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Molecular expression for dielectric friction on a rotating dipole: Reduction to the continuum theory

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Recently we presented a microscopic expression for dielectric friction on a rotating dipole. This expression has a rather curious structure, involving the contributions of the transverse polarization modes of the solvent and also of the molecular length scale processes. It is shown here that under proper limiting conditions, this expression reduces *exactly* to the classical continuum model expression of Nee and Zwanzig [J. Chem. Phys. **52**, 6353 (1970)]. The derivation requires the use of the asymptotic form of the orientation-dependent total pair correlation function, the neglect of the contributions of translational modes of the solvent, and also the use of the limit that the size of the solvent molecules goes to zero. Thus, the derivation can be important in understanding the validity of the continuum model and can also help in explaining the results of a recent computer simulation study of dielectric relaxation in a Brownian dipolar lattice.

I. INTRODUCTION

Dielectric friction, which is defined as the contribution of the long-range dipolar interactions to the total friction on a rotating dipolar molecule, has played a key role in rationalizing the experimental and theoretical studies carried out to understand orientational relaxation in dense polar liquids. A seminal study on this problem was that by Nee and Zwanzig.[1] In this elegant work the concept of dielectric friction was lucidly explained. The long-range nature and the dynamical effects of the dipolar interactions were taken into account through the frequency-dependent dielectric function. An expression for the dielectric friction ζ_{DF}, was obtained by calculating the reaction field experienced by the solute molecule. The zero-frequency limit of the dielectric friction ζ_{DF} is given by the simple expression,

$$\zeta_{DF} = \frac{2}{\beta} \frac{(\epsilon_0 - 1)^2}{\epsilon_0 (2\epsilon_0 + 1)} \tau_D, \qquad (1)$$

where $\beta = (k_B T)^{-1}$, k_B is the Boltzmann's constant, T is the absolute temperature, ϵ_0 is the dielectric constant of the solvent, and τ_D is its Debye relaxation time. Equation (1) is obtained from a more general expression by assuming that the frequency-dependent dielectric function is of Debye form. In Eq. (1) we have made the further simplifying assumption that both the solute and solvent molecules are nonpolarizable. Equation (1) is applicable only for a neat liquid as Nee and Zwanzig were interested in the dielectric relaxation of a one component dipolar liquid. Hubbard and Wolynes[2] have rewritten it in the following form which is more suitable for experimental applications where the solute molecule is different from the solvent molecules:

$$\zeta_{DF} = \frac{6\mu^2}{a^3} \frac{(\epsilon_0 - 1)}{(2\epsilon_0 + 1)^2} \tau_D, \qquad (2)$$

a is the radius of the molecular cavity that contains the solute dipole and μ is the dipole moment of the solute molecule in vacuum.

In deriving both the aforementioned expressions it was assumed that the dipolar solute molecule does not rotate significantly on the time scale of decay of the fluctuating torque acting on the solute molecule. In their important paper on orientational relaxation in dipolar liquids, Hubbard and Wolynes[2] have relaxed this assumption by evaluating the dielectric friction using a generalized Smoluchowski equation with fluctuating torques. The expression so obtained properly reduces to that of Nee and Zwanzig in the limit where the torque fluctuations are much more rapid than the reorientational relaxation of the solute. In both the theories a macroscopic continuum model was used to calculate the torque fluctuations. Similar macroscopic continuum model results were obtained for ζ_{DF} by many groups through different approaches.[3] All of them reduce to the expression of Nee and Zwanzig when proper identifications and approximations of the various parameters are made.

Madden and Kivelson[4] initiated a microscopic approach to the theory of dielectric friction by starting from a Mori continued fraction.[5] These authors evaluated the time-correlation functions by using the Zwanzig–Mori[6,7] projection operator technique. The work of Madden and Kivelson contained many nontrivial results. For example, the effects of translational motion and the anisotropic relaxation of the polarization induced by the rotating dipole in the surrounding medium, which were not taken into account in the macroscopic continuum theories, were included for the first time in this theory. The work of Madden and Kivelson remains a landmark in the field of di-

electric relaxation. Unfortunately, they used an approximate form for the pair-distribution funtion for calculating the ζ_{DF}. This approximation, even though it goes over to the correct asymptotic limit, washes out the effects of short-range interactions on the dipolar correlations and does not take into account the intermediate wave-vector contributions which are significant in the present problem. This is because the intermediate wave-vector regime is precisely the regime where the translational modes are important. Another important limitation of this theory is that it neglects the short-range structure of the liquid. Thus, the "orientational caging"[4] of a dipolar molecule in a dense dipolar liquid is neglected in the theory of Madden and Kivelson. Recent theoretical[8] and computer simulation studies[9] have shown that this "orientational caging" plays a very important role in the dynamics of dipolar liquid. Madden and Kivelson's expression for dielectric friction reduces to that of Nee and Zwanzig when the rotational motion of the solute, as well as the translational motion of the solvent molecules, were neglected. As pointed out by these authors, this is not surprising because the approximations made in the two theories are rather similar in nature.

Recently we presented a microscopic theory of dielectric friction on a rotating dipolar solute molecule.[10] This theory was based on a molecular hydrodynamic description of the coupled solute–solvent dynamics. The microscopic expression for the torque–torque correlation function involves two particle direct correlation functions of the solute–solvent interactions and also the coupled dynamics of the solute–solvent system. The contributions of the translational motion of the solvent molecules enters naturally in this theory which is similar to that of Madden and Kivelson in its objective but closer to that of Hubbard and Wolynes in spirit. The original version was somewhat limited in scope as it was based on a generalized Smoluchowski equation (derived from the extended hydrodynamic theory). The theory was subsequently extended to treat both non-Markovian and inertial regimes.[11,12] However, for the present reduction, the earlier work is sufficient. An important advantage of the molecular hydrodynamic approach is that the short-range (the nearest-neighbor) structure and interactions, which play an important role in the dynamics, can be included rather accurately.

However, the microscopic expression [given later by Eq. (6)] has a curious structure. It explicitly involves the contribution of the transverse polarization modes of the solvent. The expression is also quite complicated as it involves (in addition to the wave-vector-dependent longitudinal and transverse polarization relaxation times) the orientation-dependent pair-correlation function between the solute and the solvent molecules and also the direct correlation function for the solvent molecules themselves. Numerical calculation shows that, at moderate polarities of the solvent, the contribution of the dielectric friction can be significantly larger than the contribution of the Stokes friction due to viscosity. This effect arises because of angle-dependent short-range interactions. This implies a break-

down of the conventional Stokes relation between friction and viscosity. Because of these rather unusual predictions that the microscopic expression offers, it is important to analyze this expression carefully. Especially, it is important to show that this expression correctly goes over to the macroscopic, continuum expression of Nee and Zwanzig (also of Hubbard and Wolynes) in the appropriate limits.

The objective of this paper is to present such a derivation. In order to recover the continuum limit, we must work in the overdamped and Markovian limit of solvent dynamics. We find that by taking the asymptotic limit of the total pair-correlation functions, by neglecting the translational motion of the molecules and by considering the solute size to be much larger than the solvent molecular size our expression for ζ_{DF} goes over exactly to the Nee and Zwanzig expression. The derivation, however, is rather tricky, as we show later. We should also mention here that this derivation has been a subject of much discussion in the scientific community.[13,14]

Another motivation of the present study comes from a recent Brownian dynamics simulation study of dielectric relaxation in a simple cubic lattice (the Zwanzig lattice[15]).[16] In this work, it was discovered that the continuum model predicts too rapid a decay of the torque–torque time-correlation function to account for the observed behavior. The simulated correlation function has a much smaller value at $t=0$ and a slow long-time decay—the continuum model erred on both these accounts. Therefore, it is important to understand the approximations that are made at the microscopic level to recover the continuum model.

The organization of the rest of the paper is as follows. In Sec. II we present the microscopic expression in the overdamped, Markovian limit. In Sec. III, we present the derivation of the reduction of this expression to the continuum limit. Section IV concludes with a brief discussion of the significance of this result.

II. MICROSCOPIC EXPRESSION FOR DIELECTRIC FRICTION

As pointed out by Hubbard and Wolynes, the dielectric friction experienced by a rotating solute dipole, in the limit of a slowly rotating solute (that is solvent dynamics is faster than the solute rotation), can be expressed as a time integral over the torque–torque correlation function[2,8,10] as given by the equation

$$\zeta_{DF} = \frac{\beta}{2} \int_0^\infty dt \langle \tau[\Omega(0), t=0] \cdot \tau[\Omega(0), t] \rangle_\Omega, \qquad (3)$$

where $\langle \ \rangle_\Omega$ means an additional averaging over Ω. Here $\tau[\Omega(0), t]$ is the total torque experienced by the solute molecule with orientation $\Omega(0)$. In order to derive an expression for the fluctuating torque, we start with the following free-energy functional provided by the density-functional theory[8]

$$\beta\mathscr{F}[\rho_2(\Omega',t),\rho_1(r,\Omega,t)] = \int d\Omega'[\ln\{\rho_2(\Omega',t)\}-1]\rho_2(\Omega',t) + \int dr\, d\Omega\, \rho_1(r,\Omega,t)\left[\ln\left(\frac{\rho_1(r,\Omega,t)}{\rho_0/4\pi}\right)-1\right]$$

$$-\frac{1}{2}\int dr\, d\Omega\, dr'd\Omega'\, c_{11}(r,\Omega,r',\Omega')[\rho_1(r,\Omega,t)-(\rho_0/4\pi)][\rho_1(r',\Omega',t)-(\rho_0/4\pi)]$$

$$-\int dr\, d\Omega\, d\Omega'\, c_{12}(r,\Omega,\Omega')[\rho_1(r,\Omega,t)-(\rho_0/4\pi)][\rho_2(\Omega',t)-(1/4\pi)], \qquad (4)$$

where $\rho_2(\Omega,t)$ is the orientational density distribution of the solute and $\rho_1(r,\Omega,t)$ is the position (r) and orientation- (Ω) dependent density distribution of the solvent molecules, $c_{12}(r,\Omega,\Omega')$ is the two-particle direct correlation function between the solute (with orientation Ω') and the solvent molecules (with coordinates r and Ω). $c_{11}(r,\Omega,r',\Omega')$ is the two-particle direct correlation function of the solvent.[17] ρ_0 is the average number density of the liquid. When this free-energy functional is used in the limit of the zero solute density, the extended hydrodynamic equations provide the following expression for the torque in the Markovian overdamped limit:[10]

$$\tau(\Omega,t) = \frac{1}{\beta}\nabla_\Omega \int dr'\, d\Omega'\, c_{12}(r',\Omega',\Omega)$$

$$\times[\rho_1(r',\Omega',t)-(\rho_0/4\pi)]. \qquad (5)$$

We use this expression of torque in Eq. (3) to obtain the following expression for the dielectric friction on a dipolar solute:[10]

$$\zeta_{DF} = \frac{1}{2(2\pi)^4\beta}$$

$$\times\int dk \sum_{m=-1}^{1}[c_{12}^2(11m;k)\langle|a_{1m}(k)|^2\rangle\tau_{1m}(k)], \qquad (6a)$$

with

$$\langle|a_{1m}(k)|^2\rangle = \frac{N}{4\pi}\left(1+(-)^m\frac{\rho_0}{4\pi}h(11m;k)\right) \qquad (6b)$$

and

$$\tau_{1m}^{-1}(k) = 2D_R\left[[1+p'(k\sigma)^2]\left(1-(-1)^m\frac{\rho_0}{4\pi}(c11m;k)\right)\right], \qquad (6c)$$

where k is along the z axis of the laboratory fixed frame. The $h(11m;k)s$ are the Fourier transforms of the expansion coefficients of the total pair-correlation functions in terms of spherical harmonics.[17] In deriving Eq. (6) the pair-correlation function is assumed to be given by a linearized equilibrium theory. Hence, only the $c(11m;k)$'s are nonzero. This assumption is valid for not too strong polar dipolar liquids. The translational parameter p' is defined as $D_T/(2D_R\sigma^2)$, where D_T and D_R are the translational and rotational diffusion constants and σ is the solvent diameter. This dimensionless parameter gives a measure of the rela-tive importance of translation of the molecules to that of their rotation. Numerical calculations carried out show that p' plays an important role in determining the magnitude of ζ_{DF}. Even a small value of p' can decrease the magnitude of ζ_{DF} considerably. This is because the translational relaxation channels accelerate the relaxation of the intermediate wave-vector processes which are otherwise slow because of intermolecular correlations and make a rather large contribution to the dielectric friction. Equation (6) is interesting because of the following features. (1) It is based on a reliable microscopic theory for solute–solvent interactions. (2) The effects of molecular translation are included. (3) It incorporates the contributions from all wave vectors. (4) The structure as well as the dynamics of the liquid at intermediate and short wavelengths are taken into account through the direct correlation functions. This is in contrast to the earlier continuum theories which include the solvent dynamics only at the $k=0$ limit. (5) We have contributions from both (110) and (111) components of the solvent polarization. This anisotropic relaxation was neglected by Hubbard and Wolynes but considered by Madden and Kivelson. Note that τ_{10} and τ_{11} represent the longitudinal and transverse polarization relaxations of the dipolar solvent.[8]

III. REDUCTION TO THE CONTINUUM LIMIT

We expect the continuum limit to be valid when the interaction and also the correlation between the solute and any solvent molecule in the liquid is weak. In other words, the continuum model includes only the long-range (large r or small k) solvent effects on solute orientation. Therefore, it is appropriate to replace the solute–solvent pair correlation by its asymptotic value. It is known from the equilibrium theory of dipolar liquids that in the asymptotic limit the total pair-correlation function $h_{12}(r,\Omega,\Omega')$ is given by the simple expression[17,18]

$$h_{12}(r,\Omega,\Omega') = \frac{(\epsilon_0-1)^2}{(3Y)^2\epsilon_0}[-\beta U_{12}(r,\Omega,\Omega')], \qquad (7)$$

where $U_{12}(r,\Omega,\Omega')$ is the interaction potential between the solute dipole and a solvent molecule. $3Y=(4\pi/3)\rho_0\mu_1^2\beta$, where μ_1 is the dipole moment of the solvent. We go over to Fourier space for convenience with wave-vector k as the Fourier variable conjugate to r. Next both $U_{12}(k,\Omega,\Omega')$ and $h_{12}(k,\Omega,\Omega')$ are expanded in terms of spherical harmonics as

$$U_{12}(\mathbf{k},\Omega,\Omega') = \sum_{l_1 l_2 m} U_{12}(l_1 l_2 m;k) \, Y_{l_1 m}^{(\Omega)} Y_{l_2 \underline{m}}^{(\Omega')}, \qquad (8)$$

$$h_{12}(\mathbf{k},\Omega,\Omega') = \sum_{l_1 l_2 m} h_{12}(l_1 l_2 m;k) \, Y_{l_1 m}^{(\Omega)} Y_{l_2 \underline{m}}^{(\Omega')}. \qquad (9)$$

As mentioned before in a linearized theory only $(11m)$ components survive. We next assume that the short-range interaction between the dipolar solute and the solvent molecules is that of hard-core repulsion. That is, the solute–solvent interaction potential is dipolar hard spherical. Under this approximation, the Fourier transforms of the interaction potential harmonics are given by the following expressions:

$$U_{12}(110;k) = -2(4\pi)^2 \mu_1 \mu_2 \frac{j_1(kr_c)}{3(kr_c)}, \qquad (10)$$

$$U_{12}(111;k) = -(4\pi)^2 \mu_1 \mu_2 \frac{j_1(kr_c)}{3kr_c}, \qquad (11)$$

where μ_1 and μ_2 are the dipole moments of the solvent and solute molecules in vacuum, respectively. $j_1(kr_c)$ is the first-order spherical Bessel function and $r_c = a + \sigma/2$. Note that r_c is the distance of closest approach between the solute and the solvent molecules.

The asymptotic expression for the total correlation function [Eq. (7)] together with Eqs. (8)–(11) provide the required expressions for the Fourier transforms of the pair-correlation function harmonics. As the next ingredient, we need the following Ornstein–Zernike relation between the total and direct correlation functions

$$h_{12}(11m;k) = \frac{c_{12}(11m;k)}{1-(-1)^m c_{11}(11m;k)}. \qquad (12)$$

Next, the following approximations are also made for going over to the continuum limit. (i) The size of a solvent molecule is assumed to be negligibly small compared to the size of the dipolar solute, $r_c \simeq a$. (ii) The contribution from the translational motion of the solvent molecules is neglected by setting $p' = 0$. (iii) Onsager's expression for the dielectric constant is used for to express the interaction strength parameter $3Y$ in terms of the static dielectric constant of the medium. This expression is given by[19,20]

$$\frac{(\epsilon_0-1)(2\epsilon_0+1)}{3\epsilon_0} = 3Y. \qquad (13)$$

The aforementioned approximations lead to the following expression for the dielectric friction:

$$\zeta_{DF} = 108 \, \frac{\mu^2}{\pi a^3} \frac{(\epsilon_0-1)\epsilon_0}{(2\epsilon_0+1)^3} \frac{1}{2D_R} \int_0^\infty dy \, j_1^2(y). \qquad (14)$$

The reason for the simplicity of the integral in Eq. (14) is that the correlation function part of the relaxation time can be combined with the static correlations in Eq. (12) to give only $h^2(11m;k)$'s; the latter are given by Eqs. (10) and (11).

We are now only two steps away from the final result. An expression for $(2D_R)$ is required in the next step. The

relation between the microscopic (τ_m) and the macroscopic relaxation (τ_D) time is is given by the relation[21]

$$\tau_m \equiv (2D_R)^{-1} = \left(1 + \frac{\rho_0}{4\pi} c_{11}(111;k=0)\right)\tau_D. \qquad (15)$$

The transverse dielectric constant is related to $c_{11}(111;k)$ as[22]

$$\epsilon_T(k) = 1 + \frac{3Y}{1+(\rho_0/4\pi)c_{11}(111;k)}. \qquad (16)$$

The $k=0$ limit of $\epsilon_T(k)$ is the static dielectric constant ϵ_0. Using Eq. (16) in the $k=0$ limit with Onsager's expression for the dielectric constant, gives the following relation for $2D_R$:

$$(2D_R)^{-1} = \frac{2\epsilon_0+1}{\epsilon_0} \tau_D. \qquad (17)$$

If we substitute Eq. (17) for $(2D_R)$ in Eq. (14) and carry out the integration we obtain, for the dielectric friction,

$$\zeta_{DF} = \frac{6\mu^2}{a^3} \frac{(\epsilon_0-1)}{(2\epsilon_0+1)^2} \tau_D \qquad (18)$$

which is precisely the same as Eq. (2). This can be reduced exactly to Eq. (1) (as discussed by Hubbard and Wolynes) if Onsager's expression is used to remove μ^2/a^3 in favor of ϵ_0.

IV. CONCLUSIONS

In this article we have shown that the microscopic expression for dielectric friction derived earlier by us reduces exactly to the continuum model expression of Nee and Zwanzig. Although one would expect this reduction on physical grounds, the reduction is by no means trivial, as demonstrated by the derivation presented here. Perhaps the most interesting of the steps involved is the use of the polarization relaxation times $\tau_L(k)$ and $\tau_T(k)$ in Eq. (6) and the subsequent simplification of the expression, Eq. (14). This is certainly one of the clearest demonstrations of the reduction of a microscopic expression to a continuum limit result. This is also important because a similar reduction has not yet been possible for the translational dielectric friction on a ion moving in a dipolar liquid.[23,24] We should point out here that Hubbard[25] has performed earlier an elegant electrohydrodynamic calculation of the friction on a rotating dipole and found agreement with the Nee–Zwanzig theory in the "perfect slip" limit. The point is that hydrodynamic motions of the fluid vanish for a rotating sphere with slip but not for a translating sphere with slip.

There has been some confusion regarding the involvement of the transverse component of the polarization relaxation in solvation dynamics and in dielectric phenomena.[13,14,26–29] Loring and Mukamel[26] suggested that the transverse component of the polarization component should not contribute to solvation dynamics. However, it is shown here, and also in the work of Madden and Kivelson,[3] that the transverse component naturally enters into the picture when the dynamics of a dipolar solvent is con-

sidered. There is no contradiction between these two results as the suggestion of Loring and Mukamel pertains to the electrostatic field of a dipole which is involved in the solvation dynamics. Here we are involved in the correlation functions.

Lastly, we comment on the relation of the present study with the recent work of Zhou and Bagchi[16] who presented a detailed Brownian dynamics study of dielectric relaxation in a Brownian dipolar simple cubic lattice. It was observed that one of the main reasons of the breakdown of the continuum model of Nee and Zwanzig is that the continuum model predicts too rapid a decay of the torque–torque correlation function to account for the observed dielectric behavior. The present derivation suggests that this may be due to the neglect of the short-range orientational correlations that are known to give rise to slow decay of the longitudinal component of the solvent polarization relaxation.[8] Numerical calculations have indicated that these short-range correlation can make a significant contribution to the dielectric friction,[10] especially in the absence of the translational motion of the solvent molecules. In this respect the situation is somewhat similar to ionic solvation dynamics in the sense that a significant translational contribution can bring the microscopic result similar to the continuum model prediction,[30] as the importance of the short-range correlations decrease with the increase in the translational contribution.

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