A self-consistent theory of rotational diffusion*

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The effect of long range Coulomb and dipolar forces on the collective tumbling of rigid linear dipoles is considered. It is shown that the Debye relaxation times are modified by the presence of these long range forces in important ways. Explicit expressions for these relaxation times are derived for polar and electrolyte solutions. It is shwon that for dense solutions there are significant deviations from the Debye semicircle in the Cole–Cole plot.

I. INTRODUCTION

The problem of orientational relaxation in fluids has received much attention in the recent literature, not only because it is intrinsically interesting but also because there are applications of fluctuation spectroscopy where it is important to know how the orientational dynamics are reflected in the observed spectrum. The simplest model of orientational relaxation is that of rotational diffusion first proposed by Debye.[1] In this model each rigid molecule diffuses independently. The question immediately arises as to whether the presence of long range forces such as Coulomb, or dipolar forces would effect the results of the Debye theory. In this case each molecule not only experiences the usual frictional forces which give rise to a "diffusion equation," but also must respond to the local electric field which arises from the permanent multiple moments on the neighboring molecules. In this paper we include these added forces and torques in a generalized diffusion equation and solve this equation self-consistently with the Poisson equation. [In a sense our calculation is similar in spirit (but quite different in detail) to the lattice model proposed by Zwanzig[2] and studied recently in great detail by Cole.[3]]

In this paper the question of Debye relaxation is considered in the context of dielectric relaxation. Recently Fatuzzo and Mason[4] have shown that the autocorrelation function of the net dipole moment of a sphere embedded in a medium of the same dielectric constant (as the sphere) is related to the frequency dependent dielectric constant as

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

where $\phi(t)$ is the normalized dipole moment autocorrelation function

$$\phi(t)\equiv\frac{\langle\sum_{\alpha,\beta}\mu_\alpha(0)\cdot\mu_\beta(t)\rangle}{\langle|\sum_\alpha \mu_\alpha(0)|\rangle}\;. \tag{1.2}$$

L denotes a Laplace transform, and $\epsilon(\omega)$ and ϵ_0 are, respectively, the frequency dependent and static dielectric constant of the medium $[\epsilon_0\equiv\epsilon(0)]$. The controversy surrounding Eq. (1.1) has recently been resolved by Titular and Deutch[5] in a comprehensive review of the problem.

Further progress can be achieved only if $\phi(t)$ is calculated. In this paper we seek to generalize Debye's original calculation of $\phi(t)$ by including long range dipolar forces on the dynamics of the dipoles. For simplicity the treatment is restricted to nonpolarizable rigid linear molecules with dipole moment μ parallel to the molecular axis. We shall indicate how this model can be generalized later. We are guided in our initial formulation by the literature on electrolyte solutions.[6]

In this paper expressions are derived for the autocorrelation functions

$$C_{lm}(\mathbf{q},t)\equiv\Big\langle\sum_\alpha e^{-i\mathbf{q}\cdot\mathbf{r}_\alpha(0)}\,Y^*_{lm}(\mathbf{u}_\alpha(0))\times\sum_\beta e^{i\mathbf{q}\cdot\mathbf{r}_\beta(t)}\,Y_{lm}(\mathbf{u}_\beta(t))\Big\rangle, \tag{1.3}$$

where $\{Y_{lm}(\mathbf{u})\}$ are the spherical harmonics of rank l and projection m. The correlation function $\phi(t)$ required for dielectric relaxation is then

$$\phi(t)=\lim_{q\to 0}\frac{\sum_{m=-1}^{1}C_{1m}(q,t)}{\sum_{m=-1}^{1}C_{1m}(q,0)}. \tag{1.4}$$

It is found that when dipolar forces are taken into account $\phi(t)$ decays on two different time scales specified by the relaxation times

$$\tau_1=(2D_R)^{-1}\,, \tag{1.5a}$$

$$\tau_2=(2(1+\lambda)D_R)^{-1}\,, \tag{1.5b}$$

where D_R is the rotational diffusion coefficient, and

$$\lambda\equiv(4\pi/3K_BT)\,\mu^2\rho_0. \tag{1.5c}$$

The model is extended to binary solutions containing two polar components and to dipolar relaxation in an electrolyte solution. As far as we know, the results of this model are new. Titular and Deutch[5] also find two relaxation times in a single component polar fluid on the basis of a totally different model. It remains to be seen how these two calculations relate to each other.

II. THE SELF CONSISTENT ROTATIONAL DIFFUSION EQUATION

In the usual treatment of a fluid containing rigid linear molecules, the starting point is the "diffusion equation"

$$\partial C/\partial t=D_T\nabla_r^2 C+D_R\nabla_u^2 C,$$

where D_T and D_R are, respectively, the translational and the rotational diffusion coefficients, ∇_r is the gradient operator on the space (x, y, z), and ∇_u is the rotation operator[7] $\nabla_u=\mathbf{u}\times\partial/\partial\mathbf{u}$. In this equation $C(\mathbf{r},\mathbf{u},t)d^2u\,d^3r$ is the number of molecules with orientation $\mathbf{u}$ in the solid angle d^2u and center of mass in the neighborhood d^3r

of the point $\mathbf{r}$ at time t. The microscopic definition of C is

$$C(\mathbf{r},\mathbf{u},t) \equiv \sum_{\beta=1}^{N} \delta(\mathbf{r}-\mathbf{r}_\beta(t))\,\delta(\mathbf{u}-\mathbf{u}_\beta(t)) \, , \tag{2.1}$$

where $\mathbf{r}_\beta(t)$ and $\mathbf{u}_\beta(t)$ are, respectively, the position and orientation of molecule β at time t and the sum goes over all the molecules. The average value of C is $(1/4\pi)\rho_0$, where ρ_0 is the number density of the fluid.

Among the approximations made in deriving the diffusion equation are the neglect of inertial terms, and memory effects. The rotational and translational diffusion coefficients are assumed to contain multipolar friction terms of which the dielectric friction discussed by Zwanzig and Nee[8] is an example. It should not be too difficult to include memory effects in these equations, but we choose to consider this simple model for its pedagogical value. Strictly speaking the translational diffusion coefficient of a linear molecule is anisotropic. We shall ignore this anisotropy since it will not change any of the important conclusions.

If the linear molecules have permanent multipole moments the above equation requires modification. Long range forces and torques then arise because of long range Coulomb forces between the charge distributions on different molecules. In order to include these forces we propose to use the "forced diffusion equation" which has been used so effectively in the theory of electrolyte solutions:

$$\partial C/\partial t = -\beta D_T \nabla_r \cdot (\mathbf{F}C) - \beta D_R \nabla_u \cdot (\mathbf{N}C) + D_T \nabla_r^2 C + D_R \nabla_u^2 C, \tag{2.2}$$

where β is $(K_B T)^{-1}$, where K_B is Boltzmann's constant and T is the absolute temperature. The force and torque $\mathbf{F}(\mathbf{r},t)$ and $\mathbf{N}(\mathbf{r},t)$ acting on a molecule at $(\mathbf{r},t)$ arise from the Coulomb interactions between the molecules and can thus be expressed as

$$\mathbf{F}(\mathbf{r},t) = \int ds Z(s) \mathbf{E}(\mathbf{r}+s\mathbf{u}) \, , \tag{2.3a}$$

$$\mathbf{N}(\mathbf{r},t) = \int ds Z(s) s\mathbf{u} \times \mathbf{E}(\mathbf{r}+s\mathbf{u}) \, . \tag{2.3b}$$

To arrive at Eqs. (2.3a) and (2.3b), consider the linear molecule centered at $\mathbf{r}$ with orientation $\mathbf{u}$ and let $(\mathbf{r}+s\mathbf{u})$ be the position a distance s from the molecular center along the molecular axis. Then $\mathbf{E}(\mathbf{r}+s\mathbf{u})$ is the electric field at this point due to all charges in the system. Now let $Z(s)\,ds$ be the charge on the molecule in the neighborhood ds of the point s; that is, $Z(s)$ is the linear charge density. It is obvious that $dsZ(s)\mathbf{E}(\mathbf{r}+s\mathbf{u})$ is the electric force exerted on this charge by the surrounding fluid. Likewise $s\mathbf{u}\times dsZ(s)\mathbf{E}(\mathbf{r}+s\mathbf{u})$ is the corresponding torque. Equations (2.3a) and (2.3b) simply result from a summation of these terms over the length of the molecule.

To make Eqs. (2.2) and (2.3) self-consistent we shall eventually make use of the Poisson equation

$$\nabla_r \cdot \mathbf{E}(\mathbf{r},t) = -\nabla_r^2 \phi(\mathbf{r},t) = 4\pi\rho(\mathbf{r},t) \, , \tag{2.4}$$

where $\rho(\mathbf{r},t)$ is the charge density and $\phi(\mathbf{r},t)$ is the electrostatic potential at $\mathbf{r},t$.

The charge density is clearly

$$\rho(\mathbf{r},t) = \sum_\beta \sum_{j\in\beta} Z_j \delta(\mathbf{r}-\mathbf{r}_\beta(t) - s_j\mathbf{u}_\beta(t)) \tag{2.5}$$

where the sum first goes over the charges Z_j on molecule β and then over all the molecules in the system. After some manipulation it is found that

$$\rho(\mathbf{r},t) = \int dsZ(s) \int d^2\mathbf{u}' \int d^3x\, \delta(\mathbf{r}-\mathbf{x}-s\mathbf{u}')C(\mathbf{x},\mathbf{u}',t) \, , \tag{2.6}$$

where Eq. (2.1) has been used in addition to the definition of the molecular charge density $Z(s) \equiv \sum_j Z_j \delta(s-s_j)$. This formula is easily verified by substitution of Eq. (2.1) for $C(\mathbf{x}, u', t)$.

From Eqs. (2.3), (2.4), and (2.6) it follows that ϕ, and correspondingly $\mathbf{F}$ and $\mathbf{N}$, are linear functionals of C, so that Eq. (2.1) is a nonlinear equation in C. In the following simple treatment we shall linearize Eq. (2.2) in C because we are interested only in small fluctuations,[9] and we shall use Eq. (2.4) to express $\mathbf{N}$ and $\mathbf{F}$ in terms of C.

The final equation is now obtained by the following steps.

(a) Linearizing Eq. (2.2); that is, replacing $\nabla_r \cdot (\mathbf{F}C)$ and $\nabla_u \cdot (\mathbf{N}C)$ by $C_0\nabla_r \cdot \mathbf{F}$ and $C_0 \nabla_u \cdot \mathbf{N}$, respectively, gives

$$\partial C/\partial t = -\beta D_T C_0 \nabla_r \cdot \mathbf{F} - \beta D_R C_0 \nabla_u \cdot \mathbf{N} + D_T \nabla_r^2 C + D_R \nabla_u^2 C. \tag{2.7}$$

(b) Fourier transforming the resulting linearized equation with respect to the spatial variable $\mathbf{r}$, where

$$\rho(\mathbf{q},t) \equiv \int d^3r\, e^{i\mathbf{q}\cdot\mathbf{r}} \rho(r,t) \, , \tag{2.8}$$

$$C(\mathbf{q},\mathbf{u},t) \equiv \int d^3r\, e^{i\mathbf{q}\cdot\mathbf{r}} C(\mathbf{r},\mathbf{u},t) \tag{2.9}$$

are, respectively, the spatial Fourier transforms of $\rho(\mathbf{r},t)$ and $C(\mathbf{r},\mathbf{u},t)$.

(c) Substituting the spatial Fourier transforms of Eqs. (2.3), (2.4), (2.5), and (2.6) into the equation resulting from steps (a) and (b). This gives a linear equation for $C(\mathbf{q},\mathbf{u},t)$.

(d) $C(\mathbf{q},\mathbf{u},t)$ is now expanded in the spherical harmonics $\{Y_{lm}(\mathbf{u})\}$:

$$C(\mathbf{q},\mathbf{u},t) = \sum_{lm} a_{lm}(\mathbf{q},t) Y_{lm}^*(\mathbf{u}) \, , \tag{2.10a}$$

where the coefficient a_{lm} is obviously

$$a_{lm}(\mathbf{q},t) = \int d^2\mathbf{u}\, Y_{lm}(\mathbf{u}) C(\mathbf{q},\mathbf{u},t) \, . \tag{2.10b}$$

Substitution of Eq. (2.1) into Eq. (2.10b) then gives

$$a_{lm}(\mathbf{q},t) = \sum_\beta e^{i\mathbf{q}\cdot\mathbf{r}_\beta(t)} Y_{lm}(\mathbf{u}_\beta(t)) \, . \tag{2.10c}$$

Thus the correlation functions defined in Eq. (1.3) are simply

$$C_{lm}(\mathbf{q},t) = \langle a_{lm}^*(\mathbf{q},0) a_{lm}(\mathbf{q},t)\rangle \, . \tag{2.11}$$

Consequently what is required are the quantities $a_{lm}(q,t)$. These are found by substituting Eq. (2.10a) into the equation resulting from step (c). When the scalar product of the resulting equation with $Y_{lm}(\mathbf{u})$ is evaluated it is found that[10]

$$\frac{\partial a_{lm}(q,t)}{\partial t}+\gamma_l(q)a_{lm}(q,t)=-\sum_{JK}T_{JK}^{lm}(q)a_{JK}(q,t)\,, \quad (2.12)$$

where

$$\gamma_l(q)\equiv[q^2D_T+l(l+1)D_R]\,, \quad (2.13a)$$

$$T_{JK}^{lm}(q)\equiv(4\pi)^2\,i^{(J-l)}\beta\rho_0\gamma_l(q)$$
$$\times[Q_l^*(\mathbf{q})Q_J(\mathbf{q})/q^2]\,Y_{lm}^*(\hat{q})Y_{JK}(\hat{q})\,, \quad (2.13b)$$

$$Q_J(\mathbf{q})\equiv\int dsZ(s)j_l(qs)\,, \quad (2.13c)$$

where $\hat{q}$ is a unit vector parallel to $\mathbf{q}$, $j_l(qs)$ is a Bessel function of order l, and $Q_J(q)$ is a "multipole-moment" generating function. Equation (2.12) is the primary equation of this section.

It would thus appear that $a_{lm}(q,t)$ is coupled to many other coefficients (JK).

A considerable simplification results in the "$q\to 0$ limit." In this case the following should be noted:

$$Q_0(q)=0\,, \quad (2.14a)$$

$$Q_l(q)\xrightarrow[q\to 0]{}(\text{const})\,q^l\,, \quad (2.14b)$$

$$Q_1(q)\xrightarrow[q\to 0]{}\tfrac{1}{3}\mu q\,, \quad (2.14c)$$

where μ is the "dipole moment"

$$\mu\equiv\int dsZ(s)s\,. \quad (2.15)$$

Equation (2.14a) follows because the molecules are assumed to have no net charge; that is $\int dsZ(s)=0$. Equation (2.14b) follows from the property of the Bessel functions that $j_l(x)\to x^l$ as $x\to 0$. Therefore as $q\to 0$ the coefficient which is lowest order in q is $Q_1(q)$, and it follows that

$$T_{JK}^{lm}(q)=(\tfrac{4}{3}\pi)^3\beta\mu^2\rho_0\gamma_lY_{1m}(q)Y_{1k}^*(\hat{q})\delta_{l1}\delta_{J1}+O(q^2)\,. \quad (2.16)$$

The solution is further simplified without loss of generality if $\mathbf{q}$ is taken parallel to the Z axis. Then $Y_{1m}(0,0)=(3/4\pi)^{1/2}\delta_{m,0}$ and

$$T_{JK}^{lm}(q)=\lambda\gamma_l\delta_{l1}\delta_{J1}\delta_{m0}\delta_{k0}\,, \quad (2.17a)$$

where

$$\lambda\equiv\tfrac{4}{3}\pi\beta\mu^2\rho_0\,. \quad (2.17b)$$

Equation (2.12) then reduces to the simple form

$$\frac{\partial a_{lm}}{\partial t}=-(1+\delta_{l,1}\delta_{m,0}\lambda)\gamma_la_{lm}(q,t)\,, \quad (2.18)$$

with the solution

$$a_{lm}(q,t)=a_{lm}(q,0)\exp-[1+\delta_{l,1}\delta_{m,0}\lambda]\gamma_lt\,. \quad (2.19a)$$

Thus the correlation functions [Eq. (1.3)] are[11]

$$C_{lm}(q,t)=\langle|a_{lm}(q)|^2\rangle\exp-[1+\delta_{l,1}\delta_{m,0}\lambda]\gamma_lt\,, \quad (2.19b)$$

and the dipole correlation function of Eq. (1.4) is

$$\phi(t)=\tfrac{1}{3}(2\,e^{-2D_Rt}+e^{-(1+\lambda)2D_Rt})\,. \quad (2.19c)$$

In deriving Eq. (2.19c) we used the fact that $\gamma_l\to l(l+1)D_R$ as $q\to 0$ and $\langle|a_{lm'}|^2\rangle=\langle|a_{lm''}|^2\rangle$.

It is important to note that in the absence of a net molecular charge, the only multipole moment that contributes to the orientational relaxation in the $q\to 0$ limit is the dipole moment. This should not be surprising since only the dipolar potential is sufficiently long ranged. What is surprising is that these forces only affect the rank $l=1$ correlation functions. This is because the equation has been linearized. The major conclusion is that there are two different "Debye relaxation" times which are given by Eq. (1.5). We shall return to the ramifications of this later.

It should be noted that the "transverse" dipolar correlations are given by $C_{1\pm1}(q,t)$ and the "longitudinal" dipolar correlations are given by $C_{10}(q,t)$. Thus the two correlation times $\tau_1\equiv(2D_R)^{-1}$ and $\tau_2\equiv(2(1+\lambda)D_R)^{-1}$ that appear in Eq. (2.19c) give the decay of the transverse and longitudinal fluctuations, respectively.

III. ROTATIONAL RELAXATION IN MIXTURES

Let $C_i(\mathbf{r},\mathbf{u},t)$ denote the density of molecules of component i at $(\mathbf{r},\mathbf{u},t)$. As before this density satisfies the linearized forced diffusion equation

$$\partial C_i/\partial t=-\beta C_i^0[D_T^{(i)}(\nabla\cdot\mathbf{F}_i)+D_R^{(i)}\nabla_u\cdot\mathbf{N}_i]$$
$$+D_T^{(i)}\nabla^2C_i+D_R^{(i)}\nabla_u^2\,C_i\,, \quad (3.1)$$

where $D_T^{(i)}$ and $D_R^{(i)}$ are the translational and rotational diffusion coefficients of component i.

Proceeding as in the last section we obtain the general equation for a mixture

$$\frac{\partial a_{lm}^{(i)}(q,t)}{\partial t}+\gamma_l^{(i)}(q)a_{lm}^{(i)}(q,t)=-\sum_v\sum_{JK}T_{JK}^{lm}(iv)a_{JK}^{(v)}(q,t) \quad (3.2)$$

where

$$\gamma_l^{(i)}\equiv[q^2D_T^{(i)}+l(l+1)D_R^{(i)}]\,, \quad (3.3a)$$

$$T_{JK}^{lm}(iv)\equiv(4\pi)i^{(J-l)}\beta\rho_i\gamma_l^{(i)}(q)\,\frac{Q_l^{(i)*}(q)Q_J^{(v)}(q)}{q^2}\,Y_{lm}^*(\hat{q})Y_{JK}(\hat{q})$$

$$Q_J^{(v)}(q)=\int dsZ_v(s)j_l(qs)\,. \quad (3.3c)$$

In these equations $Z_v(s)$ is the charge density on a molecule of type v and ρ_i is the number concentration of component i. These equations are easily specialized.

We choose to consider only the simplest cases of polar and electrolyte solutions here. In all that follows only the $q\to 0$ limit is considered. Moreover without loss of generality $\mathbf{q}$ is taken parallel to the z axis.

IV. BINARY MIXTURE OF POLAR MOLECULES

In this section we consider the orientational correlation functions in a fluid mixture composed of two kinds of linear molecules denoted 1 and 2 with different dipole moments μ_1 and μ_2. In this case it is easy to show from Eq. (3.3b) that for i, $v=1,2$

$$T_{JK}^{lm}(iv)=\gamma_l^{(i)}\lambda_{iv}\delta_{lm,10}\delta_{JK,10}\,, \quad (4.1a)$$

where

$$\lambda_{iv}\equiv\tfrac{4}{3}\pi\rho_i\mu_i\mu_v \quad (4.1b)$$

and where in the $q\to 0$ limit

$$\gamma_l^{(i)} \xrightarrow[q\to 0]{} l(l+1)D_R^{(i)} . \tag{4.1c}$$

Combining Eqs. (4.1) and (3.2) it is seen that the coefficients $a_{lm}^{(i)}$ for $l \neq 1$ evolve just as predicted from the usual Debye theory; that is, they are unaffected by the long range forces. The coefficients $a_{10}^{(1)}$ and $a_{10}^{(2)}$, on the other hand, are coupled by the dipolar forces. The equations that result from substituting Eq. (4.1) into Eq. (3.5) can be expressed as the matrix equation

$$\partial \mathbf{a}_{10}/\partial t = -\mathbf{M}\cdot\mathbf{a}_{10} , \tag{4.2a}$$

where $\mathbf{a}_{10}$ is a column matrix

$$\mathbf{a}_{10}(0,t) \equiv \begin{pmatrix} a_{10}^{(1)}(0,t) \\ a_{10}^{(2)}(0,t) \end{pmatrix} \tag{4.2b}$$

and $\mathbf{M}$ is a 2×2 matrix which we call the relaxation matrix

$$\mathbf{M} = \begin{pmatrix} (1+\lambda_{11})\gamma_1 & \lambda_{12} \\ \lambda_{21} & (1+\lambda_{22})\gamma_2 \end{pmatrix} \tag{4.2c}$$

where

$$\gamma_i \equiv \gamma_1^{(i)} = 2D_R^{(i)} . \tag{4.2d}$$

Equation (4.2a) can be easily solved subject to the initial conditions. In matrix form the solution of this equation is

$$\mathbf{a}_{10}(t) = \frac{1}{(s_+ - s_-)} \begin{pmatrix} [(s_+ + (1+\gamma_{22})\gamma_2)a_{10}^{(1)} & -\gamma_1\lambda_{12}a_{10}^{(2)}] \\ [-\gamma_2\lambda_{21}a_{10}^{(1)} & +(s_+ + (1+\lambda_{11})\gamma_1)a_{10}^{(2)}] \end{pmatrix} e^{s_+ t} - \frac{1}{(s_+ - s_-)} \begin{pmatrix} [s_- + (1+\lambda_{22})\gamma_2]a_{10}^{(1)} & -\gamma_1\lambda_{12}a_{10}^{(2)}] \\ [-\gamma_2\lambda_{21}a_{10}^{(1)} & +(s_- + (1+\lambda_{11})\gamma_1] \end{pmatrix} e^{s_- t} . \tag{4.3a}$$

The other coefficients are

$$\mathbf{a}_{1\pm1}(t) = \begin{pmatrix} a_{1\pm1}^{(1)}(0)\,e^{-\gamma_1 t} \\ a_{1\pm1}^{(2)}\,e^{-\gamma_2 t} \end{pmatrix} , \tag{4.3b}$$

where the roots are

$$s_\pm = -\tfrac{1}{2}[(1+\lambda_{11})\gamma_1 + (1+\lambda_{22})\gamma_2] \pm \tfrac{1}{2}\{[(1+\lambda_{11})\gamma_1 - (1+\lambda_{22})\gamma_2]^2 + 4(\lambda_{11}\gamma_1)(\lambda_{22}\gamma_2)\}^{1/2} . \tag{4.3c}$$

Now the correlation function required for dielectric relaxation is

$$\phi(t) = \sum_{m=-1}^{1} \psi_m(t) \Big/ \sum_{m=-1}^{m} \psi_m(0) , \tag{4.4}$$

where

$$\psi_m(t) \equiv \sum_{iv} \mu_i \langle a_{lm}^{(i)*}(0) a_{lm}^{(v)}(t)\rangle \mu_v . \tag{4.5}$$

The static correlation coefficients are defined as

$$G_m(iv) \equiv \langle a_{lm}^{(i)*}(0) a_{lm}^{(v)}(0)\rangle = \left\langle \sum_{\alpha\in i} \sum_{\beta\in i} Y_{lm}^*(\mathbf{u}_\alpha) Y_{lm}(\mathbf{u}_\beta)\right\rangle . \tag{4.6}$$

These are real numbers. It is clear that $G_m(iv) = G_m^*(vi)$. Now from the preceding

$$\psi_{\pm1}(t) = \sum_v \left[\sum_i \mu_i G_{\pm1}(iv)\mu_v\right] e^{-\gamma_v |t|} . \tag{4.7}$$

These functions behave in the manner specified by Debye. $\psi_0(t)$ however decays in a more complicated manner. In fact,

$$\psi_0(t) = \frac{1}{(s_+ - s_-)}\{\psi_+ e^{s_+|t|} - \psi_- e^{s_-|t|}\} , \tag{4.8a}$$

where

$$\psi_\pm \equiv [\mu_1^2 G_0(1,1)(s_\pm + (1+\lambda_{22})\gamma_2) + \mu_2^2 G_0(2,2)(s_\pm + (1+\lambda_{11})\gamma_1) - \mu_1\mu_2 G_0(1,2)\gamma_1\lambda_{12} - \mu_2\mu_1 G_0(2,1)\gamma_2\lambda_{21}] . \tag{4.8b}$$

From Eq. (4.3c) it can be seen that the decay constants $s_\pm$ are very complicated and involve the ordinary Debye decay rates in a complicated manner.

In the event that molecule 1 is considerably larger than 2 and has a larger dipole moment (that is $\gamma_1 \ll \gamma_2$ but $\mu_1 \gg \mu_2$), then the roots simplify. To first order in γ, they become

$$\begin{aligned} s_+ &= -[(1+\lambda_{22})\gamma_2 + (1+\lambda_{11})\gamma_1] + \gamma_1\left(1 + \frac{\lambda_{11}}{1+\lambda_{22}}\right) \\ s_- &= -\gamma_1\left(1 + \frac{\lambda_{11}}{1+\lambda_{22}}\right) . \end{aligned} \tag{4.9}$$

This indicates that the smaller molecules screen the dipole moment of the larger ones, whereas the larger molecules do not screen the dipole moments of the smaller ones. This is analogous to translational diffusion in polyelectrolyte solutions where the presence of small counterions enhances the translational diffusion coefficient of the polyion.

V. ROTATIONAL RELAXATION IN ELECTROLYTE SOLUTIONS

In this section we consider the orientational correlation functions in electrolyte solutions,[12] in which the linear molecule, component 1, is assumed to have a dipole moment μ_1 and no net charge and the electrolyte solution consists of two oppositely charged spherical ions of charge z_2 and z_3 and concentration ρ_2 and ρ_3. Although H_2O is not a linear molecule, it is clear that this should reflect on aqueous electrolyte solutions. In this case it is easy to show from Eq. (3.3b) that, for $i, v = 1, 2, 3$,

$$T_{JK}^{lm}(1,1) = \lambda_1\gamma_1\delta_{lm10}\delta_{JK10} , \tag{5.1a}$$

$$T_{JK}^{lm}(1,v) = -\frac{i}{q}(\lambda_1 q_1^2)^{1/2}\left(\frac{\rho_1}{\rho_v}\right)^{1/2}\hat{z}_v\gamma_1\delta_{lm10}\delta_{JK00} , \quad v = 2,3 \tag{5.1b}$$

$$T_{JK}^{lm}(\mu,v) = \left(\frac{z_v}{z_\mu}\right) q_\mu^2 D_\mu \delta_{lm00}\delta_{JK00} , \quad \mu, v = 2, 3 \tag{5.1c}$$

$$T_{JK}^{lm}(\mu,1) = \frac{i}{q}(\lambda_1 q_\mu^2)^{1/2}\left(\frac{\rho_\mu}{\rho_1}\right)^{1/2}\hat{z}_\mu D_\mu \delta_{lm00}\delta_{JK10} , \quad \mu = 2,3 \tag{5.1d}$$

where

$$\gamma_1 = (q^2 D_1 + 2D_R) , \tag{5.2a}$$

$$\lambda_1 = \tfrac{4}{3}\pi\rho_1\mu_1^2 , \tag{5.2b}$$

$$q_v^2 = 4\pi\beta z_v^2 \rho_v , \quad v = 2, 3 \tag{5.2c}$$

and where ρ_1, ρ_2, and ρ_3, and $\hat{z}_\mu$ are, respectively, the number concentration (cm^{-3}) of the three species and $\hat{z}_\mu$ is the sign of the charge μ. In the above, q_v is the inverse Debye screening length of the ionic species $v(=2,3)$, which is proportional to $\sqrt{c}$, where c is the salt concentration.

Combining Eqs. (3.2) and (5.1) it is seen that the coefficients $a_{lm}^{(i)}$ for $lm \neq (0,0)$, (1,0) evolve just as predicted on the basis of the usual Debye theory; that is, they are unaffected by the long range forces. The coefficients $a_{10}^{(1)}$, $a_{00}^{(2)}$, and $a_{00}^{(3)}$ on the other hand are coupled by the dipolar forces. The equations that result from substituting Eq. (5.1) into Eq. (3.5) can be expressed as the matrix equation

$$\partial \mathbf{a}/\partial t = -\mathbf{M}\cdot\mathbf{a}\,, \tag{5.3a}$$

where $\mathbf{a}$ is the column vector

$$\mathbf{a}(t) = \begin{pmatrix} a_{10}^{(1)}(0,t) \\ a_{00}^{(2)}(0,t) \\ a_{00}^{(3)}(0,t) \end{pmatrix} \tag{5.3b}$$

and $\mathbf{M}$ is a 3×3 matrix which we call the relaxation matrix:

$$\mathbf{M} = \begin{pmatrix} (1+\lambda_1)\gamma_1 & -i\left(\frac{q_2}{q}\right)\gamma_1\sqrt{\lambda_1}\left(\frac{\rho_1}{\rho_2}\right)^{1/2}\hat{z}_2 & -i\left(\frac{q_3}{q}\right)\gamma_1\sqrt{\lambda_1}\left(\frac{\rho_1}{\rho_3}\right)^{1/2}\hat{z}_3 \\ iqq_2\sqrt{\lambda_1}\left(\frac{\rho_2}{\rho_1}\right)^{1/2}D_2\hat{z}_2 & (q^2+q_2^2)D_2 & \left(\frac{z_3}{z_2}\right)q_2^2D_2 \\ iqq_3\sqrt{\lambda_1}\left(\frac{\rho_3}{\rho_1}\right)^{1/2}D_3\hat{z}_3 & \left(\frac{z_2}{z_3}\right)q_3^2D_3 & (q^2+q_3^2)D_3 \end{pmatrix}. \tag{5.3c}$$

Equation (5.3) can be solved by Laplace transforms. Let

$$\mathbf{a}(s) = \int_0^\infty dt\, e^{-st}\mathbf{a}(0,t) \tag{5.4}$$

be the Laplace transform of Eq. (5.3b). Applying the Laplace transform method to the solution of Eq. (5.3a) gives

$$\mathbf{a}(s) = (s\mathbf{I}+\mathbf{M})^{-1}\cdot\mathbf{a}(0,0)\,, \tag{5.5}$$

where $\mathbf{I}$ is the 3×3 identity matrix and $(s\mathbf{I}+\mathbf{M})^{-1}$ is the reciprocal of the matrix $(s\mathbf{I}+\mathbf{M})$.

The elements of $(s\mathbf{I}+\mathbf{M})^{-1}$ are each proportional to the determinant of an element of the cofactor matrix divided by $\det(s\mathbf{I}+\mathbf{M})$. Thus it is clear that the poles of $(s\mathbf{I}+\mathbf{M})^{-1}$ are the zero's of the denominator which is the $\det(s\mathbf{I}+\mathbf{M})$. Thus the poles are found by solving the dispersion equation

$$\det(s\mathbf{I}+\mathbf{M}) = 0\,, \tag{5.6}$$

which is a cubic equation. These roots (s_1, s_2, s_3) contribute to the Laplace inversion of Eq. (5.5) in that they are the decay rates in three exponentials e^{s_1t}, e^{s_2t}, and e^{s_3t}. The solutions of Eq. (5.3b) $a_{10}^{(1)}$, $a_{00}^{(2)}$, and $a_{00}^{(3)}$, are each consequently superpositions of these three exponentials. Thus without writing out the elaborate formulas, we can find the decay rates. It then turns out that in the limit $q\to0$

$$C_{10}(t) = \langle|a_{10}^{(1)}|^2\rangle \lim_{q\to0}\left[\frac{s_1(s_1+\gamma_0)}{(s_1-s_2)(s_1-s_3)}e^{s_1|t|} + \frac{s_2(s_2+\gamma_0)}{(s_2-s_1)(s_2-s_3)}e^{s_2|t|} + \frac{s_3(s_3+\gamma_0)}{(s_3-s_1)(s_3-s_2)}e^{s_3|t|}\right], \tag{5.7}$$

where the roots are to be evaluated for $q\to0$ and where

$$\gamma_0 \equiv q_2^2D_2 + q_3^2D_3 \tag{5.8}$$

is the reciprocal of the "ionic relaxation time" τ_0. τ_0 specifies the time scale on which deviations from local electroneutrality relax by diffusion back to this condition or, more exactly, the time it takes the ions to diffuse a distance equal to the ionic screening length.

All that remains is to compute the roots $(s_1s_2s_3)$ of the dispersion equation (5.6) which follows from Eq. (5.3c). After much tedious algebra this equation becomes in the limit $q\to0$

$$s^3 + [(1+\lambda_1)\gamma_1+\gamma_0]s^2 + \gamma_1\gamma_0 s = 0\,. \tag{5.9}$$

The roots in the limit $q\to0$ are

$$s_1 = 0,\quad s_2 = s_+,\quad s_3 = s_-\,, \tag{5.10a}$$

where

$$s_\pm = -\tfrac12[(1+\lambda_1)\gamma_1+\gamma_0] \pm \tfrac12\{[(1+\lambda_1)\gamma_1+\gamma_0]^2 - 4\gamma_1\gamma_0\}^{1/2}\,. \tag{5.10b}$$

It thus follows that

$$C_{10}(t) = \langle|a_{10}(0)|^2\rangle/(s_+-s_-) \times[(s_++\gamma_0)e^{s_+|t|} - (s_-+\gamma_0)e^{s_-|t|}]\,. \tag{5.11}$$

When Eq. (5.11) is added to the unaffected functions,

$$C_{1\pm1}(t) = \langle|a_{1\pm1}(0)|^2\rangle e^{-\gamma_1|t|}\,. \tag{5.12}$$

We find

$$\phi(t) = \tfrac13\{2e^{-\gamma_1|t|} + 1/(s_+-s_-)[(s_++\gamma_0)e^{s_+|t|} - (s_-+\gamma_0)e^{s_-|t|}\}\,. \tag{5.13}$$

Thus there are three relaxation times contributing to the $l=1$ correlation functions, these are $\gamma_1^{-1} = (2D_R)^{-1}$, s_+^{-1}, and s_-^{-1}.

One of the most interesting features of this solution is that the ionic relaxation time $\tau_0 = \gamma_0^{-1}$ contributes to the orientational relaxation times through $s_\pm$. Thus the dipole either must drag or is dragged by the ions, and depending on which moves faster, the rotating dipole or the translating ions, the roots will be different. In fact we can estimate the roots by perturbation theory in two limiting cases.

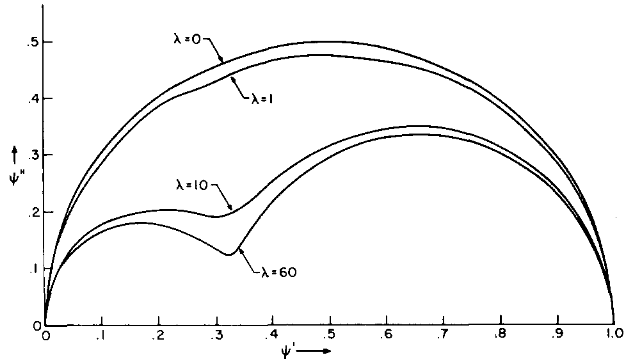

FIG. 1. Cole–Cole Plots of $\psi''(\omega)$ versus $\psi'(\omega)$ for various values of λ. $\psi'(\omega)$ and $\psi''(\omega)$ are, respectively, the real and imaginary parts of the Laplace transform of the function $\psi(t) = -d\phi(t)/dt$, where $\phi(t)$ is the orientational correlation function given by Eq. (2.19c). It should be noted that $\lambda = 0$ gives the Debye semicircle. The plots change dramatically as λ increases.

Case 1: $\gamma_1 \ll \gamma_0$. Here the ions relax much more rapidly than the period of the rotation. Then

$$\begin{aligned} s_+ &= -(\gamma_0 + \lambda_1\gamma_1) \\ s_- &= -\gamma_1 , \end{aligned} \tag{5.14a}$$

and

$$\phi(t) \simeq e^{-\gamma_1|t|} \tag{5.14b}$$

and we get the same result as in the Debye theory. Thus rapidly moving ions tend to screen the dipole–dipole interactions in such a way that we recover the original Debye relaxation.

Case 2: $\gamma_1 \gg \gamma_0$. Here the molecule rotates rapidly on the time scale of the ionic relaxation time. Then

$$s_\pm \simeq \begin{cases} -(1+\lambda_1)\gamma_1 - [\lambda_1/(1+\lambda_1)]\gamma_0 \\ -\gamma_0/(1+\lambda_1) , \end{cases} \tag{5.15a}$$

and, to a very good approximation

$$\phi(t) \simeq \tfrac{1}{3}(e^{-2\gamma_1|t|} + e^{-(1+\lambda_1)\gamma_1|t|}) . \tag{5.15b}$$

This is precisely the same form we obtained in a pure dipolar fluid. Slowly moving ions tend not to screen the dipoles. The roots are thus seen to be strongly dependent on γ_0 or concomitantly on the ionic concentration.

These effects should be seen in rotational relaxation in aqueous electrolyte solutions. As far as we know, these results are entirely new and give the only known dependence of the dielectric relaxation times on the ionic strength.

VI. CONCLUSIONS

It is clear from the foregoing simple self-consistent model that long range Coulomb and dipolar forces can "break" the symmetry usually ascribed to the Debye equation. The correlation functions $C_{lm}(q,t)$ defined by Eq. (1.3) which result from the linearized forced diffusion equation have the following properties.

(1) In the limit $q \to 0$ only monopole, and dipolar forces contribute to deviations from the Debye theory. Quadrupolar and higher multipolar forces are too short ranged to give rise to any effects.

(2) The Coulomb and dipolar forces only affect the decay of $C_{00}(q,t)$ and $C_{lm}(q,t)$ correlation functions. The higher ranked correlation functions are unaffected.

(3) In purely polar fluids the deviations from the Debye relaxation times are given by parameters like $\lambda_v = \frac{4}{3}\pi\beta\mu_v^2\rho_v$. These parameters can be substantial (~ 1) for dense fluids. For a neat fluid $1+\lambda$ is of order ϵ so that the longitudinal relaxation time has a screening of order $1/\epsilon$.

(4) In electrolyte solution, the deviations from the Debye relaxation times are not only determined by the parameters λ_v but also by the ionic relaxation times in such a way that at low ionic strengths, the relaxation times are $(1+\lambda_1)\gamma_1$, whereas for high ionic strengths, they are the same as in the Debye theory.

(5) In the polar mixtures the fast dipoles screen the dipole moments of the slow dipoles, whereas the slow dipoles do not effectively screen the dipole moments of the fast dipoles.

(6) Let

$$\psi(t) \equiv -d\phi/dt$$

and

$$\psi(\omega) = L\psi(t) = \psi'(\omega) - i\psi''(\omega) .$$

The Cole–Cole plot of $\psi''(\omega)$ versus $\psi'(\omega)$ of Fig. 1 shows that for attainable values of $\lambda(\sim 1)$, the Cole–Cole plot corresponding to Eq. (2.19c) deviates significantly from the Debye semicircle.

If the equation is not linearized, we conjecture that these conclusions will change in that all the C_{lm} will be affected. We hope to turn to this question in a subsequent paper where we shall use the techniques of mode-mode coupling theory.

In this paper the molecules were taken to be unpolarizable linear rigid dipoles. No real solution corresponds to this simplification. When the polarizability is included the problem becomes more complicated, for then the local forces should depend on gradients of expressions like $\frac{1}{2}\mathbf{E}\cdot\overleftrightarrow{\alpha}\cdot\mathbf{E}$ where $\overleftrightarrow{\alpha}$ is the local polarizability density and $\mathbf{E}$ is the local field (with analogous terms for the torques). This is clearly a nonlinear problem, and we hope to consider it in our subsequent work. To estimate the effects of polarizability, it might suffice to replace $4\pi\rho$ in the Poisson equation by $(4\pi/\epsilon_\rho$, where ϵ_ρ is a dielectric constant due to the polarizability $[(\epsilon_\rho - 1)/(\epsilon_\rho + 2) = \rho_0\alpha]$. Also the dipole moment of the linear molecules might be taken as an effective dipole moment.

Thus this paper should be regarded as a study of a simple model. The conclusions certainly point to interesting consequences of long range forces.

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[7] The operator $\nabla_u \equiv u \times \partial/\partial u$ is related to $\hat{l} \equiv -i(u \times \partial/\partial u)$, the dimensionless angular momentum operator of quantum mechanics; that is, $\nabla_u = i\hat{l}$ and $\nabla_u^2 = -\hat{l}^2$. It should be recalled that the spherical harmonics $Y_{lm}(u)$ are eigenfunctions of $\hat{l}^2$ corresponding to the eigenvalue $l(l+1)$.

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[9] It is nevertheless clear that a more complete theory must reckon with this nonlinear equation. Because the forces are long ranged, a kind of mode–mode coupling theory may be required. we hope to return to this in a future publication.

[10] This equation follows only after a Rayleigh expansion of the terms $e^{iq\cdot us}$ and use of the properties of l^2; that is, $l^2 Y_{lm} = l(l+1) Y_{lm}$.

[11] It should be noted that if $C_{1m}(q,t)$ of Eq. (2.19b) is spatially Fourier transformed, we find

$$C_{1m}(\mathbf{r},t) = [4\pi D_T(1+\delta_{m0}\lambda)t]^{-3/2} < |a_{lm}(0)|^2 > \times e^{-r^2/4(1+\lambda\delta_{m0})D_T|t|} e^{-2(1+\lambda\delta_{m0})D_R|t|} .$$

If this result is integrated over a spherical region of radius a, we find the $\phi(t)$ for a spherical region to be

$$\phi_{\text{sph}}(t) = \tfrac{2}{3} F_1(t) e^{-2D_R t} + \tfrac{1}{3} F_0(t) e^{-2D_R(1+\lambda)|t|},$$

where

$$F_m(t) = 4\pi[4\pi(1+\lambda\delta_{m0})D_T|t|]^{-3/2} \times \int_0^a dr\, r^2 e^{-r^2/4(1+\lambda\delta_{m0})D_R|t|}.$$

Thus the dielectric relaxation of a spherical region should contain effects of translational diffusion which give rise to fluctuations in the number of molecules in the sphere. Only for sufficiently large spheres or slow diffusors should particular effects be important if ever. Also if and when these effects are important, other hydrodynamic effects should be considered.

[12] Solutions consisting of two ions where ions of type 1 are linear molecules of charge z_1 and "dipole moment" μ_1 and ions of type 2 are spherical ions of charge z_2 behave in precisely the same manner.