^2\langle\mathbf{u}_i(0)\cdot\mathbf{u}_i(t)\rangle$, where $\mathbf{u}_i$ is the unit vector associated with the dipole moment $\boldsymbol{\mu}_i$. For a medium in which all the dipoles are equivalent (*e.g.*, liquid chlorobenzene), all the $\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle$'s are equal and

$$\sum\nolimits_i\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle = N\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle = N\mu_i^2\Gamma_{ii}(t)$$

where $\Gamma_{ii}(t) = \langle\mathbf{u}_i(0)\cdot\mathbf{u}_i(t)\rangle$. This dipole autocorrelation function $\Gamma_{ii}(t)$ has the limiting values $\Gamma_{ii}(0) = 1$, $\Gamma_{ii}(t \to \infty) \to 0$. It is appropriate to express what $\Gamma_{ii}(t)$ means for the (classical) reorientation of a dipole in the liquid state. Consider a dipole i at $t = 0$ whose orientation may be represented as $\mathbf{u}_i(0)$. As time develops, the dipole reorients in space, so that at a later time t it would have an average direction $\langle\mathbf{u}_i(t)\rangle_{\mathbf{u}_{i(0)}}$, where this means the average direction at t given that its direction at $t = 0$ was $\mathbf{u}_i(0)$. Since in a liquid all initial directions are equally probable $\mathbf{u}_i(0)\cdot\langle\mathbf{u}_i(t)\rangle_{\boldsymbol{\mu}_{i(0)}} = \langle\mathbf{u}_i(0)\cdot\mathbf{u}_i(t)\rangle = \langle\cos\theta\ (t)\rangle$. As time develops so the average projection of the vector on the original direction decreases, so $\Gamma_{ii}(t)$ decreases and eventually reaches zero. The cross-correlation terms $\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_{i'}(t)\rangle$ in eq 17 express the time-dependent orientation correlations between the dipoles i and i'. The cross-correlation term is evaluated as the weighted sum of the decay terms obtained for given initial relative orientations of i and i', where the weighting factors are the equilibrium probabilities of obtaining the given relative orientations.

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Equation 17 is in a sense expressing the dynamic function which is required in order to generalize the Kirkwood equilibrium theory to time-dependent phenomena. Steele[41] has discussed the general properties of the autocorrelation and cross-correlation terms, while Cook, Watts, and Williams[22,45] have discussed their significance with particular reference to dipolar polymeric chains. The case of polymers is of special interest since the orientation correlation between dipoles along a chain is determined by fixed bond lengths and the conformational (internal rotation) properties of a given chain. The equilibrium correlation of dipole orientations in polymers is well understood[46,47] and the generalization to time-dependent correlations *via* eq 17 should be of considerable value.[21,45]

The cross-correlation terms in eq 17 will be necessarily involved when dielectric relaxation experiments or pure rotational absorption experiments (gaseous media) are made. However, Gordon[42] has made the important deduction that the shape of infrared and Raman vibrational lines may yield information on the autocorrelation term contained in eq 17. If **u** is a unit vector along the direction of the transition dipole moment of the vibrator, we may write a correlation function $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$. The vibrational line will be modulated by the rotation of the molecule, and this has the result that $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ may be obtained as the Fourier transform of the normalized spectral density (see eq 13) for the infrared vibration–rotation line. For the classical case $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle = \langle \cos\theta(t)\rangle$, and this clearly indentifies with the dipole autocorrelation function $\Gamma_{ii}(t)$. Gordon[4,42] notes that the interference (cross-correlation) terms are absent in the vibrational case because of the assumed lack of coupling between the vibrations of different molecules.

Since the infrared vibration rotation spectra may yield $\Gamma_{ii}(t)$, and the Raman spectrum may lead to a different correlation function of the reorientation of molecules,[4] it is important to see if the correlation function from one experiment can be transformed in some way to predict the values of a different correlation function. For the dipole case the simplest quantity is that for a reference molecule i, and we write

$$\Gamma_{ii}(t) = \langle \mathbf{u}_i(0)\cdot\mathbf{u}_i(t)\rangle \tag{18}$$

$\mathbf{u}_i(t)$ is the direction of the dipole moment vector at time t given that it was $\mathbf{u}_i(0)$ at $t = 0$. For Brownian motion, $\Gamma_{ii}(t)$ will decay continuously from unity at $t = 0$ to zero as $t \rightarrow \infty$. This correlation function is obtained (omitting the subscript ii) by the relation[6]

$$\Gamma(t) = \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta \sin\theta \cos\theta\, \bar{P}(\theta,\phi,t) \tag{19}$$

$\bar{P}(\theta,\phi,t) \sin\theta\, \mathrm{d}\theta \mathrm{d}\phi$ is the probability at time t that the dipole is orientated in the direction of the solid angle $\sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi$. It is important to remember that the dipole correlation function is only one of many correlation functions relating to molecular reorientation. The correlation function in Raman scattering, the depolarization of fluorescence, and certain nuclear magnetic resonance experiments is given by $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$, where $P_2(x)$ is the Legendre polynomial of index 2 and **u** is the unit vector along a threefold or higher axis in a molecule.[4] Thus $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle = \langle P_1[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ and $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ probe different aspects of the same basic molecular motion (as expressed by $\bar{P}(\theta,\phi,t)$. A connection between the two correlation functions is of value since it brings the results of different experimental techniques together. Berne and Harp[6] have outlined an approximate method whereby a knowledge of $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ at a given time would lead to an approximate value of $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ and *vice versa*. The method[6] involves maximizing the information entropy of the distribution $\bar{P}(\theta,\phi,t)$. Using the definition

$$\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(\mathrm{t})]\rangle = \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta \sin\theta \left[\frac{3\cos^2\theta - 1}{2}\right] \bar{P}(\theta,\phi,t) \tag{20}$$

and eq 19, Berne and Harp[6] obtain the approximate relations

$$\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle \approx \left[\coth\beta(t) - \frac{1}{\beta(t)}\right] \tag{21}$$

$$\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle \approx 1 + \frac{3}{\beta(t)}\left[\frac{1}{\beta(t)} - \coth\beta(t)\right] \tag{22}$$

$\beta(t)$ is a Lagrange undetermined multiplier. Knowing $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ at t gives $\beta(t)$; hence $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ is obtained from eq 22. Berne and Harp[6] tested this procedure by comparing it with exact results for $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ and $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ obtained by the method of "molecular dynamics,"[6] *i.e.*, computer experiments, on simulation models for CO molecules in the dense phase. They found that this approximate method (eq 21 and 22) gave a fair approximation to the true correlation function, $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$ obtained by the method of molecular dynamics. This procedure may be of use in relating results obtained in dielectric experiments to those obtained in Raman scattering, fluorescence depolarization, and nuclear spin lattice relaxation. It is important to note that for the special case of an ensemble of linear free rotator molecules, Gordon[39] has given an exact relationship between $\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle$ and $\langle P_2(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle$.

B. COMPLEX PERMITTIVITY AND DIPOLE CORRELATION FUNCTION

The two main difficulties with the relationship between $\epsilon^*(i\omega)$ and a dipole moment correlation function are (i) local field effects and (ii) orientation correlations between dipoles. In Glarum's development[9] of the Kubo method for dielectric relaxation, he considered in the first instance the case of rigid dipoles, thus avoiding the problems of induced moments. The latter factors were brought in at a late stage of the theory, and he obtained the result for a liquid containing only one type of dipole.

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \left[1 + \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty}\{[G(\omega)]^{-1} - 1\}\right]^{-1} \tag{23}$$

$$G(\omega) = \int_0^{\infty} \mathrm{d}t\, [\exp(-i\omega t)]\left[\frac{-\mathrm{d}\Gamma(t)}{\mathrm{d}t}\right] \tag{24}$$

$\Gamma(t)$ is the dipole correlation function $\langle \boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(t)\rangle/\mu^2$ for a reference dipole in the liquid medium (see eq 17 above). The factor $[3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)]$, which lies between 1.0 and 1.5, is due to local field effects. If $\Gamma(t)$ is given by

$$\Gamma(t) = \exp(-t/\tau_\mu) \tag{25}$$

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(46) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience, New York, N. Y., 1963.

(47) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

then it follows from eq 23 that

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau_{\mathrm{M}}} \tag{26}$$

where $\tau_{\mathrm{M}} = [3\epsilon_0/(2\epsilon_0 - \epsilon_\infty)]\tau_\mu$. This is the familiar relationship between a "macroscopic" relaxation time τ_{M} and a "microscopic relaxation time" τ_μ, which has been given by Powles.[48] Thus eq 23–26 predict that a single microscopic relaxation time will always lead to a process governed by single macroscopic relaxation time.

One further point should be stressed. If the internal field factor $[3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)]$ is set equal to unity, then eq 24 becomes

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \mathrm{d}t\,[\exp(-i\omega t)]\left[\frac{-\mathrm{d}\Gamma(t)}{\mathrm{d}t}\right] \tag{27}$$

A comparison of eq 1 and 27 would lead in this special case to the relation $\phi(t) = \Gamma(t)$, and the macroscopic and molecular time quantities would be the same. If the internal field factor is included, the relationship between $\phi(t)$ and $\Gamma(t)$ is rather complicated, but it would be correct to say, for approximate work, that in this case again, $\phi(t) \approx \Gamma(t)$ (for an example of the relationship between macroscopic and microscopic relaxation times using eq 23, see Cole[40]).

Scaife,[11] Cole,[40] Zwanzig,[49] Steele,[41] Fatuzzo and Mason,[50] Klug, Kranbuehl, and Vaughan,[51] Gordon,[4] Nee and Zwanzig,[52] O'Dwyer and Harting,[12] and Keller, Ebersold, and Kneubühl[37] have given accounts of the relationship between the macroscopic complex permittivity $\epsilon^*(i\omega)$ and the molecular dipole correlation function. In the important paper by Cole,[40] the earlier work of Glarum[9] was generalized so as to include the deformation polarizability of molecules at the initial stage of the theory. Of the several relations deduced by Cole,[40] his result for the Onsager model of a dielectric coincides with eq 23. The Glarum treatment and that of Cole have been criticized by Fatuzzo and Mason.[50] These authors evaluated the special case of nonpolarizable molecules and obtained the relation

$$\left[\frac{\epsilon^*(i\omega) - 1}{\epsilon_0 - 1}\right]\left[\frac{\epsilon_0}{\epsilon^*(i\omega)}\right]\left[\frac{2\epsilon^*(i\omega) + 1}{2\epsilon_0 + 1}\right] = \int_0^\infty \mathrm{d}t\,[\exp(-i\omega t)]\left[\frac{-\mathrm{d}\Gamma_1(t)}{\mathrm{d}t}\right] \tag{28}$$

$$\Gamma_1(t) = \frac{\langle \boldsymbol{\mu}(0)\cdot\mathbf{m}(t)\rangle}{\langle \boldsymbol{\mu}(0)\cdot\mathbf{m}(0)\rangle} \tag{29}$$

$\boldsymbol{\mu}$ is the dipole moment of a representative dipole which is located at the center of a small sphere whose instantaneous dipole moment is $\mathbf{m}(t)$ at time t. Klug, Kranbuehl, and Vaughan[51] generalized the model of Fatuzzo and Mason in order to include the deformation polarizability of the molecules, for the special case of the Onsager model of a dielectric. They obtain the equation

$$\left[\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}\right]\left[\frac{\epsilon_0}{\epsilon^*(i\omega)}\right]\left[\frac{2\epsilon^*(i\omega) + \epsilon_\infty}{2\epsilon_0 + \epsilon_\infty}\right] = \int_0^\infty \mathrm{d}t\,[\exp(-i\omega t)]\left[\frac{-\mathrm{d}\Gamma(t)}{\mathrm{d}t}\right] \tag{30}$$

where $\Gamma(t)$ is given by $\langle \boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(t)\rangle/\mu^2$. Thus the equation of Glarum and Cole (eq 23) and the equation of Klug, Kranbuehl, and Vaughan (eq 30) differ by the inclusion of $\{\epsilon_0(2\epsilon^* + \epsilon_\infty)/[\epsilon^*(2\epsilon_0 + \epsilon_\infty)]\}$ in eq 30. Nee and Zwanzig[52] have also obtained eq 30. Clearly there will be a difference between $\epsilon^*(i\omega)$ calculated from eq 23 and from eq 30 given a particular $\Gamma(t)$. This difference may not be large, and Klug, Kranbuehl, and Vaughan[51] have stated that for $\Gamma(t) = \exp[-t/\tau]$, the two equations cannot be distinguished by experiment. Certainly for approximate work it might be considered more convenient to evaluate $\epsilon^*(i\omega)$ from eq 23, given a particular form for $\Gamma(t)$. Cook, Watts, and Williams[22] have generalized one approach of Fatuzzo and Mason,[50] which is a combination of the Fröhlich and Kubo theories, to include deformation polarization, and obtain

$$\left[\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}\right]\left[\frac{\epsilon_0}{\epsilon^*(i\omega)}\right]\left[\frac{2\epsilon^*(i\omega) + \epsilon_\infty}{2\epsilon_0 + \epsilon_\infty}\right] = \int_0^\infty \mathrm{d}t\,[\exp(-i\omega t)]\left[\frac{-\mathrm{d}\Lambda(t)}{\mathrm{d}t}\right] \tag{31}$$

where $\Lambda(t)$ is given by eq 17. For a system in which there are no orientation correlations between molecules, the cross-correlation terms in $\Lambda(t)$ would be zero; thus $\Lambda(t) = \Gamma(t)$ in this case and eq 31 reduces to eq 30.

Kneubühl and Keller[53] and Keller, Ebersold, and Kneubühl[37] have outlined a different approach to the relationship between macroscopic and molecular dielectric quantities in an attempt to overcome the local field difficulties. They write the macroscopic electric dipole moment per unit volume $\mathcal{P}(t)$ as a superposition relation

$$\mathcal{P}(t) = \frac{1}{4\pi}\int_0^\infty \mathrm{d}t' E_{\mathrm{loc}}(t - t')\mathrm{K}(t') \tag{32}$$

$$\mathrm{K}(t' < 0) = 0$$

$E_{\mathrm{loc}}(t)$ is the local field, and is related to the macroscopic applied field by a further superposition relation

$$E_{\mathrm{loc}}(t) = E(t) + 4\pi\int_0^\infty \mathrm{d}t'\,\mathcal{P}(t-t')\mathrm{L}(t')$$

$$\mathrm{L}(t' < 0) = 0 \tag{33}$$

$\mathrm{K}(t')$ and $\mathrm{L}(t')$ are the dielectric response functions. A combination of the Fourier transforms of eq 32 and 33 and use of the convolution theorem gives

$$\epsilon^*(i\omega) - \epsilon_\infty = [\mathrm{K}(\omega)^{-1} - \mathrm{L}(\omega)]^{-1} = \mathrm{K}(\omega)\frac{E_{\mathrm{loc}}(\omega)}{E(\omega)} \tag{34}$$

Equations 32 to 34 are macroscopic and are related to the microscopic dipole correlation functions by the relation given by Scaife[11] and O'Dwyer and Harting[12]

$$\epsilon^*(i\omega) - \epsilon_\infty = C\int_0^\infty \mathrm{d}t\,[\exp(-i\omega t)]\left[\frac{-\mathrm{d}\Lambda(t)}{\mathrm{d}t}\right] \tag{35}$$

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(48) J. G. Powles, *J. Chem. Phys.*, **21**, 633 (1953).

(49) R. Zwanzig, *ibid.*, **38**, 2766 (1963).

(50) E. Fatuzzo and P. R. Mason, *Proc. Phys. Soc., London*, **90**, 741 (1967).

(51) D. D. Klug, D. E. Kranbuehl, and W. E. Vaughan, *J. Chem. Phys.*, **50**, 3904 (1969).

(52) T. W. Nee and R. Zwanzig, *ibid.*, **52**, 6353 (1970).

(53) F. Kneubühl and B. Keller, *Phys. Lett. A*, **29**, 88 (1969).

$$\Lambda(t) = \left\langle \left[\sum_i \boldsymbol{\mu}_i(0) + \mathbf{M}_{\text{ind}}(0) \right] \left[\sum_i \boldsymbol{\mu}_i(t) + \mathbf{M}_{\text{ind}}(t) \right] \right\rangle \tag{36}$$

$\mathbf{M}_{\text{ind}}(t)$ represents the induced polarization not localized at the $\boldsymbol{\mu}_i(t)$. They state that $\langle \boldsymbol{\mu}_i(0) \cdot \mathbf{M}_{\text{ind}}(t) \rangle = 0$ and assume $\sum_i \langle \boldsymbol{\mu}_i(t) \cdot \mathbf{M}_{\text{ind}}(0) \rangle = 0$. They then identify the first time derivative of the autocorrelation term in eq 36 with the response function $\mathrm{K}(t)$ in eq 32. We have

$$\mathrm{K}(t) = -\frac{\mathrm{d}}{\mathrm{d}t} [\langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_i(t) \rangle] NC \tag{37}$$

and we write

$$\mathrm{K}_1(t) = -\frac{\mathrm{d}}{\mathrm{d}t} \left[\sum_i \sum_{i'} \langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_{i'}(t) \rangle + \langle \mathbf{M}_{\text{ind}}(0) \cdot \mathbf{M}_{\text{ind}}(t) \rangle \right] C \tag{38}$$

Hence eq 35 becomes

$$\epsilon^*(i\omega) - \epsilon_\infty = [\mathrm{K}(\omega) + \mathrm{K}_1(\omega)] \tag{39}$$

$\mathrm{K}_1(\omega)$ is the Fourier transform of $\mathrm{K}_1(t)$. A comparison of eq 34 and 39 gives

$$\mathrm{L}(\omega) = \frac{\mathrm{K}_1(\omega)}{\mathrm{K}(\omega)[\mathrm{K}(\omega) + \mathrm{K}_1(\omega)]} \tag{40}$$

$$\frac{E_{\text{loc}}(\omega)}{E(\omega)} = 1 + \frac{\mathrm{K}_1(\omega)}{\mathrm{K}(\omega)} \tag{41}$$

Thus the $\mathrm{L}(\omega)$ term is expressed in terms of $\mathrm{K}(\omega)$ and $\mathrm{K}_1(\omega)$. Keller, Ebersold, and Kneubühl[37] suggest that dielectric dispersion measurements, which yield $\mathrm{K}(\omega) + \mathrm{K}_1(\omega)$, and infrared vibration rotation spectra, which may yield $\mathrm{K}(\omega)$, may be combined so that $\mathrm{K}_1(\omega)$ (the cross-correlation terms) and $\mathrm{L}(\omega)$ (the local field terms) may be deduced. They emphasize however that the decision with regard to the leading term in $\mathrm{K}_1(t)$ will be difficult. Note that $\mathrm{K}_1(t)$ still contains nonspecified induced moment terms. Equation 35 (when normalized to include $(\epsilon_0 - \epsilon_\infty)$ is numerically quite similar to eq 31 above.

The relationship between the experimental absorption and the correlation functions for vibration–rotation spectra and dielectric relaxation have been given by Gordon,[4,38,39,42] Berne and Harp,[6] and Keller, Ebersold, and Kneubühl.[37] It is of interest to see how the quantum mechanical equations are related to eq 23, 31, and 34 above. For the simple case of molecules which have no orientation correlations between them, the quantum mechanical correlation function from an infrared vibration rotation line or from dielectric relaxation is $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$. Consider now the classical limit in the relation given by Gordon[4] for the normalized spectral density.

$$\hat{I}(\omega) = \frac{3\hbar}{4\pi^2} \frac{\epsilon''(\omega)}{[1 - \exp(-\hbar\omega/kT)] N \boldsymbol{\mu}^2} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}t\, [\exp(-i\omega t)] \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle \tag{42}$$

For the classical limit, $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ is a real even function of time, and $\hbar\omega/kT \ll 1$. Thus eq 42 yields

$$\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} = \omega \int_0^\infty \mathrm{d}t\, [\cos \omega t] \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \int_0^\infty \mathrm{d}t\, [\sin \omega t] \left[-\frac{\mathrm{d}\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle}{\mathrm{d}t} \right] \tag{43}$$

Here we have used the classical Debye relation $(\epsilon_0 - \epsilon_\infty) = 4\pi N \mu^2/(3kT)$. Equation 43 is the same as the imaginary part of eq 27. If the term $[\epsilon_0(2\epsilon^* + \epsilon_\infty)/\epsilon^*(2\epsilon_0 + \epsilon_\infty)]$ is set equal to unity in eq 30, then that equation reduces to eq 27 and the relationship to eq 43 is obvious. Note that Lassier and Brot[54] have stated the formulations of Gordon[4,42] and of Cole[40] are equivalent for the classical case.

IV. Application of the Dipole Correlation Function

A. INTRODUCTION

The dipole correlation functions $\Gamma(t)$ and $\Lambda(t)$ may be obtained from experimental data *via* the inversion of the appropriate equations given in section III above. For example, if we take the simplest relation, eq 27, which neglects local field effects and dipole orientational correlations, then

$$\Gamma(t) = \frac{2}{\pi} \int_0^\infty \frac{\mathrm{d}\omega}{\omega} \left[\frac{\epsilon_0 - \epsilon'(\omega)}{\epsilon_0 - \epsilon_\infty} \right] \sin \omega t = \frac{2}{\pi} \int_0^\infty \frac{\mathrm{d}\omega}{\omega} \left[\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} \right] \cos \omega t \tag{44}$$

Note the similarity between eq 4 and 44. Thus in this special case, the plot of $[\epsilon''/(\epsilon_0 - \epsilon_\infty)] \cos \omega t_i$ against $\log \omega$ for $t = t_i$ gives $\Gamma(t_i)$ from eq 44. Although in principle experimental data should be converted into the dipole correlation function, this has only been done in a few cases; see, for example, Gordon[4,42] Keller, Ebersold, and Kneubühl,[37] and Rothschild,[55] who have deduced the dipole correlation function from vibration–rotation spectra,[56] and Cook, Watts, and Williams,[22] Mountain,[5] Le Roy, Constant, and Desplanques,[23a] and Le Roy and coworkers,[23b] for the evaluation of the dipole correlation function from dielectric relaxation measurements on polymers and simple liquids. It has become more customary to construct an analytical or numerical correlation function, to transform it into the frequency dependent complex permittivity, and then compare with experiment. The correlation functions obtained using different models for molecular reorientation will be described below. In doing so it is convenient to regard the work to date as falling very generally into two categories. The first involves the "short time" behavior of the dipole correlation function, and the second involves the "longer time" behavior of this correlation function. The term "short time" is somewhat arbitrary but may be taken to mean up to about 2×10^{-12} sec in time. This would correspond to a frequency which is higher than about 10^{11} Hz, *i.e.*, the high-frequency region for microwave radiation and the far-infrared region. The "long time" behavior consequently corresponds to times greater than about 2×10^{-12} sec or frequencies less than about 10^{11} Hz (and indeed extending all the way down to 10^{-4} Hz). The important difference between the two time scales is as follows. For motional processes occurring in the "short time" scale, the inertial effects of molecules are of great importance. For example, in the case of the classical free rotator the correlation function[4] has $\gamma_2 = (2kT/I)$ (see eq 15 above). For processes occurring in the "longer time" scale the inertial effects are less important, and the motions may be associated with the classical reorien-

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(54) B. Lassier and C. Brot, *Chem. Phys. Lett.*, **1**, 581 (1968).

(55) W. G. Rothschild, *Macromolecules*, **1**, 43 (1968).

(56) See Gordon[4,42] for a detailed outline of the evaluation of the dipole correlation function from vibration–rotation spectroscopy.

tation of molecules (or parts of molecules) in Brownian motion. Note that the largest part of the orientation polarization in most liquids and solids is relaxed in the frequency range 10^{-4} to 10^{11} Hz.[10,17,67] This necessarily means that in these systems the largest portion of the drop in the dipole correlation function from 1 to 0 occurs at times greater than about 2×10^{-12} sec.

B. "SHORT TIME" BEHAVIOR

The series of papers by Gordon[4,38,42,58–61] provide a detailed account of the relationship between correlation functions and vibration–rotation spectra, nonresonant absorption, Raman spectra, and nuclear magnetic resonance processes. The theory for the dipole correlation function for molecular reorientation has been given by Steele,[62] Shimizu,[63,64] and Lassier and Brot.[54] In the above work, dipole correlation functions were evaluated analytically. There has been a new and significant development in the numerical calculation of the dipole correlation function and other correlation functions. This has been called "molecular dynamics," and in these calculations the equations of motion of a model system are solved numerically. The technique was first employed by Alder and Wainwright,[65] and was followed by Rahman[66] who simulated the dynamical properties of liquid argon. The dipole correlation function and several other correlation functions have been calculated by Berne and Harp[6,7] and Lassier and Brot[67] for model systems. Köhler and Bellemans,[68] Bellemans, Köhler, and Gancberg,[43,69] and Quentrec and Brot[70] have also evaluated the dipole correlation function for model systems by the method of molecular dynamics. As Berne and Harp[6] remark, there are a number of compelling reasons for making a study of the molecular dynamics of model systems. Among these are that a realistic and detailed picture of how individual molecules rotate and translate is obtained, the effect of different potentials upon the motional behavior can be examined, and the various stochastic assumptions for molecular motion that would simplify the *N* body problem can be assessed. Some indication of the sophistication and degree of difficulty of the molecular dynamics calculations of Berne and Harp[6] may be obtained by noting that in their calculation for the modified Stockmayer simulation for 512 carbon monoxide molecules, approximately 151 hr of IBM 7094 time was required. The experimental study of dielectric behavior in the far-infrared has been made by Le Roy and coworkers,[23] Constant and coworkers,[71] and Davies and coworkers.[72] For reviews and further references, see ref 23, 72, and 73, and ref 57b, pp 298–311. It would not be possible to give a detailed account of the analytical and numerical theoretical work and the experimental work here, so only a brief account will be given, indicating some of the essential features.

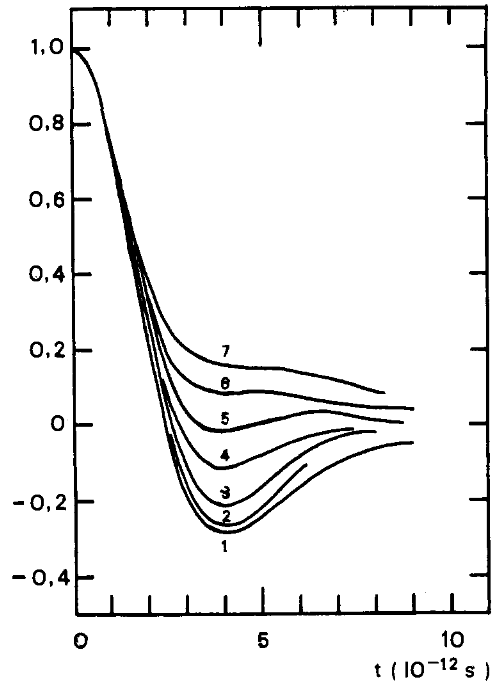

Figure 1. A schematic illustration of the dipole correlation function for CO in different environments (after Gordon [42]). Curve 1 is the free rotator correlation function. Curves 2, 3, and 4 refer to CO in argon at 66,270 and 510 amagat units, respectively. Curves 5, 6, and 7 refer to CO in liquid *n*-heptane, CCl_4, and $CHCl_3$, respectively. Reprinted by permission of the author and the American Institute of Physics from R. G. Gordon, *J. Chem. Phys.*, **43**, 1307 (1965).

First of all it should be stressed that a simple exponential dipole correlation function, eq 25, is not acceptable for times $t \ll \tau_\mu$. It does not obey eq 9a and it is not an even function of time. Other difficulties are discussed by Berne and Harp (ref 6, p 148) and by Birnbaum and Cohen.[74] The great objection, from an experimental point of view, is that the absorption coefficient $\alpha = \epsilon''\omega/nc$, where n is the real part of the complex refractive index and c is the velocity of light in a vacuum, would reach a constant value $(\epsilon_0 - \epsilon_\infty)/nc\tau$ if the correlation function is given by $\exp(-t/\tau)$. It would mean that all polar liquids would be opaque in the far-infrared region and at higher frequencies, which is certainly not the case. Thus the exponential decay is inadequate and must be replaced by a function which allows for the finite inertia of molecules, and obeys the requirements for a classical correlation function. Such functions have been deduced analytically[4,39,54,62–64,74] and numerically.[43,65–68] Consider first the dipole correlation function for a classical free rotator[4,67]

$$\Gamma(t) = \sum_{l=0}^{\infty}(-1)^l\left[\frac{t^2kT}{I}\right]^l\frac{1}{1\cdot3\cdot5\cdots(2l-1)} \tag{45}$$

The plot of $\Gamma(t)$ against t according to eq 45 is indicated schematically in Figure. 1. The correlation function has zero

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(57) (a) C. P. Smyth, "Dielectric Behaviour and Structure," McGraw-Hill, New York, N. Y., 1955; (b) N. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "Dielectric Properties and Molecular Behaviour," Van Nostrand, New York, N. Y., 1969.

(58) R. G. Gordon, *J. Chem. Phys.*, **45**, 1635 (1966).

(59) R. G. Gordon, *ibid.*, **45**, 1643 (1966).

(60) R. G. Gordon, *ibid.*, **45**, 1649 (1966).

(61) R. G. Gordon, *ibid.*, **42**, 3658 (1965).

(62) W. A. Steele, *ibid.*, **38**, 2411 (1963).

(63) H. Shimizu, *ibid.*, **43**, 2453 (1965).

(64) H. Shimizu, *ibid.*, **48**, 2494 (1968).

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(66) A. Rahman, *Phys. Rev. A*, **136**, 405 (1964).

(67) B. Lassier and C. Brot, *Discuss. Faraday Soc.*, **48**, 39 (1969).

(68) M. Köhler and A. Bellemans, *J. Chem. Phys.*, **47**, 1261 (1967).

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(71) E. Constant, L. Galatry, Y. Le Roy, and D. Robert, *J. Chim. Phys.*, **65**, 1022 (1968).

(72) M. Davies, G. W. F. Pardoe, J. E. Chamberlain, and H. A. Gebbie, *Trans. Faraday Soc.*, **64**, 847 (1968).

(73) G. W. F. Pardoe, *ibid.*, **66**, 2699 (1970).

(74) G. Birnbaum and E. R. Cohen, *J. Chem. Phys.*, **53**, 2885 (1970).

slope at $t = 0$ and is an even function of time. The negative values of $\Gamma(t)$ mean[4] that after a certain time it is more probable that a molecule has moved to point in the opposite direction to that which it had at $t = 0$. Such an easy rotation would tend not to be allowed in the liquid state, so that in the liquid $\Gamma(t)$ is in most cases a positive quantity.[4–7,22]

Gordon[4,42] has given dipole correlation functions for carbon monoxide in the gas phase (with argon) and in different organic solvents. The results follow those indicated schematically in Figure 1. In this case Gordon[4,42] obtained the dipole correlation function from an analysis of the vibration–rotation spectrum in the infrared region. This technique has been used by Rothschild[55] to study the reorientation of methylene dichloride in polystyrene, and by Keller, Ebersold, and Kneubühl[37] for the motion of $CHCl_3$, HCl, DCl, and HBr in different solvents. For the liquid state the results of Gordon[4,42] and Keller, Ebersold, and Kneubühl indicate some oscillation of $\Gamma(t)$ followed by a monotonous decay to zero. Gordon[4,39] considered his results for CO in terms of two models for rotational diffusion. In the m diffusion model the free rotational step of a molecule is terminated by randomizing the components of the angular momentum of molecular rotation J. In the J diffusion model the magnitude of J was distributed over a Boltzmann distribution at the end of each step in addition to randomizing the components of J. He found that the $\Gamma(t)$ data for CO in the different environments could be represented quite well in terms of these models, and the m diffusion model was particularly good. One feature of Gordon's models is that they allow for large angular displacement between collisions. However, Berne and Harp[6] remark that Gordon's model does not correctly predict the angular momentum correlation function. Berne and Harp[6] carried out their molecular dynamics calculations for CO using three different models. (1) The Stockmayer simulation employed a Lennard-Jones 6–12 potential between the centers of mass for two molecules together with a dipole–dipole interaction term, $\mu = 0.1172$ D. (2) The Stockmayer simulation was as in (1) except μ was set at 1.172 D. (3) The modified Stockmayer simulation was the same as (1) except that additional quadrupole–quadrupole and quadrupole–dipole terms were included. The simulation (1) gave $\Gamma(t)$ nearly the same as the free rotator $\Gamma(t)$. This suggests that the dipole–dipole term is unimportant in CO due to its small value. The $\Gamma(t)$ from (2) resembles curve 7 in Figure 1, as does the $\Gamma(t)$ from (3). The quadrupole–quadrupole term was found to exert a strong influence on the decay of $\Gamma(t)$.

Lassier and Brot[54] considered a model in which a rotator may undergo librations in a potential well prescribed by neighboring molecules, and under the action of strong collisions might reorient from one well to another. The analysis leads to two processes at low temperatures—a small high frequency librational motion and a much larger reorientational process—while at higher temperatures the two processes tend to merge. The feature of this work is that the absorption coefficient α exhibits a peak in the frequency plot and tends to zero as $\omega \rightarrow \infty$, and also reaches its limit n^2 through values of $\epsilon'(\omega) < n^2$; *i.e.*, the high-frequency region has "resonance" character. Thus the transparency in the high-frequency region is recovered. Note that the question of $\alpha \rightarrow 0$ as $\omega \rightarrow \infty$ has been discussed without the aid of correlation functions by Rocard,[75] Powles,[76] and Herzfeld,[77] and more recently using the correlation function by Le Roy and coworkers[23] and Constant and coworkers.[71] These authors and Davies and coworkers[72] have given extensive accounts of the behavior of $\alpha(\omega)$ against ω for a variety of molecules in the liquid state, and the reader is referred to these accounts for a discussion of the fit obtained to experimental data using the calculated absorption coefficient. Lassier and Brot[67] have carried out a numerical calculation of the dipole correlation function (and the angular momentum correlation function and $\langle P_2[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$) for the model of a classical linear rotator hindered by a two-well potential and submitted to random torque impulses. The potential $W(\theta) = V \sin^2 \theta$, and θ is the polar angle. For the special case of $V = 0$ (their zero potential case), $\Gamma(t)$ is given by eq 45 only when the impacts are rare. For numerous impacts, *i.e.*, the mean time $\langle\tau_i\rangle$ between collisions is small, then $\Gamma(t)$ departs radically from eq 45 and has a quantitative similarity to the $\Gamma(t)$ calculated by Gordon (his "J" diffusion model), and a qualitative similarity to the upper curves shown in Figure 1. For very frequent impacts $\Gamma(t)$ approaches an exponential decay in time and yet retains the necessary condition that $[\mathrm{d}\Gamma(t)/\mathrm{d}t]_{t=0} = 0$. The plots of $\alpha(\omega)$ deduced from this simulation exhibit peaks and the transparency for high ω is recovered with ϵ' reaching its limit n^2 through values of $\epsilon' < n^2$. The Cole–Cole plots of $\epsilon''/(\epsilon_0 - n^2)$ against $(\epsilon' - n^2)/(\epsilon_0 - n^2)$ show only one continuous dispersion–absorption region and are strongly asymetrical. Lassier and Brot[67] also carried out a simulation for $V = kT$ and $V = 3kT$. Their results for $V = 3kT$ indicate that for $\langle\tau_i\rangle$ large (*i.e.*, infrequent impacts), then $\Gamma(t)$ decays initially in an oscillatory manner, and at later time tends to the exponential decay in time. Physically this means that the dipole librates in the potential minima and occasionally crosses the barrier between minima. For $\langle\tau_i\rangle$ small (*i.e.* frequent impacts), $\Gamma(t)$ retains its very short time oscillations, but this changes over into an exponential decay sooner than for $\langle\tau_i\rangle$ large. The plots of $\alpha(\omega)$ against ω for $V = 3kT$ and $\langle\tau_i\rangle$ as a variable show that the larger $\langle\tau_i\rangle$ is, the larger is $\alpha_{\max}$. The transparency, *i.e.*, $\alpha \rightarrow 0$, as $\omega \rightarrow \infty$, at high frequencies is again recovered in this simulation, and the results are to be compared with the earlier analytic work of Lassier and Brot.[54] To summarize the work of Lassier and Brot,[54,67] they show that the inclusion of (i) a potential barrier, (ii) the moment of inertia of the molecule, and (iii) the randomization rate of the angular velocity $(2\langle\tau_i\rangle)^{-1}$ have a significant effect on the plots of $\alpha(\omega)$ against ω. The inertial term recovers the transparency of the medium at high frequencies. $\langle\tau_i\rangle$ plays a very important part in the transformation of oscillatory behavior of $\Gamma(t)$ to exponential behavior at longer times.

Bellemans, Köhler, and Gancberg[43] used the molecular dynamics technique to evaluate the dielectric response function $\varphi_r(t) = [-\mathrm{d}\Lambda(t)/\mathrm{d}t]$ for a two-dimensional system of dipoles, where the dipoles are located on a rigid square lattice and the specimen is circular. They considered two types of coupling: (a) dipole–dipole interactions and (b) classical exchange interactions which would lead in one case to parallel and in another case to antiparallel preferential orientation between molecules. The calculations were carried out for 101, 193, and 421 dipoles. They evaluated $\varphi_r(t)$ and hence the real and imaginary parts of the complex dielectric susceptibility within the terms of their two-dimensional model. It was found that the dielectric behavior in the presence of dipole

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(75) Y. Rocard, *J. Phys. Radium*, 4, 247 (1933).

(76) J. G. Powles, *Trans. Faraday Soc.*, 44, 802 (1948).

(77) K. F. Herzfeld, *J. Amer. Chem. Soc.*, **86**, 3468 (1964).

interactions was not very different from that for the free rotator. They concluded that dipolar interactions exert only a weak influence on the dielectric relaxation of their model system. The exchange interactions had a considerable influence on the dielectric relaxation, and the reader is referred to ref 43 for the necessary details. Note that Boon and Köhler[44] have given an analytical formulation for $\Lambda(t)$ which agrees with the molecular dynamics calculations of Bellemans, Köhler, and Gancberg[43] for the system where dipolar interactions are considered.

Quentrec and Brot[70] carried out a molecular dynamics calculation for the dipole correlation function of a two-dimensional system of rigid diatomics with their centers fixed on the sites of a square lattice. Using a Lennard-Jones 6–12 potential between the atoms in the system, and a total of 100 molecules, they found the following. At low temperatures the dipole correlation function undergoes a few damped oscillations followed by a slow decrease with increasing time. At high temperatures the correlation function approaches the free rotator result. They conclude that the atom–atom potential has a far greater effect on the correlation function than does dipolar interaction.

Birnbaum and Cohen[74] have considered an empirical dipole correlation function which is a real and even function of time (thus has zero slope in the limit of zero time) and in addition takes the form of an exponential decay in linear time at long times. This function is given by

$$\Gamma(t) = \exp\{\delta - [\delta^2 + (t/\tau_1)^2]^{1/2}\} \qquad (46)$$

where δ and τ_1 are parameters. They used this function to calculate $(\epsilon' - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)$, $\epsilon''/(\epsilon_0 - \epsilon_\infty)$, and the absorption coefficient α as a function of frequency for given values of δ and τ_1. If $\delta = 0$, eq 46 reduces to the exponential decay function. For $\delta = 0.01$ and $\delta = 0.1$, Birnbaum and Cohen showed that the loss curve was narrower than the single relaxation time curve, and that ϵ' reached its limiting value of ϵ_∞ through values less than ϵ_∞. This is quite similar to the findings of Lassier and Brot.[54,67] The plot of α against ω for $\delta = 0.01$ and 0.1 shows a maximum, and at much higher frequencies α decreases exponentially with increasing frequency, thus recovering the transparency of the system. The loss curves based on eq 46 are quite similar to those calculated from the Rocard[75] and Powles[76] relations for suitably chosen parameters. Birnbaum and Cohen[74] attempted to fit the experimental absorption results obtained in the far-infrared region for liquid methyl chloroform[72] to the theoretical absorption based on eq 46. It was found that the theoretical curves, with or without internal field corrections, did not give an adequate representation of the experimental data. The theory predicts too small a maximum value for α and too large an absorption (α) at very high frequencies, in comparison with the experimental results. A similar discrepancy is obtained if the Rocard[75] or Powles[76] relations are used. They conclude[74] that dielectric relaxation is not the only mechanism responsible for the far-infrared absorption in liquid methyl chloroform.

C. "LONGER TIME" BEHAVIOR

1. Dipole Reorientation in Liquids

a. Introduction

As indicated in section IV.B above, inertial effects are of great importance in determining the "short time" behavior of $\Gamma(t)$ or the high-frequency behavior of $\epsilon''(\omega)$ and $\alpha(\omega)$. However if the plot of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ is made against log ω, then for the majority of dipolar molecules in the liquid and solid states the larger part of the dispersion magnitude $(\epsilon_0 - \epsilon_\infty)$ is relaxed in the low frequency ($f < 10^{11}$ Hz) or long time ($t > 2 \times 10^{-12}$ sec) range. Thus only a small part of the dielectric dispersion region may be influenced by the inertia effects described in section IV.B above. Note that the presentation of dielectric information as $\alpha(\omega) = \epsilon''\omega/nc$ tends to emphasize the high frequency region compared with the presentation as $\epsilon''(\omega)$. The presentation as $\alpha(\omega)$ is common in the far-infrared region since it is the quantity that is obtained directly from the measurements.

The "long time, low frequency" region for dielectric relaxation has been the subject of many detailed investigations over the years, and a number of texts which summarize the findings are available.[10,17,57,78–80] In the present account we are concerned with the applications of the dipole correlation function to specific systems and to specific mechanisms for dielectric relaxation. The Debye theory[78] for a molecule reorienting in a viscous continuum has been expressed in terms of the dipole correlation function by Cole.[40] The correlation function approach has been used for models of cooperative relaxation in liquids by Glarum,[81] Adam,[82] Anderson,[83] Anderson and Ullman[84] and Ullman.[85] It has also been used for the reorientation of molecules having groups capable of internal reorientation by Provder and Vaughan[86] and by Williams.[87,88] It is of interest to discuss this work in a little more detail.

b. Cooperative Motions

Glarum[81] noted that certain alkyl halides[89,90] in the liquid state gave plots of $\epsilon''(\omega)$ against log ω which were nonsymmetrical about the frequency of maximum loss and were approximately represented by the empirical relation of Davidson and Cole.[26,27] Glarum considered that this might not be due to a distribution of relaxation times but might be due to a cooperative relaxation process. He took a simple one-dimensional model of equivalent polar molecules in which each molecule (dipole) is supposed to be able to reorient with a single relaxation time τ. In addition it was supposed that there are defects in the system whose motions are described by a diffusion equation. When a defect reaches a dipole it relaxes completely and instantly. The introduction of a diffusion equation immediately leads to a dipole correlation function which has a natural nonexponential dependence on time. This emphasizes the fact that a loss curve which is broader than a single relaxation time process need not be considered as a weighted sum of single relaxation time pro-

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(79) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier, New York, N. Y., 1952.

(80) V. V. Daniel, "Dielectric Relaxation," Academic Press, London, 1967.

(81) S. H. Glarum, *J. Chem. Phys.*, **33**, 639 (1960).

(82) G. Adam, *ibid.*, **43**, 662 (1965).

(83) J. E. Anderson, *ibid.*, **47**, 4879 (1967).

(84) J. E. Anderson and R. Ullman, *ibid.*, **47**, 2178 (1967).

(85) R. Ullman, *ibid.*, **49**, 831 (1968).

(86) T. Provder and W. E. Vaughan, *ibid.*, **46**, 848 (1967).

(87) G. Williams, *Trans. Faraday Soc.*, **64**, 1219 (1968).

(88) G. Williams, *ibid.*, **64**, 1934 (1968).

(89) D. J. Denney, *J. Chem. Phys.*, **27**, 259 (1957).

(90) D. J. Denney, *ibid.*, **30**, 1019 (1959).

cesses, *i.e.*, a distribution of relaxation times (see section II, eq 6). Glarum's dipole correlation function is given by

$$\Gamma(t) = [\exp(-t/\tau_0)][1 - p(t)] \tag{47}$$

where $p(t)$ is the probability that the defect has reached an arbitrary dipole at time t. The final relation is

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau_0} + \left\{\frac{i\omega\tau_0}{1 + i\omega\tau_0}[1 + a_0^{1/2}(1 + i\omega\tau_0)^{1/2}]^{-1}\right\} \tag{48}$$

$a_0 = l_0^2/D\tau_0$ where l_0 is the average distance of a defect from a given dipole and D is the diffusion coefficient for a defect. Glarum has discussed the shape of the dispersion and absorption curves obtained from eq 48. For $a_0 \gg 1$, eq 48 reduces to a single relaxation time expression and the relaxation involves the "intrinsic" relaxation time τ_0, with diffusion not being involved. For $a_0 = 1$ eq 48 is very similar to the Davidson–Cole empirical relation with a parameter of 0.5, while for $a_0 = 0$ eq 48 is similar to the Cole–Cole empirical equation[24] with a parameter of 0.5. Although Glarum's model is simple, it does indicate that dielectric relaxation arising from a diffusion process (in part) may depart significantly from the single relaxation time expression eq 5.

A different approach to cooperative relaxation in liquids and solids has been outlined by Adam.[82] He assumed that a cooperative region, containing Z lattice sites, would participate in the reorientation of a reference dipole. The number of holes in such a cooperative region is a variable $\bar{a}$ which may vary, over all cooperative regions in a sample, from $\bar{a} = 0$ to $\bar{a} = Z$. The fraction of cooperative regions which have $\bar{a}$ holes may be expressed by a Bragg–Williams relation

$$q_{\bar{a}} = \left[\frac{Z!}{\bar{a}!(Z - \bar{a})!}\right]\left[\frac{F^{\bar{a}}}{(1 - F)^{\bar{a} - z}}\right] \tag{49}$$

where F is the fraction of vacant cells in the entire sample. Adam assumed that a cooperative region containing $\bar{a}$ holes would have a single exponential correlation function in time

$$\Gamma_{\bar{a}}(t) = \exp(-t/\tau_{\bar{a}}) \tag{50}$$

so that the overall correlation function is given by

$$\Gamma(t) = \sum_{\bar{a}=0}^{z} q_{\bar{a}}\Gamma_{\bar{a}}(t) = \sum_{\bar{a}=0}^{z} \frac{Z!}{\bar{a}!(Z - a)!}\frac{F^{\bar{a}}}{(1 - F)^{\bar{a} - z}} \exp(-t/\tau_{\bar{a}}) \tag{51}$$

and from eq 27

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_{\bar{a}=0}^{z} \frac{Z!F^{\bar{a}}}{\bar{a}!(Z - \bar{a})!(1 - F)^{\bar{a} - z}}\frac{1}{(1 + i\omega\tau_{\bar{a}})} \tag{52}$$

Thus the dielectric relaxation is given as a weighted sum of single relaxation processes. This distribution of relaxation times has arisen since a region containing $\bar{a}$ holes is characterized by a relaxation time $\tau_{\bar{a}}$. It would appear that the system relaxes without a redistribution of the holes between cooperative systems, whereas in the Glarum treatment above the diffusion of a defect is one mechanism for relaxation. Adam[82] assumed that a cooperative region would require an activation energy of $Q_{\bar{a}} = Zu_1 - \bar{a}u_2$, where Zu_1 is the activation energy for a region without holes, and $\bar{a}u_2$ is the reduction in $Q_{\bar{a}}$ due to the presence of $\bar{a}$ holes. Hence $\tau_{\bar{a}}$ may be written as $\tau_0 \exp(Zu_1/kT) \exp(-\bar{a}u_2/kT)$ and eq 52 may be evaluated for given values of F, u_2, and τ_0 at different values of T. Adam found that the plots of $\epsilon''(\omega)$ against $\epsilon'(\omega)$ may be similar to a single relaxation time process, two relaxation processes, a Cole–Cole empirical relation, or a Cole–Davidson empirical relation, depending upon the choice of parameters. The experimental data for solid HBr, DBr, HCl, HI, and DI, and liquid alkyl halides could be represented in terms of eq 52.

Anderson and Ullman[84] considered the model in which a representative dipole is allowed to relax by its environment. The "free volume" V_f about any molecule fluctuates about an average value $\langle V_f\rangle$, and it is these fluctuations which determine the ability of a molecule to reorient. The kinetics of the free volume fluctuations were evaluated using a diffusion equation, and with the aid of the dipole correlation function a numerical evaluation of $\epsilon^*(i\omega)$ was made. The loss curves range from single relaxation time profiles to curves resembling the Cole–Cole and Davidson–Cole empirical representations, depending upon the parameters of the model. They conclude that if the free volume fluctuations (in time) are much slower than the rates of individual molecular reorientation, then the molecules reorient at their own rates and a distribution of relaxation times is present. For free volume fluctuations that are fast, a single relaxation time results, since a molecule experiences one average environment during its reorientation. When the rate of the environment fluctuation and the individual molecular reorientation are comparable, they predict the "skewed arc" behavior similar to the Davidson–Cole empirical function. Thus a fluctuating environment may lead to a variety of shapes for loss factor curves, as does the model of Glarum and of Adam. In a later paper Ullman[85] has given a more phenomenological treatment for the (dipole) correlation function. He considers that a system which is relaxing from an initial state obeys the relation

$$\frac{\mathrm{d}f(t)}{\mathrm{d}t} + \eta(t)f(t) = 0 \tag{53}$$

where f is a generalized displacement and $\eta(t) = \bar{\eta} + \delta(t)$, where $\bar{\eta}$ is the mean value of the fluctuating coefficient of friction $\eta(t)$. The general solution to eq 53 is

$$f(t) = f_0 \exp(-\bar{\eta}t) \exp[-X(s,t)] \tag{54}$$

and

$$X(s,t) = \int_s^{s+t} \delta(q)\mathrm{d}q \tag{55}$$

Ullman assumed that the probability of $X(s,t)$ might be given by a Gaussian function, or that $[X(s,t) + \bar{\eta}t]$ might be given by a Poisson distribution function. This leads to expressions for the correlation function $\langle f\rangle/f_0$ in terms of $\bar{\eta}$, time, and $\langle X^2\rangle$. He then considered two forms for $\langle X^2\rangle$, one based on a Markov process and the other on a Gaussian elemental process. The details will not be given here. It suffices to say that the correlation function, and hence the complex (dielectric) susceptibility, was calculated for (i) Gaussian distribution of X, Markov microscopic fluctuations; (ii) Gaussian distribution of X, Gaussian microscopic fluctuations; and (iii) Poisson distribution of X, Markov microscopic fluctuations. In all cases, for very long times $\Gamma(t)$ is exponential in time. The deviations from the exponential decay occur at times smaller than, or of the order of, the characteristic time of local fluctuations. In case (i) the Cole–Cole plots were flat but rather symmetrical; in (ii) bimodal loss curves emerge; and in (iii) asymmetric Cole–Cole plots are obtained. Thus again, a variety of shapes for the relaxation curves may result depending upon the parameters used and the assumptions made in the theory involving fluctuations. Anderson[83] has outlined a model for relaxation in which the molecule may exist in either of two "environments." The molecule may relax in a given environment, or it may change its environment and subsequently relax. Anderson calculates $\Gamma(t)$ and obtains one large single relaxation time process and one small (but faster) single relaxation time process.

To summarize, the correlation function obtained from the models of Glarum,[81] Anderson and Ullman,[84] and Ullman[85] are of a nonexponential nature since diffusion or fluctuations may naturally lead to such behavior. This seems perfectly reasonable and emphasizes the fact that a relaxation process which is broader than a single relaxation time process need not involve a distribution of relaxation times. The theories of Adam[82] and Anderson[83] lead to equations involving a weighted sum of single relaxation time processes and may not fully accommodate the possibility that diffusional processes are involved in cooperative relaxation.

c. Internal Reorientation

Provder and Vaughan[86] have used the dipole correlation function in evaluating the dielectric relaxation for a hindered internal rotator whose polar groups are of equal size and have a common rotation axis. The hindering potential for internal rotation was taken as (i) a singly periodic cosine potential, (ii) a doubly cosine potential, (iii) a singly periodic parabolic potential, and (iv) a doubly periodic parabolic potential. Each case was worked out and compared with the result for a free rotator, which has a single relaxation time process with $\tau^{-1} = kT(\rho^{-1} + \rho_1^{-1})$, where ρ and ρ_1 are the friction coefficients for internal and overall rotation of the molecule, respectively. It was found that the deviations of the dispersion and absorption curves from the free rotator were most marked for the single and double parabolic potentials.

Williams[87,88] examined the dielectric relaxation for different structures which were capable of internal reorientation in addition to molecular rotation. Examples are phenols, aromatic amines, and methoxybenzenes. The theory involved the dipole correlation function approach of Cole[40] and was applied to such molecules as triphenylamine, aniline, *p*-phenylenediamine, and *p*-dimethoxybenzene. In these cases the total mean square dipole moment may be partially relaxed by internal reorientation of the dipolar groups in the molecule. It is instructive to consider the correlation function for two special cases. Figure 2a shows the dynamic equilibrium between the two internal states of the $C_6H_5NR_2$ molecule, while Figure 2b shows the dynamic equilibrium for $R_2NC_6H_4NR_2$. For $C_6H_5NR_2$ the dipole correlation function is given by[87]

$$\Gamma(t) = \frac{\mu_z^2}{\mu^2}\gamma_{\text{mol}}(t) + \frac{\mu_x^2}{\mu^2}\gamma_{\text{mol}}(t)\psi(t) \qquad (56)$$

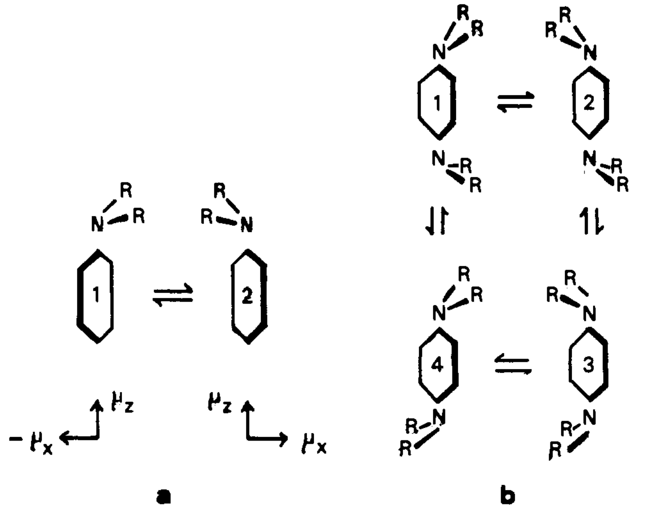

Figure 2. The dynamic equilibria between (a) the two internal states of the $C_6H_5NR_2$ molecule, and (b) the four internal states for the $R_2NC_6H_4NR_2$ molecule.

$\gamma_{\text{mol}}(t) = \exp(-t/\tau_{\text{mol}})$ and $\psi(t) = \exp(-t/\tau')$. Here τ_{mol} and τ' are the relaxation times for the overall molecular rotation and internal reorientation, respectively, and $\mu^2 = \mu_x^2 + \mu_z^2$. Thus for $\tau' \ll \tau_{\text{mol}}$, eq 56 predicts two relaxation regions; the higher frequency process (short time) has a relaxation time τ' and has a magnitude proportional to (μ_x^2/μ^2). The lower frequency process has a relaxation time τ_{mol} and has a magnitude proportional to (μ_z^2/μ^2). For the other extreme, if $\tau' \gg \tau_{\text{mol}}$, then $\Gamma(t) = \gamma_{\text{mol}}(t)$, and one relaxation process, the molecular rotation process, is predicted. It is important to note that the above has a simple physical interpretation which allows one to predict the result for a more complex situation without the use of detailed theory. If internal reorientation is fast compared with molecular tumbling, then the internal reorientation will relax a portion of μ^2. The molecular tumbling will relax the square of the average dipole moment $\langle \boldsymbol{\mu} \rangle$ left in a molecule when the component moment associated with the intramolecular motion is abstracted. For Figure 2a, $\langle \boldsymbol{\mu} \rangle = \boldsymbol{\mu}_z$, so the molecular tumbling carries with it a magnitude proportional to μ_z^2. The magnitude of the internal reorientation process is proportional to $\mu^2 - \mu_z^2 = \mu_x^2$. Clearly this is consistent with eq 56 when $\tau' \ll \tau_{\text{mol}}$. For $\tau' \gg \tau_{\text{mol}}$, the result $\Gamma(t) = \gamma_{\text{mol}}(t)$ simply means that the molecule tumbles many times between conformational changes; hence μ^2 is relaxed completely by molecular tumbling. For Figure 2b, the correlation function is evaluated as[87]

$$\Gamma(t) = \gamma_{\text{mol}}(t)\psi(t) \qquad (57)$$

where $\gamma_{\text{mol}}(t)$ and $\psi(t)$ are the same as defined above. Thus the relaxation occurs by a combination of overall molecular rotation and internal reorientation. For $\tau' \ll \tau_{\text{mol}}$, $\Gamma(t) \approx \psi(t)$, while for $\tau' \gg \tau_{\text{mol}}$, $\Gamma(t) \approx \gamma_{\text{mol}}(t)$. Note that for fast internal reorientation, all of $\langle \mu^2 \rangle$ is relaxed by internal reorientation. The value of $\langle \boldsymbol{\mu} \rangle$ in this case is zero. Williams[87,88] has discussed the occurrence of internal reorientation processes in a number of aromatic molecules containing flexible groups, such as NR_2, CH_2Cl, and OCH_3.

2. Dipole Reorientation in Solids

a. Introduction

The dipole correlation function approach has been applied to reorientation in ice by Onsager and Runnels,[91] to the cooperative relaxation of solid substituted benzenes by Brot and Darmon,[92] and to the dielectric behavior of polymer chains

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(91) L. Onsager and L. K. Runnels, *J. Chem. Phys.*, **50**, 1089 (1969).

(92) C. Brot and I. Darmon, *ibid.*, **53**, 2271 (1970).

by Work and Fujita,[93] Cook, Watts, and Williams,[22] Anderson,[94] and Dubois-Violette and coworkers.[95] It is appropriate to consider the work of Onsager and Runnels in section D below and to indicate briefly the work on solid substituted benzenes and polymers in sections 2.b and 2.c below.

b. Substituted Benzenes

It is well known that in certain substituted benzenes in the crystalline state, the molecules may exhibit rotation about the axis perpendicular to the ring plane. Brot and Darmon[92] showed that in 1,2-dichloro-3,4,5,6-tetramethylbenzene (DCTMB) and 1,2,3-trichlorotrimethylbenzene (TCTMB), although rotation occurs in the solid state, there is a fall in the static permittivity $\epsilon_0(T)$ at lower temperatures, indicative of a progressive (antiparallel) orientational ordering of the dipolar molecules on the lattice. The dielectric relaxation curves broaden markedly as the temperature is lowered in the (ordering) transition region. Brot and Darmon[92] made a Monte Carlo calculation of $\epsilon_0(T)$ based upon the electrostatic energy of the crystal and found that at low temperatures such crystals would be orientationally ordered (ϵ_0 small), while, as the temperature was raised, disorder increased so that $\epsilon_0(T)$ increased rapidly over a temperature range of $\sim$30°K. This is in agreement with experiment. They evaluated $\Lambda(t)$ by a Monte Carlo method, including the local barrier to reorientation and the electrostatic contributions to the barrier system. They found that their model calculation leads to a single exponential decay at high temperatures, while at lower temperatures (in the region of orientational ordering) $\Lambda(t)$ was consistent with a distribution of relaxation times. These calculations are entirely consistent with their experimental data for DCTMB and TCTMB. Since the calculations were made for an assembly of molecules, it is not strictly possible to describe the motions of a given molecule. However, as Brot and Darmon remark, an intuitive interpretation would be that at high temperatures the fair amount of orientational disorder in neighboring molecules will lead to a cancellation of the differences in depth of potential wells, and there will be an almost constant jump probability (*i.e.*, a single exponential decay). At low temperatures, the few disoriented molecules produce around themselves potential differences of opposite signs for different neighbors, hence a greater variability of the potential wells, and this leads to a large distribution in jump probabilities.

c. Polymeric Solids

The dipole correlation function approach is of considerable value in discussing the dielectric relaxation of solid polymers. This approach has been employed by Work and Fujita,[93] Cook, Watts, and Williams,[22] Dubois-Violette and coworkers,[95] Williams and Watts,[96] and Anderson.[94] In the paper by Cook, Watts, and Williams,[22] it was shown that the normalized complex permittivity was given by eq 31. Thus a convenient approach to the dielectric behavior of polymers is through $\Lambda(t)$. Now $\Lambda(t)$ is expressed in terms of the autocorrelation terms $\langle \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle$ and the cross terms $\langle \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_{i'}(t)\rangle$ within a given polymer chain. The orientation correlation terms between dipoles were shown to decrease in magnitude with increasing separation of the dipoles along the chain[22] by reference to a series of model polyethers. They also remark that if the dipoles were very widely separated, then the dielectric behavior would reflect only the autocorrelation term $\langle \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle$. From experimental evidence for copolymers, it would appear that $\langle \boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_i(t)\rangle$ is nonexponential in time. Rather than regard this as evidence for a distribution of relaxation times, it might be best to regard it simply as an experimental result, whose explanation may be found if the cooperative motions of chain segments could be evaluated (see section IV.C.1.b above). The approach of Cook, Watts, and Williams[22] does not consider the detailed mechanical motions of chains. Work and Fujita,[93] Dubois-Violette and coworkers,[95] and Anderson[94] have considered the dipole correlation function for model chains in which the exact modes of motion are prescribed.

Work and Fujita[93] evaluated the dipole correlation function for an infinitely long array of equally spaced, rigid permanent electric dipoles oriented at right angles to a linear axis, with freedom to rotate around this axis. Interactions within the chain were included by means of a time-dependent angular correlation function. The theory was developed using a generalization of Glauber's dynamical theory[97] of the one-dimensional Ising model. It was shown that there were two characteristic times associated with the dielectric relaxations. One time constant was given by the time required to establish the equilibrium angular correlations for the rotators within the chain, while the second time constant was associated with the relaxation of correlated chain segments. When the statistical correlation function is achieved in a time which is short compared with the relaxation time of the correlated unit, a single relaxation time process is obtained. When the statistical correlation function takes an appreciable time to be established (they term this "retarded correlations"), a significant deviation from single relaxation time behavior is obtained, and Work and Fujita demonstrate that in some cases bimodal loss curves are obtained. Thus, within the terms of their model, correlations along the chain may lead to very broad relaxation curves.

Anderson[94] considered a chain in which the individual elements may or may not be dipolar, but the orientation of each element can always be found in one of two directions in space. Denoting these two orientations as 0 and 1, then the possible arrangements for a triad in the chain are 000, 111, 101, 010, 011, 001, 100, and 110. Anderson expressed the rate equations for the chain dynamics in terms of Glauber's dynamical theory for the one-dimensional Ising model.[97] The quantity $R = (k_2/k_1)$ expressed the coupling between chain elements. Here k_2 and k_1 are the rate coefficients in the transformations

$$000 \underset{2k_2}{\overset{2k_1}{\rightleftharpoons}} 010; \quad 111 \underset{2k_2}{\overset{2k_1}{\rightleftharpoons}} 101; \quad 011 \underset{(k_1 + k_2)}{\overset{(k_1 + k_2)}{\rightleftharpoons}} 001$$

Anderson first considered a single dipole situated in a chain which constituted an infinite ring. For R small (*i.e.*, not very different from unity), the dipole correlation function was a simple exponential decay in time; thus the Cole–Cole plot of $\epsilon''(\omega)$ against $(\epsilon'(\omega) - \epsilon_\infty)$ was a semicircle. For R large, *i.e.*, strong coupling between chain elements, the behavior de-

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[93] R. N. Work and S. Fujita, *J. Chem. Phys.*, **45**, 3779 (1966).

[94] J. E. Anderson, *ibid.*, **52**, 2821 (1970).

[95] E. Dubois-Violette, F. Geny, L. Monnerie, and O. Parodi, *J. Chim. Phys.*, **66**, 1865 (1969).

[96] G. Williams and D. C. Watts in "NMR, Basic Principles and Progress," Vol. 4, Springer-Verlag, Berlin, 1971, p 271.

[97] R. J. Glauber, *J. Math. Phys.* (*N. Y.*), 4, 294 (1963).

parted significantly from a single relaxation time process, and in the limit of very large R, asymmetric behavior, numerically equivalent to the Davidson–Cole empirical function, was obtained. It should be emphasized that the broadening of the relaxation behavior here is only due to the complex motions of the model chain. The strong coupling of the (nonpolar) elements to the single dipolar element prescribes the motion of that dipolar element. He then considered the influence of the cross-correlation terms $\langle \mathbf{\mu}_i(0)\cdot\mathbf{\mu}_{i'}(t)\rangle$ on the dipole correlation function. For the case of a chain where the dipoles tend to align in a parallel manner, then for $R = 100$, when the dipoles were 49 elements apart, the Cole–Cole plot was asymmetrical of Davidson–Cole type. For only seven elements apart, the Cole–Cole plot becomes less asymmetric, and $\epsilon''_{\max}/(\epsilon_0 - \epsilon_\infty)$ has increased over that for a spacing of 49 elements. For a dipole spacing of three elements the plot is nearly a semicircle. For the case of a chain where the dipoles tend to align in an antiparallel manner, then for $R = 100$, for a separation of 49 elements, the Cole–Cole plot was a Davidson–Cole type and very similar to that for $R = 100$, parallel dipoles 49 elements apart mentioned above. This reflects the fact that at a separation of 49 elements $\langle \mathbf{\mu}_i(0)\cdot\mathbf{\mu}_{i'}(t)\rangle$ terms are not important. However for a dipole separation of seven elements and for three elements the Cole–Cole plots tend to bimodal behavior in the antiparallel case. As Anderson points out, these model calculations must be viewed with caution when considering their application to real polymer chains. It is, however, significant that the model chain dynamics naturally lead to broad relaxation curves (in the log frequency plot) for a single dipole in a chain. It is also important that cross-correlation terms would appear to influence the shape of the dielectric relaxation curves.

Monnerie and Geny[98–100] have outlined a simulation of the Brownian motion of a macromolecular chain on a tetrahedral lattice, using a Monte Carlo method. These calculations have been successful in describing the equilibrium statistical properties of a polymer chain[99] and the dynamic properties of a chain.[95,100] In particular, they evaluated the correlation function $\langle \cos^2 \theta_i(t)\rangle$, where $\theta_i(t)$ is the angle the ith bond has turned after t trials. This correlation function is of importance to studies of the depolarization of fluorescence. They also made[95] an analytical evaluation of $\langle \cos^2 \theta_i(t)\rangle$ and $\langle \cos \theta_i(t)\rangle$, the dipole correlation function, for a chain element moving on a tetrahedral lattice. It was shown that $\langle \cos \theta_i(t)\rangle$ varies as $t^{-1/2}$ or $t^{-2/3}$ at long times, depending upon the hydrodynamic conditions. The results of this work do not appear to have been applied to experimental dielectric relaxation data for polymers in solution or in the liquid state.

It should be clear from the above work on the dielectric relaxation of polymer molecules that the dipole correlation function provides a direct and informative method of proceeding from a given model to its dielectric relaxation behavior. The alternative approach, involving the solution of the chain dynamics in the presence and absence of an applied electric field, would be extremely difficult to evaluate.

D. BARRIER THEORIES

The "long time" relaxation of molecules in a prescribed barrier system was considered in a series of elegant papers by Hoffman and coworkers.[101–104] In this work, the rate equations for the occupational probabilities of the stable sites were solved, and the dielectric relaxation behavior was evaluated by a consideration of the time dependence of the occupational probabilities when a steady electric field is removed from the system. Cole[40] showed that the dipole correlation function provides a straightforward method for the evaluation of the dielectric behavior if the solution of the rate equations is known. Wachtman[105] and Onsager and Runnels[91] showed that the rate equations for an octahedral site model, where all the sites were of equal energy in the absence of an applied field, could be solved with the aid of "group theory." The combined group theory and dipole correlation approach is a convenient method for evaluating the dielectric relaxation in site model systems. Williams and Cook[106] have used this combined approach for equivalent energy site models and, in addition, have applied it to cases where the sites are not equivalent in energy. Since the motion in site situations is of importance in crystalline solids,[105,107–109] for mechanical and dielectric relaxation, it is of interest to give a brief indication of the method used. Consider the example of a three-site model, Figure 3a, in which site 1 is lower in energy than the two equivalent energy sites 2 and 3. Figure 3b shows the transition probabilities for motion between adjacent sites. The rate equation for the conditional occupational probabilities of the sites may be expressed in matrix form[91,106] and has the solution

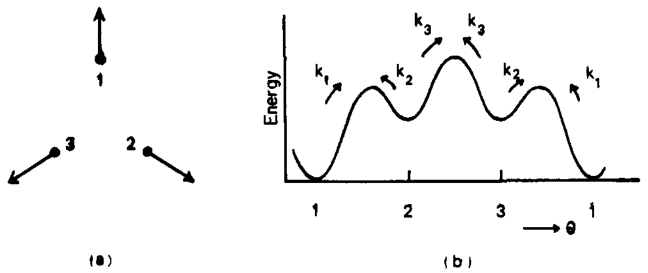

Figure 3. (a) Three-site model showing the dipole direction in the sites. (b) The local free energy barrier as a function of the coordinate of reorientation.

$$\mathbf{P}(t) = \exp(\mathbf{T}t) \tag{58}$$

The general element of $\mathbf{P}(t)$ is $P_{ji}(t)$ where this is the conditional probability of obtaining site j at time t, given that the molecule was in site i at $t = 0$. $\mathbf{T}$ is the transition matrix, which for the three-site model of Figure 3 is given by

$$\mathbf{T} = \begin{bmatrix} -2k_1 & k_2 & k_2 \\ k_1 & -(k_2 + k_3) & k_3 \\ k_1 & k_3 & -(k_2 + k_3) \end{bmatrix} \tag{59}$$

$\mathbf{P}(t)$ would be known from eq 58 if the transformation $\mathbf{S}^{-1}\mathbf{T}\mathbf{S} = \mathbf{D}$ could be performed. $\mathbf{S}$ is the matrix that diagonal-

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izes **T**, and **D** is the diagonal matrix. Group theory is used for this purpose,[106] and an orthogonal matrix **Q** is generated by taking the sites themselves as the basis of a reducible representation, forming the columns of **Q** with the aid of the projection operator. This matrix is then used to perform $\mathbf{Q}^{-1}\mathbf{TQ} = \mathbf{W}$, and **W** will be a partitioned matrix, blocked out on its diagonal. The eigenvalues and eigenvectors of the smaller matrices in **W** are readily determined so that the diagonal matrix **D** is obtained from $\mathbf{U}^{-1}\mathbf{WU} = \mathbf{D}$. For the example in Figure 3 we have the C_{2v} point group and

$$\mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \beta & \beta \\ 0 & \beta & -\beta \end{bmatrix}$$

$$\mathbf{W} = \begin{bmatrix} -2k_1 & 2\beta k_2 & 0 \\ 2\beta k_1 & -k_2 & 0 \\ 0 & 0 & -(k_2 + 2k_3) \end{bmatrix}$$

$$\mathbf{U} = \begin{bmatrix} \alpha & \gamma & 0 \\ \alpha x/\beta & -\gamma/2\beta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{D} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & -(k_2 + 2k_1) & 0 \\ 0 & 0 & -(k_2 + 2k_3) \end{bmatrix}$$

$x = (k_1/k_2)$; $2\beta^2 = 1$; $\alpha^2(1 + 2x^2) = 1$; ${}^3/_2\gamma^2 = 1$. Hence $\mathbf{P}(t)$ is readily obtained as

$$\mathbf{P}(t) = \mathbf{QU}[\exp(\mathbf{D}t)]\mathbf{U}^{-1}\mathbf{Q}^{-1} \qquad (60)$$

The dielectric relaxation is evaluated[40] using the dipole correlation function

$$\Gamma(t) = \sum_i {}^0P_i\xi_i(t) \qquad (61)$$

$$\xi_i(t) = \sum_j P_{ji}(t)\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \qquad (62)$$

$\xi_i(t)$ is the dipole decay function for dipoles which were in site i at $t = 0$; ${}^0P_i$ is the equilibrium occupational probability of site i. Thus $\Gamma(t)$ is the weighted sum of the individual decay terms. For the example of Figure 3, eq 60–62 yield[40,106]

$$\Gamma(t) = \frac{1}{(1 + 2x)^2}[(1 + 2x \cos \theta_{12})^2 + 2x(1 - \cos \theta_{12})^2 \times \psi_2(t) + 2x(1 + 2x)(1 - \cos^2 \theta_{12})\psi_3(t) \qquad (63)$$

θ_{12} is the angle between the dipole direction in site 1 and site 2. $\psi_2(t) = \exp[-(k_2 + 2k_1)t]$; $\psi_3(t) = \exp[-(k_2 + 2k_3)t]$. Note that two of the eigenvalues of **D** are the reciprocal of time constants in $\psi_2(t)$ and $\psi_3(t)$. It is instructive to note that the time-independent term in eq 63 represents that part of μ^2 which cannot be relaxed in the barrier system. This term must be omitted from the $\Gamma(t)$ in eq 63, and when this is done[106] the complex dielectric permittivity follows from eq 27 as

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{c_2}{1 + i\omega\tau_2} + \frac{c_3}{1 + i\omega\tau_3} \qquad (64)$$

where $c_2 = (1 - \cos \theta_{12})\eta$; $c_3 = (1 + 2x)(1 + \cos \theta_{12})\eta$; and $\eta^{-1} = 2[1 + x(1 + \cos \theta_{12})]$. The relaxation times are $\tau_2 = (k_2 + 2k_1)^{-1}$ and $\tau_3 = (k_2 + 2k_3)^{-1}$.

Thus the rate eq 58 may be solved with the aid of group theory if the barrier system processes a degree of symmetry. The dielectric relaxation is evaluated using the dipole correlation function together with $\mathbf{P}(t)$. The combined group theory and correlation function approach represents a direct means of evaluating the dielectric behavior of dipoles in a barrier system possessing a large number of sites, but having a degree of symmetry.

It should be emphasized that the barrier theories considered in this section do not include the "short time" part of the correlation function. This was considered by Lassier and Brot[54,67] and was discussed in section IV.B above.

E. CHEMICAL RELAXATION

Anderson and Smyth[110] and Schwarz[111,112] have considered that a dynamic equilibrium between reactants and products may be observed in a dielectric relaxation experiment. They used a theory involving a perturbation of the chemical system with a weak electric field. Scheider[113] used a correlation function method to evaluate the dielectric relaxation for a system in which a dissolved macromolecule is in chemical equilibrium with a free ionic species, while Williams[114] has shown that the models considered by Schwarz[111] could be evaluated very conveniently using the dipole correlation function. One advantage of the correlation function method is that all dielectric relaxation processes, both orientational and chemical, are included in the theory.[87] Scheider[115] has commented on the earlier work[111–114] and has distinguished between a chemical equilibrium involving reactants and products which are ionic and those which are not ionic. Thus the systems $A_1 \rightleftharpoons A_2$, $A + B \rightleftharpoons C$, where A_1, A_2, A, B, and C will (in general) be dipolar molecules, should be distinguished from the system $HZH^+ + A^- \rightleftharpoons {}^-ZH^+ + HA$. According to Scheider[115] the formulations of Schwarz[111] and Williams[114] are correct for nonionic systems, since these are evaluated on the basis that the system comes to a thermodynamic equilibrium in the presence of a steady electric field. The ionic systems are different since a steady electric field results in charge transport to the electrodes. With this difference in mind, it is of interest to see how chemical relaxation may lead to an active dielectric relaxation process, and how the correlation function provides a direct evaluation of a given model. Consider the simple case[111,114]

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2$$

where A_1 is nondipolar and A_2 is dipolar. For a macroscopic unit volume, the dipole moment arising from permanent dipoles at $t = 0$ is given by

$$\mathbf{M}(0) = \sum_{i=1}^{N_{A_2}} \boldsymbol{\mu}_{A_{2i}}(0)$$

where $\boldsymbol{\mu}_{A_{2i}}(0)$ is the dipole moment of the ith A_2 molecule at $t = 0$, and $N_{A_2}(0)$ is the number of A_2 molecules at $t = 0$. At a later time t, $\mathbf{M}(t) = [\mathbf{M}_{A_2}(t)]_{A_2} + [\mathbf{M}_{A_2}(t)]_{A_1}$, where the bracket subscript indicates that the A_2 molecules at time t were A_2 at $t = 0$ or A_1 at $t = 0$. Since there is no orientation correlation

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between molecules which are A_2 at $t = 0$ and those which are A_1 at $t = 0$, it follows[114] that

$$\langle \mathbf{M}(0)\cdot\mathbf{M}(t)\rangle = \langle \mathbf{M}_{A_2}(0)\cdot[\mathbf{M}_{A_2}(t)]_{A_2}\rangle \tag{65}$$

Williams[114] evaluated the conditional moment $[\mathbf{M}_{A_2}(t)]_{A_2}$ with the aid of the rate equations governing the chemical equilibrium, and obtained

$$\Lambda(t) = \frac{\langle \mathbf{M}(0)\cdot\mathbf{M}(t)\rangle}{\langle \mathbf{M}(0)\cdot\mathbf{M}(0)\rangle} = \gamma_{A_2}(t)\frac{[K^* + \psi(t)]}{[K^* + 1]} \tag{66}$$

$K^* = (k_{12}/k_{21})$ is the equilibrium constant for the system, $\gamma_{A_2}(t)$ is the molecular reorientation decay function for A_2 molecules, and $\psi(t) = \exp[-(k_{12} + k_{21})t]$. Writing $\gamma_{A_2}(t) = \exp[-t/\tau_{A_2}]$ and using eq 31 with the factor $\{\epsilon_0(2\epsilon^* + \epsilon_\infty)/[(\epsilon^*)(2\epsilon_0 + \epsilon_\infty)]\}$ set equal to unity gives

$$\frac{\epsilon^*(i\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{K^*}{[1 + K^*]}\frac{1}{[1 + i\omega\tau_{A_2}]} + \frac{1}{[1 + K^*]}\frac{1}{[1 + i\omega\tau]} \tag{67}$$

$\tau^{-1} = \tau_{A_2}^{-1} + \tau_{ch}^{-1}$, where $\tau_{ch} = (k_{12} + k_{21})^{-1}$. The time constant τ_{ch} is called the chemical relaxation time. For the special case $\tau_{ch} \ll \tau_{A_2}$, the chemical exchange between A_1 and A_2 is faster than the reorientation of A_2 molecules, and according to eq 67 two relaxation processes are predicted, the higher frequency process being due to chemical relaxation. For $\tau_{ch} \gg \tau_{A_2}$, then $\tau = \tau_{A_2}$ in eq 67. Thus chemical relaxation would not be detected in this case, the dielectric relaxation occurring by the reorientation of A_2 molecules. Note that the correlation function treatment for chemical relaxation is quite similar to that for internal reorientation in molecules (section IV.C.1.c).

If chemical relaxation occurs at a far slower rate than the reorientation of dipolar molecules, then the dielectric experiment will not detect the chemical relaxation process. The simple physical explanation for this result is that the mean-square dipole moment will be relaxed by the faster process, which for most simple chemical equilibria would correspond to the reorientation of molecules. Schwarz has discussed experiments in which the chemical relaxation might be observed in a dielectric experiment,[111-112] and it is hoped that this will become a very useful application of the dielectric technique.

V. Summary

The dipole correlation function approach to dielectric relaxation provides a very direct means for proceeding from a specified mechanism for molecular motion to the predicted dielectric behavior. This is true despite the local field problems discussed in section III.B above. The considerable interest in this approach, as evidenced by the large number of recent publications, owes much to the work of Glarum,[9] Cole,[40] Gordon,[4,38,42] and Scaife.[11] Its success is evident from the work described in section IV above and needs no further comment in this summary. As to the future, it is to be anticipated that the molecular-dynamics method for evaluating the dipole moment correlation function will provide much valuable information for motion in molecular crystals and for cooperative motions in liquids. With the advent of accurate experimental methods working in the time domain at long times[116] and short times,[117,118] it seems likely that approximate dipole correlation functions will be obtained directly from experiments in the time domain, thus removing (for certain systems) the present complication of transforming frequency dependent data, obtained over a limited frequency range, into the time domain with the aid of the Fourier transformation. As the experimental information on the dipole moment correlation function is accumulated and is related to the correlation functions obtained from different experimental techniques, there is little doubt that our understanding of the molecular dynamic interactions in liquids and in solids possessing rotational freedom will improve significantly. It would appear that the dielectric technique, with its capability of covering a wide frequency range (10^{-4} to 10^{12} Hz) or wide time range (10^{-10} to 10^{3} sec), will play a very important part in future studies of the details of molecular motion.[119]

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