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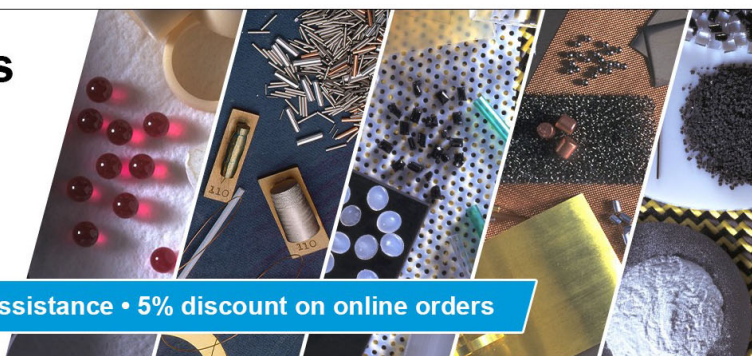J. Chem. Phys. **17**, 686 (1949); 10.1063/1.1747370

Dielectric friction and polar molecule rotational relaxation

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Using the Onsager cavity model the frequency dependent torque due to the long range dipole–dipole interaction is derived for an electric dipole rotating in a polar liquid. This generalizes to all orders the result first order in the angular velocity derived by Fatuzzo and Mason and by Nee and Zwanzig. For a constant angular velocity the dielectric frictional torque on a rotor is shown to depend upon the complex permittivity only at the frequency of rotation and has no zero frequency contribution as given by the first order theory. The effect of dielectric friction upon the rotational Einstein relation and the second fluctuation–dissipation theorem is derived. Unlike the first order theory and consistent with the suggestion of Hubbard and Wolynes this theory invalidates the rotational Einstein relation when long range dipolar coupling effects are included in the theory of rotational relaxation. The first order theory is valid only for high angular frequencies above $(2kT/I_{\perp})^{1/2}$. The formulation presented in this report is most conveniently applicable when significant inertial effects are present. In a sample calculation for highly compressed polar gases it is shown that dielectric friction produces a contribution to the angular momentum relaxation time second order in the gas density. This contribution is significant for rapidly rotating polar molecules of small moment of inertia at number densities above 2×10^{21} cm^{-3}.

I. INTRODUCTION

In the Onsager cavity model for the dielectric constant of a nonassociative polar liquid, one considers a molecule at the center of a spherical cavity inside the dielectric treated as a continuum at the cavity walls. The extension of this model to the frequency dependent complex permittivity has been considered by many authors.[1-8] This model is an approximation to more general theories relating the complex permittivity to the dipole autocorrelation function of an embedded microsphere sufficiently large to be treated as a material with a complex permittivity the same as that of the whole dielectric specimen.[9-12] The cavity model is employed to make tractable the calculation of the complex permittivity in terms of individual molecular processes. The justification for this is that a microscopic model of slowly rotating molecules in Onsager cavities gives a relation between the dipole autocorrelation function and the complex permittivity consistent with the more general theories.[5,9] In this paper the cavity model is employed for both polar liquids and dense polar gases as an approximate theoretical basis for calculating the effect of the long range dipole–dipole forces on molecular rotational relaxation.

Dielectric friction is the common name ascribed to the essentially many body coupling of a polar molecule with its surroundings by the long range dipole–dipole interaction. It refers in practice to the torque exerted by the reaction field on the molecule as it rotates in the cavity. This torque has been approximated to first order in the angular velocity by several authors[4,5,8,13,14] by assuming that the dipole rotation is sufficiently "slow." Such derivations do not provide a precise criterion for slow rotation as distinct from "fast" rotation, nor do they present an analysis of whether dipole rotation in actual polar liquids satisfy the slow rotation criterion. Hubbard and Wolynes[15] have pointed out that slow rotation corresponds to a molecular reorientational relaxation time which is large compared with the character-

istic relaxation time of spontaneous cavity field fluctuations. This condition is not satisfied in pure polar liquids but can be for large foreign polar molecules dissolved in a relatively fast relaxing polar solvent. Employing a rotational Smoluchowski equation, Hubbard and Wolynes extend the slow rotation theory to cover the pure dipole liquid case correctly and apply it to the calculation of all Legendre polynomial time correlation functions of dipole orientational relaxation. As they suggest, dielectric friction for permanent dipole dielectrics may be observable by comparing the results from a battery of experiments sensitive to different orders of orientational relaxation.

This paper presents an alternative, and in formal terms, a more general treatment of the rotational dielectric friction problem than the approach of Hubbard and Wolynes. The approach here is to calculate the frequency dependent dielectric frictional torque to all orders in the angular velocity and then to deduce the resultant consequences for the rotational Einstein relation and the second fluctuation–dissipation theorem. Both this and the Hubbard and Wolynes treatment emphasize the general inadequacy of the slow rotation approximation where only a first order angular velocity treatment is used. Indeed, the theory presented here shows that a constant angular frequency equal to $\omega_{\perp} = (2kT/I_{\perp})^{1/2}$ characteristic of the Maxwell–Boltzmann distribution should be regarded as a fast rotation rather than a slow rotation for the purpose of calculating dielectric friction effects. Whereas the rotational Einstein relation fails in the Hubbard and Wolynes treatment because the characteristic relaxation time for cavity field spontaneous fluctuations is not significantly smaller than the dipolar reorinetation time, the rotational Einstein relation fails in our formulation because all powers of the angular velocity contributing to the dielectric friction effect are needed.

Unfortunately, the theory presented here is not easily applied to the small angle rotational diffusion case considered by Hubbard and Wolynes because the general ex-

pression for the frequency dependent rotational diffusion constant is dynamical model dependent and not expressible in terms of the complex permittivity alone as is possible with the first order theory. The theory is more appropriately applicable to large angle rotational diffusion or quasifree rotational motion. In this case the generalized second fluctuation–dissipation theorem may be applied to deduce the frequency dependent friction tensor and hence the dielectric friction contribution to the angular momentum relaxation rate $\tau_{J_\perp}^{-1}(\omega)$ may be deduced. A calculation of $\tau_{J_\perp}^{-1}(0)$ including dielectric friction effects is performed in Sec. V for polar molecules in a highly compressed rigid dipolar gas. This is believed to be the first attempt to perform such a calculation and is made possible only by the development for the cavity model of the formally exact solution to the dielectric friction problem. Dielectric friction in gas phase rotational relaxation proves to be important only for highly polar molecules of small moment of inertia and for number densities above 2×10^{21} cm^{-3}. The contribution to $\tau_{J_\perp}^{-1}(0)$ due to dielectric friction is quadratic in the gas density.

An important result is that the first order theory remains true at angular frequencies much larger than $\omega_\perp$ for a gas phase, quasifree rotation theory. In liquids the situation for high frequency rotational relaxation is less clear; however, one may expect on physical grounds the first order theory to apply down to the much lower frequencies nearer $\omega_\perp$. As pointed out in an earlier paper,[16] the functional dependence upon the complex permittivity $\epsilon(\omega)$ of the first order dielectric friction contribution to the orientational relaxation time for a rigid dipole dielectric is the same as the total dielectric friction effect in a harmonic oscillator dielectric satisfying the well-known frequency dependent Clausius–Mosotti relation. This enables dipolar plasmons to be treated within the context of a single pseudo-oscillator theory which incorporates the harmonic oscillator dielectric and the plasma as other special examples. The approximate validity of the first order theory for dipolar dielectrics at high frequencies enables the original Lobo, Robinson, and Rodriguez[17] theory of dipolar plasmons to be retained.

II. DERIVATION OF THE DIELECTRIC FRICTION TORQUE

We follow Nee and Zwanzig,[8] who considered a molecule of vacuum permanent electric dipole moment $\mu_v(t)$ and isotropic polarizability χ_∞ at the center of a spherical cavity of radius a. The polarizability is related to the dielectric constant ϵ_∞ by $(\epsilon_\infty - 1)/(\epsilon_\infty + 2) = \chi_\infty/a^3$ at frequencies where the refractive index $n = \epsilon_\infty^{1/2}$ is insensitive to molecular rotation. We assume that the appropriate electric dipole moment undergoing rotational diffusion is the shielded moment $\mu(t) = \frac{1}{3}(\epsilon_\infty + 2)\mu_v(t)$.

A reaction field $\mathbf{R}(t)$ is produced at the molecule due to its polarization of the surrounding dielectric, approximated as a continuum. There is a dielectric frictional torque $\mathbf{N}(t) = \mu(t) \times \mathbf{R}(t)$ exerted on the molecule. The reaction field is related to $\mu(\theta)$ for all $\theta \leqslant t$ by

$$\mathbf{R}(t) = \int_{-\infty}^{t} \mu(\theta) g(t - \theta) \, d\theta, \tag{1}$$

where

$$g(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{+i\omega\tau} \tilde{g}(\omega) d\omega \quad \tau \geqslant 0$$
$$= 0 \qquad\qquad\qquad \tau < 0$$

and

$$\tilde{g}(\omega) = \frac{2(\epsilon(\omega) - \epsilon_\infty)}{\epsilon_\infty(2\epsilon(\omega) + \epsilon_\infty)} \frac{1}{a^3}, \tag{2}$$

where $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ is the complex permittivity. Defining $\tilde{\mathbf{N}}(\omega) = \int_{-\infty}^{\infty} \mathbf{N}(t)e^{-i\omega t}dt$, we may write

$$\tilde{\mathbf{N}}(\omega) = \int_0^\infty g(\tau)e^{-i\omega\tau}d\tau \int_{-\infty}^\infty e^{-i\omega\theta}\mu(\theta + \tau) \times \mu(\theta)d\theta. \tag{3}$$

$\mu(\theta + \tau)$ can be expanded out as a Taylor series in τ. Let us define

$$\mathbf{S}_n^j(\theta) = \left(\frac{1}{i\omega}\right)^{n+j} \mu^{(n)}(\theta) \times \mu^{(j)}(\theta), \tag{4}$$

where $\mu^{(n)}(\theta)$ denotes the nth derivative with respect to θ.

Also define the vectors

$$\mathbf{T}_j(\omega;\tau) = \sum_{n=j+1}^{\infty} \frac{(i\omega\tau)^n}{n!} \int_{-\infty}^{\infty} e^{-i\omega\theta}\mathbf{S}_n^j(\theta)d\theta;$$
$$\tau \geqslant 0, \quad j = 0, 1, 2, \ldots$$
$$= 0 \quad \tau \leqslant 0. \tag{5}$$

Equation (3) is just

$$\tilde{\mathbf{N}}(\omega) = \int_0^\infty g(\tau)\mathbf{T}_0(\omega;\tau)e^{-i\omega\tau}d\tau. \tag{6}$$

Later analysis shows that $\tilde{\mathbf{N}}(\omega)$ is best written as a convolution of the Fourier–Laplace transforms of $g(\tau)$ and $\mathbf{T}_0(\omega;\tau)$. Thus, we may write

$$\tilde{\mathbf{N}}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{g}(\omega')\tilde{\mathbf{T}}_0(\omega;\omega - \omega')d\omega', \tag{7}$$

where

$$\tilde{\mathbf{T}}_0(\omega;\omega - \omega') = \int_0^\infty e^{-i(\omega - \omega')\tau}\mathbf{T}_0(\omega;\tau)d\tau.$$

Note that the displacement $\omega \to \omega - i\delta$, δ small and positive, is to be made so that the integrands go to zero for $\tau \to \infty$.

If we regard dielectric friction as turned on asymptotically at $\theta \to -\infty$, we may derive the useful identity

$$\int_{-\infty}^{+\infty} e^{-i\omega\theta}\mathbf{S}_n^j(\theta)d\theta = \int_{-\infty}^{\infty} e^{-i\omega\theta}\mathbf{S}_{n-1}^j(\theta)d\theta - \int_{-\infty}^{\infty} e^{-i\omega\theta}\mathbf{S}_{n-1}^{j+1}(\theta)d\theta. \tag{8}$$

Equation (8) may be used to set up a hierarchy of coupled equations for the $\mathbf{T}_j(\omega;\tau)$. The case $n = j + 1$ in Eq. (8) leads to a trivial result because $\mathbf{S}_{j+1}^j(\theta) = -\mathbf{S}_j^{j+1}(\theta)$. Also, $\mathbf{S}_j^j(\theta) = 0$. The Fourier Transform of $\mathbf{S}_{j+1}^j(\theta)$ is not further reducible using Eq. (8) and must enter as an independent quantity in the final formula for the torque. By differentiating $\mathbf{T}_j(\omega;\tau)$ with respect to τ once and using Eq. (8) for $n > j + 1$, we find

$$\frac{dT_j(\omega, x)}{dx} - T_j(\omega, x)$$

$$= \frac{x^j}{j!} X_j - T_{j+1}(\omega, x); \quad j = 0, 1, 2, \ldots, \tag{9}$$

where $x = i\omega\tau$ and

$$X_j = \int_{-\infty}^{\infty} e^{-i\omega\theta} S_{j+1}^j(\theta) d\theta. \tag{10}$$

Equation (9) can be solved by Fourier–Laplace transforms. We write $\tilde{T}_j(\omega; \omega - \omega') = \tilde{T}_j(\omega, s)$, where $s = (1 - \omega'/\omega)$ and where

$$\tilde{T}_j(\omega; s) = \frac{1}{i\omega} \int_0^{\pm i\infty} e^{-sx} T_j(\omega; x) dx.$$

The sign of the upper limit here depends upon the sign of ω. Again taking care that the integrands go to zero as $\tau \to \infty$, we find the following hierarchy of equations:

$$(s - 1)\tilde{T}_0(\omega; s) = \frac{1}{i\omega} \frac{1}{s} X_0 - \tilde{T}_1(\omega; s),$$

$$(s - 1)\tilde{T}_1(\omega; s) = \frac{1}{i\omega} \frac{1}{s^2} X_1 - \tilde{T}_2(\omega; s),$$

$$\vdots$$

$$(s - 1)\tilde{T}_j(\omega; s) = \frac{1}{i\omega} \frac{1}{s^j} \tilde{X}_j - \tilde{T}_{j+1}(\omega; s)$$

$$\vdots$$

from which the required solution is

$$\tilde{T}_0(\omega; \omega - \omega') = \frac{1}{i\omega} \sum_{k=0}^{\infty} X_k \left(\frac{-1}{s(s-1)}\right)^{k+1}$$

$$= \sum_{k=0}^{\infty} \tilde{Y}_k(\omega) \left(\frac{1}{\omega'(\omega' - \omega)}\right)^{k+1}, \tag{11}$$

where

$$\tilde{Y}_k(\omega) = \int_{-\infty}^{\infty} e^{-i\omega\theta} \mu^{(k)}(\theta) \times \mu^{(k+1)}(\theta) d\theta. \tag{12}$$

Substituting Eq. (11) into Eq. (7) leads to

$$\tilde{N}(\omega) = \sum_{k=0}^{\infty} \tilde{Y}_k(\omega) \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{g}(\omega') \left(\frac{1}{\omega'(\omega' - \omega)}\right)^{k+1} d\omega'. \tag{13}$$

Causality requires that $\tilde{g}(\omega')$ has all singularities above the real ω' axis. The other singularities in the integrand of Eq. (13) are at $\omega' = 0 - i\delta$, $\omega' = \omega - i\delta$ and are below the real ω' axis. The contour integrations can can be completed below the real ω' axis so that only these two singularities contribute.

It can be shown by induction that

$$\left(\frac{1}{\omega'(\omega' - \omega)}\right)^{k+1} = \left(\frac{1}{\omega}\right)^{k+1} \sum_{l=0}^{k} \left(\frac{(-1)}{\omega}\right)^l \frac{(k+l)!}{l! k!}$$

$$\times \left[\left(\frac{1}{\omega' - \omega}\right)^{k+1-l} + \left(\frac{-1}{\omega'}\right)^{k+1-l}\right]. \tag{14}$$

The proof of Eq. (14) is facilitated by the relations

$$\sum_{l=0}^{n} \frac{(k+l)!}{l! k!} = \frac{(k+1+n)!}{n!(k+1)!} \quad 0 \le n < k,$$

$$\sum_{l=0}^{k} \frac{(k+l)!}{l! k!} = \frac{1}{2} \frac{(2k+2)!}{(k+1)!(k+1)!},$$

$$\left(\frac{1}{\omega' - \omega}\right)^n \frac{1}{\omega'} = \left(\frac{(-1)}{\omega}\right)^n \frac{1}{\omega'} - \sum_{m=0}^{n-1} \left(\frac{(-1)}{\omega}\right)^{m+1} \left(\frac{1}{\omega' - \omega}\right)^{n-m},$$

$$\left(\frac{(1)}{\omega'}\right)^n \frac{1}{\omega' - \omega} = \left(\frac{(1)}{\omega}\right)^n \frac{1}{\omega' - \omega} - \sum_{m=0}^{n-1} \left(\frac{(1)}{\omega}\right)^{m+1} \left(\frac{(1)}{\omega'}\right)^{n-m}.$$

Employing Eq. (14) in Eq. (13) and completing the contour integral below the real ω' axis term by term for each k and l produces the final result

$$\tilde{N}(\omega) = \frac{1}{i\omega} \sum_{k=0}^{\infty} \sum_{l=0}^{k} (-1)^l \left(\frac{(1)}{\omega}\right)^{k+l} \tilde{Y}_k(\omega) \frac{(k+l)!}{l! k!}$$

$$\times (\tilde{g}(\omega)^{(k-l)} - (-1)^{k-l} \tilde{g}(0)^{(k-l)}). \tag{15}$$

Equation (15) is valid for arbitrary dipole motion as no particular assumptions about it have been made. When the dipole $\mu(t)$ is rigid, that is, when there is no significant vibration on a time scale shorter than one full dipole rotation, we can define a set of ω dependent vectors $\tilde{\Omega}_k(\omega)$ by $\tilde{Y}_k(\omega) = \mu^2 \tilde{\Omega}_k(\omega)$ and the set of friction coefficients $\tilde{\zeta}_k(\omega)$ so that Eq. (15) becomes

$$\tilde{N}(\omega) = -\sum_{k=0}^{\infty} \tilde{\zeta}_k(\omega) \tilde{\Omega}_k(\omega).$$

The first term, $k = 0$, of Eq. (14) is exactly the first order result of Nee and Zwanzig[8] where $\tilde{\Omega}_0(\omega) = \Omega_\perp(\omega)$ is the Fourier transform of the component of the angular velocity $\Omega(t)$ perpendicular to $\mu(t)$. For $k > 0$, $\Omega_k(\omega)$ cannot be simply expressed in terms of $\tilde{\mu}(\omega)$ and $\tilde{\Omega}_\perp(\omega)$ alone. Indeed, $\mu^{(k)}(t) \times \mu^{(k+1)}(t)$ depends upon $\mu(t)$ and $\Omega(t)$ and the time derivatives of $\Omega(t)$. In the following sections we shall be mainly concerned with special cases where the $k > 0$ terms are relatively simple, in particular where the molecular rotation is perturbed significantly only on a time scale longer than one full rotation of the molecule. However, more generally applicable expressions for the angular momentum correlation tensor and the second fluctuation–dissipation theorem are also derived. Application to particular problems cannot be divorced from specific kinematical and dynamical considerations of molecular reorientation and the theory loses the inherent simplicity of the first order theory which can be expressed in terms of the complex permittivity alone.

III. APPLICATION TO CONSTANT ANGULAR VELOCITY ROTATION

A difficulty arises if we attempt to use Eq. (15) to obtain the $k \ge 1$ corrections to the first order theory $(k = 0)$. To demonstrate this we consider the case of a constant precessional angular velocity Ω_J for a symmetric top molecule with the electric dipole moment along the symmetric axis. Let $I_\parallel$ and $I_\perp$ denote the moments of inertia parallel to and perpendicular to the figure axis, respectively. Ω_J is related to the angular momentum J by $\Omega_J = J/I_\perp$ and of course must be distinguished from the total angular velocity Ω which relates to J through the moment of inertia tensor I by the equation $J = I \cdot \Omega$.

Let θ be the angle between $\mu(t)$ and Ω_J. Let $\hat{k}$ be the unit vector parallel to Ω_J and let $\hat{n}(t)$ be the unit vector perpendicular to $\hat{k}$ and passing through the symmetry axis. We write $\hat{u}(t) = \mu(t)/\mu$ for the unit vector along μ.

Then we have

$$\hat{u}(t) = \cos\theta\,\hat{k} + \sin\theta\,\hat{n}(t),$$

where

$$\hat{n}(t) = \hat{i}\,\cos\Omega_J t + \hat{j}\,\sin\Omega_J t.$$

$\Omega_0(t) = \hat{u} \times \hat{u}^{(1)}$ leads to the result

$$\Omega_0(\omega) = 2\pi\delta(\omega)\sin^2\theta\Omega_J - \Omega_J\sin\theta\cos\theta\,\hat{n}(\omega), \tag{16}$$

where $\delta(\omega)$ is the Dirac δ function and

$$\hat{n}(\omega) = \hat{i}\,\frac{i\omega}{\Omega_J^2 - \omega^2} + \hat{j}\,\frac{\Omega_J}{\Omega_J^2 - \omega^2}. \tag{17}$$

For $k \geq 1$, $\hat{u}^{(k)}(t) \times \hat{u}^{(k+1)}(t)$ is easily calculated whereupon it is found that $\hat{n}(\omega)$ does not contribute to $\tilde{\Omega}_k(\omega)$ and we obtain

$$\tilde{\Omega}_k(\omega) = 2\pi\delta(\omega)\sin^2\theta\,\Omega_J^{2k}\,\Omega_J. \tag{18}$$

We see that only $\omega = 0$ determines the contribution to the frictional torque from the higher order $k \geq 1$ terms.

In the limit $\omega \to 0$ we take the complex permittivity given by the Debye formula

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau_M},$$

which leads to

$$\tilde{g}(\omega) - \tilde{g}(0) = \tilde{g}(0)\,\frac{-i\omega\tau_G}{1 + i\omega\tau_G}, \tag{19a}$$

where

$$\tilde{g}(0) = \frac{2(\epsilon_0 - \epsilon_\infty)}{\epsilon_\infty(2\epsilon_0 + \epsilon_\infty)}\,\frac{1}{a^3} \tag{19b}$$

and

$$\tau_G = \frac{3\epsilon_\infty}{2\epsilon_0 + \epsilon_\infty}\,\tau_M. \tag{19c}$$

Using Eqs. (18) and (19) in Eq. (15) we find that all terms for $k \geq 1$ individually diverge for $\omega \to 0$. Thus, the first order theory or slow rotation theory breaks down, at least in the constant angular velocity case, as it is the first term of a series, all subsequent terms of which individually diverge. The series as a whole does converge however.

To evaluate $\tilde{N}(\omega)$ it is more convenient to return to Eq. (13) and perform the summation over k before doing the contour integration. We find

$$\sum_{k=0}^{\infty} \tilde{\Omega}_k(\omega)\left(\frac{1}{\omega'(\omega'-\omega)}\right)^{k+1}$$
$$= \frac{2\pi\Omega_J\delta(\omega)\sin^2\theta}{\omega'(\omega'-\omega) - \Omega_J^2} - \frac{\Omega_J\sin\theta\cos\theta\,\hat{n}(\omega)}{\omega'(\omega'-\omega)}.$$

The first term on the RHS has poles at $\omega_\pm$, where

$$\omega_\pm = \tfrac{1}{2}\omega \pm \tfrac{1}{2}(\omega^2 + 4\Omega_J^2)^{1/2}. \tag{20}$$

The integrals over ω' can be evaluated leading to the result

$$\tilde{N}(\omega) = \frac{-2\pi\mu^2\sin^2\theta\,\delta(\omega)\Omega_J}{i(\omega^2 + 4\Omega_J^2)^{1/2}}\,[(\tilde{g}(\omega_-) - \tilde{g}(\omega_+)]$$
$$- \frac{\mu^2\sin\theta\cos\theta\,\Omega_J\,\hat{n}(\omega)}{i\omega}\,(\tilde{g}(\omega) - \tilde{g}(0)], \tag{21a}$$

whereas the first order approximation gives

$$\tilde{N}_0(\omega) = -\mu^2\,\tilde{\Omega}_\perp(\omega)\frac{[(\tilde{g}(0) - \tilde{g}(\omega)]}{i\omega}. \tag{21b}$$

Both $\tilde{N}(\omega)$ and $\tilde{N}_0(\omega)$ agree on the contribution to the frequency dependent torque proportional to $\hat{n}(\omega)$. This torque tends to flip Ω_J, and it is convenient to denote this "flip" torque as $N_f(t)$. The explicit time dependent torque may be written as

$$N(t) = N_f(t) - \mu^2\Omega_J\sin^2\theta\,\frac{\tilde{g}(-\Omega_J) - \tilde{g}(\Omega_J)}{2i\Omega_J}, \tag{22a}$$

$$N_0(t) = N_f(t) - \mu^2\,\Omega_J\sin^2\theta\lim_{\omega\to 0}\frac{\tilde{g}(0) - \tilde{g}(\omega)}{i\omega}. \tag{22b}$$

It is quite evident that the exact theory Eq. (22a) produces for a rotor a frictional torque which depends on the complex permittivity only at the frequency of rotation $\Omega_J/2\pi$, whereas the first order theory has a contribution from the zero frequency complex permittivity. This result for the exact theory is quite sensible physically as it simply means that the response of the dielectric surrounding the cavity to the rotating dipole field is at the *driving frequency* and depends upon the dielectric properties only at that frequency. The first order approximation, on the other hand, does not reflect this basic expectation of the theory of dielectric friction. Note that for $\theta \neq \pi/2$, a zero frequency dipole component exists with a corresponding zero frequency complex permittivity contribution to $N_f(t)$.

To proceed further it is convenient to introduce real and imaginary parts of $\tilde{g}(\omega)$ as $\tilde{g}'(\omega)$ and $\tilde{g}''(\omega)$, where in terms of $\epsilon'(\omega)$ and $\epsilon''(\omega)$,

$$\tilde{g}'(\omega) = \frac{2}{a^3\epsilon_\infty}\,\frac{(\epsilon'(\omega) + \epsilon_\infty)(2\epsilon'(\omega) + \epsilon_\infty) + 2\epsilon''(\omega)^2}{(2\epsilon'(\omega) + \epsilon_\infty)^2 + 4\epsilon''(\omega)^2},$$

$$\tilde{g}''(\omega) = \frac{6}{a^3}\,\frac{\epsilon''(\omega)}{(2\epsilon'(\omega) + \epsilon_\infty)^2 + 4\epsilon''(\omega)^2}.$$

Equation (22a) can be simplified to give

$$N(t) = -\mu^2\sin^2\theta\tilde{g}''(\Omega_J)\hat{k} - \mu^2\sin\theta\cos\theta$$
$$\times[\tilde{g}''(\Omega_J)\hat{n}(t) + (\tilde{g}(0) - \tilde{g}'(\Omega_J))\hat{m}(t)], \tag{23}$$

where

$$\hat{m}(t) = \hat{i}\,\sin\Omega_J t - \hat{j}\,\cos\Omega_J t$$

is a unit vector forming a mutually perpendicular set of unit vectors with $\hat{k}$ and $\hat{n}(t)$. Equation (23) is derived using the general properties[12] $\epsilon'(\omega) = \epsilon'(-\omega)$, $\epsilon''(\omega) = -\epsilon''(-\omega)$ which lead to $\tilde{g}'(\omega) = \tilde{g}'(-\omega)$ and $\tilde{g}''(\omega) = -\tilde{g}''(-\omega)$.

We may now use Eq. (23) to define the distinction between slow rotation and fast rotation for the purpose of deriving the dielectric frictional torque. Only the first part of Eq. (23) giving N_J parallel to Ω_J need be used, as the "flip" component is the same for Eq. (23) and the slow rotation first order approximation. Using the Debye formula we find

$$N_J = -\frac{\mu^2\tilde{g}(0)\,\tau_G\sin^2\theta}{1 + (\Omega_J\tau_G)^2}\,\Omega_J, \tag{24a}$$

whereas Eq. (22b) may be employed to give the first order result

$$N_{J0} = - \mu^2 \tilde{g}(0) \tau_G \sin^2\theta \, \Omega_J \,. \qquad (24b)$$

Clearly, slow rotation requires $(\Omega_J \tau_G)^2 \ll 1$.

To determine whether molecular rotation in actual polar liquids corresponds to fast rotation rather than slow rotation, consider the following relation between the relaxation time τ_1 for the dipole autocorrelation function and the molecular angular velocity relaxation time $\tau_{J_\perp}$. This relation is well known and is given by[12]

$$\tau_1 = (I_\perp / 2kT\tau_{J_\perp}) \,. \qquad (25)$$

Take $\tau_1 \simeq \tau_M$, which is easily demonstrated from the general theory of dielectric relaxation.[12] Then we find

$$\omega_\perp \tau_M \simeq (\omega_\perp \tau_{J_\perp})^{-1} \,,$$

where

$$\omega_\perp = (2kT/I_\perp)^{1/2} \qquad (26)$$

is the rms quantity $\langle \Omega_\perp^2 \rangle^{1/2}$. For small angle rotational diffusion $\omega_\perp \tau_{J_\perp} \ll 1$ and thus $\omega_\perp \tau_M \gg 1$, and provided ϵ_0 is not too large τ_M can be replaced by τ_G and suggests that $\omega_\perp \tau_G > 1$. Taking $\Omega_J \simeq \omega_\perp$ we obviously find that molecular rotation in liquids corresponds to fast rotation and the first order theory is inadequate.

The above analysis uses a free rotation approximation and assumes that the Debye formula is adequate over the whole range $0 \le \omega \le \omega_\perp$. In practice, τ_1 is ω dependent via a frequency dependent angular momentum relaxation rate $\tau_{J_\perp}(\omega)^{-1}$. Thus, although molecular rotation may be strongly overdamped at low frequencies so that Eq. (25) actually applies for $\tau_1(0)$ and $\tau_{J_\perp}(0)$, Eq. (25) may fail for $\omega \simeq \omega_\perp$ and the resultant high frequency underdamping may be observed as a peak in the absorption coefficient near $\omega_\perp$. With $\Omega_J \simeq \omega_\perp$, Eq. (24b) still fails on the quite general ground that the complex permittivity of a liquid at low or microwave frequencies is quite different from that at far-infrared frequencies. The condition $(\Omega_J \tau_G)^2 \ll 1$ for slow rotation still holds and is simply the requirement that Ω_J lie in the microwave region. In principle the slow rotation condition may be satisfied for heavy foreign molecules dissolved in a relatively fast relaxing dielectric but $(\Omega_J \tau_G)^2 \ll 1$ is actually much too restrictive in that it is based upon a free rotational calculation which ignores the effect of rotational damping. It is evident from the treatment of Hubbard and Wolynes[15] that the presence of intermolecular collisions or short range viscous damping slows down the net reorientation rate and indeed, as might be expected on physical grounds, the deviation from the first order theory is much less than indicated by the free rotation calculation. This is demonstrated in Sec. IV with an explicit calculation of the dielectric friction coefficient. Both the exact and the free rotation calculations agree, however, in that the slow rotation approximation overestimates the low frequency dielectric friction coefficient.

IV. CONSIDERATION OF THE EINSTEIN RELATION AND FLUCTUATION–DISSIPATION THEOREM WITH DIELECTRIC FRICTION

It is generally necessary to deal with a body fixed frame of reference in which the moment of inertia tensor

and the friction tensor are time independent. For our purposes this is not necessary, as our considerations will be confined to symmetric top molecules with μ along the figure axis. For this case one need only use a quasi-body-fixed reference frame defined to rotate with the symmetric top molecule at the angular velocity $\Omega_J(t)$ because the additional component adding to Ω_J to produce Ω is directed only along the figure axis and does not contribute to dipole rotation. The advantage of the quasi-body-fixed frame is that J is constant in this frame in the free rotation case which facilitates the setting up of the second fluctuation–dissipation relation between the random torque tensor and the friction tensor. Quasi-body-fixed time derivatives will be denoted by $\delta/\delta t$ and the laboratory frame time derivative of any vector A will be related to that in the quasi-body-fixed frame by the usual equation $dA/dt = \delta A/\delta t + \Omega_J \times A$. Thus, Ω_k may be expressed in quasi-body-fixed terms by repeated application of the time derivative transformation to obtain $\hat{u}^{(k)}$ and the definition $\Omega_k = \hat{u}^{(k)} \times \hat{u}^{(k+1)}$ applied.

It is quite apparent from Eq. (15) that the dielectric frictional torque $N(t)$ can be written as a sum of convolution of $\Omega_k(t)$ with friction memory functions $\zeta_k(t)$. We shall also assume a short range viscous friction memory tensor $\zeta_S(t)$. The structure of these two contributions to the frictional torque suggests that the generalized Langevin equation of motion for $J(t)$ in the quasi-body-fixed frame can be employed. This requires introducing a random torque $N_R(t)$, thereby leading to the equation of motion

$$\frac{\delta J(t)}{\delta t} + \int_0^t \zeta_S(\tau) \cdot \Omega_J(t - \tau) \delta\tau$$

$$+ \sum_{k=0}^{\infty} \int_0^t \zeta_k(\tau) \Omega_k(t - \tau) \delta\tau = N_R(t) \,. \qquad (27)$$

To proceed further rigorously is not possible, and it is necessary to ascribe to the random torque certain statistical properties guided by the results of more rigorous developments of the fluctuation–dissipation theorem,[18] in particular the Mori projection operator formalism[19] and the reviews of Berne and Harp[20] and of Berne.[21] $J(0)$ is uncorrelated with $N_R(t)$, thereby giving $\langle N_R(t) J(0) \rangle = 0$; however, by virtue of the equation of motion $\dot{J}(t) = N_R(t) + N_F(t)$, where N_F is the friction torque due to molecular rotation, the angular momentum $J(t)$ begins to correlate with the random torque $N_R(t')$ for $0 < t' \le t$. Similarly, $\Omega_k(t)$ becomes correlated with $N_R(t')$ so that in general $\langle N_R(t')J(t)\rangle \neq 0$ and $\langle N_R(t')\Omega_k(t)\rangle \neq 0$.

Postmultiplying Eq. (27) by $J(0)$ and taking the ensemble average we find that $N_R(t)$ is eliminated and an equation of motion for the tensor $\langle J(t)J(0)\rangle$ is obtained in terms of the $\langle \Omega_k(t)J(0)\rangle$. Taking the Fourier–Laplace transform gives

$$\langle \tilde{J}(\omega)J(0)\rangle = (i\omega 1 + \tilde{\zeta}_S(\omega)I_\perp^{-1})^{-1}$$

$$\times \left[\langle J(0)J(0)\rangle - \sum_{k=0}^{\infty} \tilde{\zeta}_k(\omega)\langle \tilde{\Omega}_k(\omega)J(0)\rangle \right] \,. \qquad (28)$$

As will be seen later, Eq. (28) is closely related to the rotational Einstein relation. Because the Einstein relation requires $\langle \tilde{J}(\omega)J(0)\rangle$ to relate to some friction

tensor $\tilde{\zeta}(\omega)$ and $\langle J(0)J(0)\rangle$ alone it is already evident from Eq. (28) that dielectric friction invalidates the Einstein relation through the introduction of the additional tensors $\langle \tilde{\Omega}_k(\omega)J(0)\rangle$.

The second fluctuation–dissipation theorem is obtained by postmultiplying Eq. (27) by $N_R(0)$, employing $N_R(0) = (\delta J/\delta t)_0$ on the LHS and taking the ensemble average. One may use the relation

$$\left\langle A(t)\left(\frac{\delta J}{\delta t}\right)_0\right\rangle = -\left\langle \frac{\delta A}{\delta t} J(0)\right\rangle,$$

which follows from the independence of time correlation functions from the choice of the initial time.[20] The resultant equation is

$$-\frac{\delta^2\langle J(t)J(0)\rangle}{\delta t^2} - \int_0^t \zeta_S(t-\tau)\cdot\left\langle \frac{\delta\Omega_J(\tau)}{\delta\tau}J(0)\right\rangle\delta\tau$$

$$-\sum_{k=0}^\infty \int_0^t \zeta_k(t-\tau)\left\langle \frac{\delta\Omega_k(\tau)}{\delta\tau}J(0)\right\rangle\delta\tau = \langle N_R(t)N_R(0)\rangle.$$

Taking the Fourier–Laplace transform, we find

$$\langle \tilde{N}_R(\omega)N_R(0)\rangle = -(i\omega 1 + \tilde{\zeta}_S(\omega)I_1^{-1})\cdot[i\omega\langle \tilde{J}(\omega)J(0)\rangle - \langle J(0)J(0)\rangle]$$

$$-\sum_{k=0}^\infty \tilde{\zeta}_k(\omega)[i\omega\langle \tilde{\Omega}_k(\omega)J(0)\rangle - \langle \Omega_k(0)J(0)\rangle].$$

This can be simplified by eliminating $\langle J(0)J(0)\rangle$ and the $\langle \tilde{\Omega}_k(\omega)J(0)\rangle$ by using Eq. (28). We find then the second fluctuation–dissipation theorem

$$\langle \tilde{N}_R(\omega)N_R(0)\rangle = \tilde{\zeta}(\omega)\cdot\langle \Omega_J(0)J(0)\rangle, \qquad (29a)$$

where

$$\tilde{\zeta}(\omega) = \tilde{\zeta}_S(\omega) + \tilde{\zeta}_D(\omega), \qquad (29b)$$

and the dielectric friction tensor is given by

$$\tilde{\zeta}_D(\omega) = \sum_{k=0}^\infty \tilde{\zeta}_k(\omega)\langle \Omega_k(0)J(0)\rangle\cdot\langle \Omega_J(0)J(0)\rangle^{-1}. \qquad (29c)$$

If the dielectric friction and the frequency dependence of these tensors are omitted, then Eqs. (28) and (29a) resemble the usual results of rotational Brownian motion.[22] The results of the earlier work differ only in that for nonspherical molecules actual body-fixed coordinates are used rather than the quasi-body-fixed frame employed in this report. Thus, whereas the friction tensor in other works is associated with the total angular velocity Ω, the present work associates the friction tensor with Ω_J. $N_R(t)$ used in this paper, therefore, is not the total random torque acting on the molecule; however, it is a reasonable assumption that the omitted component of the random torque which is along the symmetry axis of the symmetric top molecule is statistically uncorrelated with $N_R(t)$, so that if so desired one can simply add this omitted contribution to the friction tensor to obtain the total friction tensor. This is of no consequence for the dielectric friction problem when μ is along the symmetry axis.

The rotational Brownian motion theory leads to the definition of the frequency dependent rotational diffusion tensor[12,23] $\tilde{D}(\omega) = \langle \tilde{\Omega}(\omega)\Omega(0)\rangle$, and since we have μ along the symmetry axis we may employ the more restricted diffusion tensor

$$\tilde{D}_J(\omega) = \langle \tilde{\Omega}_J(\omega)\Omega_J(0)\rangle = I_1^{-2}\langle \tilde{J}(\omega)J(0)\rangle. \qquad (30)$$

Suppose now that for all k

$$\langle \tilde{\Omega}_k(\omega)J(0)\rangle = \langle \Omega_k(0)J(0)\rangle\cdot\langle J(0)J(0)\rangle^{-1}\cdot\langle \tilde{J}(\omega)J(0)\rangle. \qquad (31)$$

Then combining this with Eq. (28), solving for $\langle \tilde{J}(\omega)J(0)\rangle$, and employing the definition of $\tilde{\zeta}(\omega)$ from Eqs. (29b) and (29c), we find

$$\langle \tilde{J}(\omega)\tilde{J}(0)\rangle = (i\omega 1 + I_1^{-1}\tilde{\zeta}(\omega))^{-1}\cdot\langle J(0)J(0)\rangle, \qquad (32)$$

which when combined with Eq. (30) is just the generalized rotational Einstein relation. The usual well-known Einstein relation is the zero frequency case $\omega = 0$.

The Einstein relation is valid, even in the presence of dielectric friction, only if Eq. (31) holds for all k. For $k = 0$, Eq. (31) holds since it is easily shown from the rotational kinematics of a symmetric top that

$$\langle \Omega_1(0)J(0)\rangle\cdot\langle J(0)J(0)\rangle^{-1}\cdot\langle \tilde{J}(\omega)J(0)\rangle = \langle \tilde{\Omega}_1(\omega)J(0)\rangle.$$

For $k \geq 1$, however, $\Omega_k(0)$ is not simply expressed in terms of kinematics alone but involves contributions from $N_R(0)$ and its time derivatives, and so there is no general reason for Eq. (31) to hold. Thus the Einstein relation holds only to first order ($k = 0$) but generally breaks down when higher approximations are included. This result is qualitatively consistent with the conclusion of Hubbard and Wolynes.[15] In their model, the Einstein relation fails because a molecule can reorientate significantly on the same time scale of spontaneous fluctuations of the local cavity field which couple to the electric dipole to produce the random torque N_R. The Einstein relation requires a slow reorientation compared with fluctuations of the cavity field, and the inclusion of the higher order terms $k \geq 1$ is just the formal manner of introducing the fast reorientation process and the resultant failure of the Einstein relation.

The method of Hubbard and Wolynes is not fundamentally different from the approach in this paper, but whereas they are restricted to small angle rotational diffusion the present approach is more general and may be extended to the situation of significant inertial effects and large angle rotational diffusion. For small angle rotational diffusion one only requires to find the component $\tilde{D}_{J_1}(\omega) = I_1^{-2}\langle \tilde{J}(\omega)J(0)\rangle_1$ for rotation perpendicular to μ but to use Eq. (28) one must choose a specific dynamical model. One suitable model has in fact already been analyzed by Hubbard and Wolynes who derived a rotational Smoluchowski equation giving the time evolution of the orientational distribution function under the influence of the random cavity field fluctuations. In this approach it is not necessary to use Eq. (28) to get $\tilde{D}_{J_1}(\omega)$ nor Eq. (29c) to get $\tilde{\zeta}_D(\omega)$, but one may calculate the orientational correlation functions and their respective correlation times more directly from the Smoluchowski equation and calculate $\tilde{\zeta}_D(\omega)$ directly from the spontaneous cavity field fluctuations via Eqs. (29a) and (29b). This is just a method of dealing with full summations over k and l, which is very necessary because all individual terms $\tilde{\zeta}_k(\omega)$, $k \geq 1$, actually diverge at $\omega = 0$ for Debye relaxation.

In the latter approach it is necessary to know the

random cavity field time autocorrelation function $\langle \delta G(t) \cdot \delta G(0) \rangle$. The random torque autocorrelation function, consistent with Eqs. (29a) and (29b), may be taken to be the sum of a short range viscous part and the long range cavity field part. The long range part is

$$\langle \mathbf{N}_{RD}(t) \, \mathbf{N}_{RD}(0) \rangle_{\perp} = \tfrac{1}{2}\langle (\boldsymbol{\mu}(t) \times \delta \mathbf{G}(t)) \cdot (\boldsymbol{\mu}(0) \times \delta \mathbf{G}(0)) \rangle$$

$$\cong \tfrac{1}{3}\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle \langle \delta \mathbf{G}(0) \cdot \delta \mathbf{G}(t) \rangle . \quad (33)$$

This latter relation approximates $\boldsymbol{\mu}(t)$ as remaining uncorrelated with $\delta \mathbf{G}(t)$, which is not of course perfectly accurate but is roughly correct if dielectric friction is only a small part of the total friction effect. $\langle \delta \mathbf{G}(0) \cdot \delta \mathbf{G}(t) \rangle$ may be obtained by imagining a heavy foreign molecule in the liquid that reorientates slowly on the time scale of $\delta G(t)$. Thus, for this molecule $\boldsymbol{\mu}'(t) \simeq \boldsymbol{\mu}'(0)$, so that

$$\langle \mathbf{N}'_{RD}(t)\mathbf{N}'_{RD}(0) \rangle_{\perp} \cong \tfrac{1}{3}\mu'^2 \langle \delta \mathbf{G}(0) \cdot \delta \mathbf{G}(t) \rangle ,$$

and since the first order approximation ($k = 0$) to Eq. (29c) is sufficient we have

$$\tilde{\zeta}_0(\omega) \langle \mathbf{\Omega}_\perp(0)\mathbf{J}(0) \rangle_\perp \cong \tfrac{1}{3}\mu'^2 \langle \delta \mathbf{G}(0) \cdot \delta \tilde{\mathbf{G}}(\omega) \rangle ,$$

which can be inverted to give[15]

$$\langle \delta \mathbf{G}(0) \cdot \delta \mathbf{G}(t) \rangle = \frac{3kT}{\mu'^2} \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t}\, \tilde{\zeta}_0(\omega)d\omega ,$$

and using Eq. (19)

$$\frac{1}{\mu'^2}\, \tilde{\zeta}_0(\omega) = \frac{\tilde{g}(0) - \tilde{g}(\omega)}{i\omega} = \tilde{g}(0)\, \frac{\tau_G}{1 + i\omega\tau_G} ,$$

we obtain the $\epsilon_\infty \neq 1$ generalization of Hubbard and Wolynes' result

$$\langle \delta \mathbf{G}(0) \cdot \delta \mathbf{G}(t) \rangle = \frac{6kT(\epsilon_0 - \epsilon_\infty)}{a^3 \epsilon_\infty (2\epsilon_0 + \epsilon_\infty)}\, e^{-t/\tau_G}. \quad (34)$$

Taking in the Debye or long time limit $\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle = \mu^2 e^{-t/\tau_1}$ in Eq. (33), applying the Fourier–Laplace transform, and using Eqs. (29a) and (29b) to obtain $\tilde{\zeta}(\omega)$, we find, again in the Debye or low frequency limit,

$$\tilde{\zeta}_{D_\perp}(\omega) \cong \frac{\mu^2 \tilde{g}(0)\tau_D}{1 + i\omega\tau_D} , \quad (35a)$$

where

$$\tau_D = \tau_G \tau_1 (\tau_G + \tau_1)^{-1} . \quad (35b)$$

We see that the deviation from the slow rotation or first order approximation for the $\omega = 0$ dielectric friction coefficient is by the factor $\tau_1/(\tau_G + \tau_1)$ which on using Eq. (19c) and the relation[16,17] $\tau_M = \tau_1(2\epsilon_0 + \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty^2 \epsilon_0^{-1})^{-1}$ comes to $[1 + 3\epsilon_\infty (2\epsilon_0 + \epsilon_\infty^2 \epsilon_0^{-1})^{-1}]^{-1}$, which is typically ($\epsilon_0 = 5$, $\epsilon_\infty = 2$) of the order of 0.64. The fast reorientation process therefore leads to a significant reduction of $\tilde{\zeta}_{D_\perp}(0)$ relative to the first order theory and this agrees qualitatively with the Hubbard and Wolynes model of the dielectric friction contribution to τ_1.

Writing $C_1(t) = (1/\mu^2)\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle$ it can be shown that[12,23]

$$\frac{dC_1(t)}{dt} = -2 \int_0^t D_{J_\perp}(t)C_1(t - \tau)d\tau ,$$

so that

$$\tau_1(\omega) = (2\tilde{D}_{J_\perp}(\omega))^{-1} . \quad (36)$$

Suppose now that Eq. (31) is accepted, tantamount to a convenient choice of the statistical properties of the random cavity field. One may then obtain $\tau_1(\omega)$ by substituting Eq. (35a) into Eq. (32) and then employing Eq. (36). This enables us to compare this model with the result obtained by Hubbard and Wolynes,[15] which is

$$\tau_1 = (2\bar{D}_{J_\perp}(0))^{-1} = \tau_0 + \gamma(0)\frac{\mu^2 \tilde{g}(0)\tau_G}{2kT} , \quad (37a)$$

where

$$\gamma(0) = \tau_0/(3\tau_G + \tau_0) \quad (37b)$$

and

$$\tau_0 = \tilde{\zeta}_{J_\perp}(0)/2kT. \quad (37c)$$

As shown in the earlier paper, $\gamma(0)$ may be regarded as a variable dielectric friction coupling coefficient of a pseudooscillator model of dielectric relaxation.[16] The slow rotation theory corresponds to $\gamma(0) = 1$. If one were to employ Eq. (35a) in an Einstein relation, then a result similar to Eq. (37a) would be obtained except that $\gamma(0)$ is replaced by $\gamma'(0) = \tau_1(\tau_G + \tau_1)^{-1}$. Thus, taking $\epsilon_0 = 5$, $\epsilon_\infty = 2$, one would obtain $\gamma'(0) = 0.64$, whereas it may be shown that[16] $\gamma(0) = 0.36$. In both cases the failure of the slow rotation approximation is significant. Also, the failure of the Einstein relation, measured by the difference between $\gamma(0)$ and $\gamma'(0)$, is significant in the Hubbard and Wolynes model.

V. EFFECT OF DIELECTRIC FRICTION ON HIGHLY COMPRESSED POLAR GAS ANGULAR MOMENTUM RELAXATION TIMES

There has been considerable interest in recent years in observing experimentally the systematic relationship between the angular momentum relaxation time $\tau_{J_\perp}(0)$ and various reorientational relaxation times. Systematic variations may be obtained by density and temperature changes and the results compared with theoretical models. A great deal of success has been achieved with the extended rotational diffusion models[24] originally proposed for linear rotors by Gordon[25] and later extended to spherical top[26] and symmetric top[27] molecules by McClung and others and by Bliot et al.[28] For highly polar fluids there is expected to be a significant contribution to these relaxation times from dielectric friction. To prove this by experimental means is not simple, however. Thus, although dielectric friction enters small angle rotational diffusion in the way indicated by Eq. (37a), the relation that can be tested experimentally by present means is Eq. (25) and its generalization to other correlation functions. However, Eq. (25) does not separate out the dielectric friction contribution, necessitating other experimental approaches for detecting dielectric friction. Temperature and density variations may be considered; however, such studies suffer from a deficiency in knowledge about how τ_0 is so affected in the liquid state. A systematic study of different types of reorientation relaxation times as suggested by Hubbard and Wolynes[15] can in principle circumvent this problem. In this section, the possibility of observing the contribution of dielectric friction to the angular momentum relaxation time directly is considered. Our analysis is restricted to highly compressed, highly polar gases for

which the cavity model is expected to provide, at least for the present heuristic purposes, a reasonable estimate. The fingerprint of dielectric friction is a quadratic density dependence of $\tau_{J_\perp}^{-1}(0)$ which can be changed with temperature and with foreign gas mixing in a reliably predictable manner.

The formal theory of the angular momentum autocorrelation function can be developed in terms of Mori memory functions.[19-21] If we retain at this stage a full tensorial notation the theory requires a memory tensor $\mathbf{K}_1(\tau)$ appropriate to a dense gas such that

$$\frac{\delta \langle \mathbf{J}(t)\mathbf{J}(0)\rangle}{\delta t} = -\int_0^t \mathbf{K}_1(\tau) \cdot \langle \mathbf{J}(t-\tau)\mathbf{J}(0)\rangle \delta\tau , \qquad (38)$$

where in general

$$\mathbf{K}_1(0) = \langle \mathbf{N}_R(0)\mathbf{N}_R(0)\rangle \cdot \langle \mathbf{J}(0)\mathbf{J}(0)\rangle^{-1} .$$

Because in a gas $\langle \mathbf{N}_R(t)\mathbf{N}_R(0)\rangle$ decays rapidly with $\langle \mathbf{J}(t)\mathbf{J}(0)\rangle$[12,29] it is justifiable to use Eq. (38) and the associated relation

$$\mathbf{K}_1(\tau) = \langle \mathbf{N}_R(\tau)\mathbf{N}_R(0)\rangle \cdot \langle \mathbf{J}(0)\mathbf{J}(0)\rangle^{-1} ,$$

which by Eq. (29a) is equivalent to[30]

$$\tilde{\mathbf{K}}_1(\omega) = I_\perp^{-1} \tilde{\zeta}(\omega) . \qquad (39)$$

Equations (38) and (39) together are equivalent to Eq. (32), but Eq. (32) requires Eq. (31) to be satisfied for all k. It is readily checked that Eq. (31) is satisfied for all k if Eq. (18) of the free rotation theory is employed. This corresponds physically to a rapidly changing random long range torque which is associated with the dipole directions of molecules in the surrounding fluid rapidly changing compared with their angular momentum vectors. Although our particular problem does not concern perfectly free rotating molecules, we shall regard our present quasifree rotation problem as sufficiently similar to enable Eq. (39) to be employed. Thus we are restricted to $\omega_\perp \tau_{J_\perp}(0) \geq 2\pi$, or in other words, at least one full molecular rotation on the time scale of $\tau_{J_\perp}(0)$ but high enough gas densities to justify use as a first approximation of the cavity model.

The frequency dependent angular momentum relaxation time is defined via the relation

$$\frac{\langle \tilde{\mathbf{J}}(\omega)\mathbf{J}(0)\rangle_\perp}{\langle \mathbf{J}(0)\mathbf{J}(0)\rangle_\perp} = \frac{1}{i\omega + \tau_{J_\perp}^{-1}(\omega)} , \qquad (40)$$

and from Eq. (38)

$$1/\tau_{J_\perp}(\omega) = (\tilde{\mathbf{K}}_1(\omega))_\perp . \qquad (41)$$

Using $\langle \mathbf{J}(0)\mathbf{J}(0)\rangle_\perp = \tfrac{1}{2}I_\perp^2 \langle \Omega_\perp^2\rangle = \tfrac{1}{2}I_\perp^2 \omega_\perp^2$ and Eqs. (40) and (30), we find for the small angle rotational diffusion model,

$$\tilde{D}_{J_\perp}(\omega) = kT I_\perp^{-1}\tau_{J_\perp}(\omega)(1+i\omega\tau_{J_\perp}(\omega))^{-1} , \qquad (42)$$

which for $\omega = 0$ and combined with Eq. (36) reproduces the well-known Eq. (25). For $\omega \neq 0$ the factor $(1+i\omega\tau_{J_\perp}(\omega))^{-1}$ produces the important inertial effects for $\omega \geq \omega_\perp$ originally discussed for the dielectric friction problem and high frequency dipolar plasmons by Lobo, Robinson, and Rodriguez.[16,17] Using Eqs. (25) and (37a), we have

$$1/\tau_{J_\perp}(0) = \frac{2kT\tau_0}{I_\perp} + \gamma(0)\frac{\mu^2\tilde{g}(0)}{I_\perp}\tau_G , \qquad (43a)$$

or after using the Onsager equation to get the result

$$\frac{\mu^2\tilde{g}(0)}{I_\perp\omega_\perp^2} = \frac{(\epsilon_0-\epsilon_\infty)^2}{3\epsilon_0\epsilon_\infty}$$

we obtain in dimensionless terms

$$\frac{1}{\omega_\perp\tau_{J_\perp}(0)} = \omega_\perp\tau_0\left(1 + \frac{(\epsilon_0-\epsilon_\infty)^2}{3\epsilon_0\epsilon_\infty}\frac{\tau_G}{3\tau_G+\tau_0}\right) . \qquad (43b)$$

The angular momentum relaxation is evidently locked into the fluid viscous relaxation process via $\tau_G \simeq \tau_0$ making independent observation of dielectric friction effects difficult. As we show below, this no longer occurs in the quasifree rotation limit.

Using Eqs. (41), (39), (29b), and (29c), noting that all tensors are diagonal, we get for quasifree rotation

$$\frac{1}{\tau_{J_\perp}(\omega)} = \frac{\tilde{\zeta}_{S_\perp}(\omega)+\tilde{\zeta}_0(\omega)}{I_\perp} + \sum_{k=1}^{\infty}\tilde{\zeta}_k(\omega)\frac{\langle \Omega_k(0)\,J(0)\rangle_\perp}{\langle J(0)\,J(0)\rangle_\perp} . \qquad (44)$$

From Eqs. (16) and (18), we have for all k

$$\langle \Omega_k(0)\,J(0)\rangle_\perp = \tfrac{1}{2}I_\perp\langle \Omega_\perp^2\,\Omega_J^{2k}\rangle , \qquad (45)$$

where $\Omega_\perp^2 = \sin^2\theta\,\Omega_J^2$. We have used $\langle \sin\theta\cos\theta\rangle = 0$, which eliminates the angular momentum flip component associated with the $k=0$ term. Thus, dielectric friction in the quasifree rotation limit affects only the magnitude of the angular momentum, not its direction. The resultant expression for $\tau_{J_\perp}(0)$ therefore cannot be employed in the extended rotational diffusion models which associate $\tau_{J_\perp}(0)$ with a randomization of the direction of the angular momentum.[24-28] This difference plus the fact that the angular momentum relaxation time is now frequency dependent implies that molecular band shapes of strongly polar gases with significant dielectric friction should deviate from the extended rotational diffusion model results; however, no attempt is made in this report to develop this theme. Instead, we restrict ourselves to a heuristic consideration of the circumstances where dielectric friction is important.

Combining Eqs. (44) and (45), we find

$$\frac{1}{\tau_{J_\perp}(\omega)} = \frac{\tilde{\zeta}_{S_\perp}(\omega)}{I_\perp} + \frac{\mu^2}{I_\perp}\frac{1}{2\pi\langle\Omega_\perp^2\rangle}$$

$$\times \int_{-\infty}^{\infty}\tilde{g}(\omega')\left\langle \sin^2\theta\sum_{k=0}^{\infty}\left(\frac{\Omega_J^2}{\omega'(\omega-\omega')}\right)^{k+1}\right\rangle d\omega' ,$$

which may be evaluated analogously to Sec. III to give

$$\frac{1}{\tau_{J_\perp}(\omega)} = \frac{\tilde{\zeta}_{S_\perp}(\omega)}{I_\perp} + \frac{\mu^2}{I_\perp\langle\Omega_\perp^2\rangle}\left\langle \Omega_\perp^2\frac{(\tilde{g}(\omega_-)-\tilde{g}(\omega_+))}{i(\omega^2+4\Omega_J^2)^{1/2}}\right\rangle , \qquad (46)$$

where $\omega_\pm$ are again given by Eq. (20). It is interesting to note that for $\omega^2 \gg 4\Omega_J^2$, which is well satisfied by $\omega \geq 5\omega_\perp$,

$$\frac{1}{\tau_{J_\perp}(\omega)} \simeq \frac{\tilde{\zeta}_{S_\perp}(\omega)}{I_\perp} + \frac{\mu^2}{I_\perp}\frac{\tilde{g}(0)-\tilde{g}(\omega)}{i\omega} . \qquad (47)$$

This is equivalent to assuming the first order approximation and gives rise to the important conclusion that the slow rotation theory is valid at high frequencies with significant inertial effects even if it fails at low frequencies $\omega < \omega_\perp$. The slow rotation approximation merely requires the characteristic dipole rate of change to be

slow compared with the probe angular frequency ω. Thus one would expect the generalizations[17,31] of the original Fatuzzo–Mason[5] and Nee–Zwanzig[8] theories based on the first order approximation to the high frequency range to be valid. Furthermore, Eq. (47) inserted into Eq. (42) should be valid for angular frequencies ω well below $5\omega_1$ due to the effect of rotational damping in the main dispersion region making the slow rotation approximation more widely applicable than for the free rotation case. The importance of this point for the theory of dipolar plasmons has been emphasized in an earlier paper.[16] To avoid major revision, the plasmon theory requires the first order theory to work down to $\omega \cong \omega_1$ at least. Due to rotational damping, this requirement is almost certainly justified but as yet still requires a formal proof. This point is returned to in Sec. VI.

The angular momentum relaxation time $\tau_{J_1}(0)$ may be obtained from the NMR spin–lattice relaxation time.[24] Thus we may confine our attention to $\omega = 0$, whereupon the dielectric friction contribution to τ_J^{-1} is purely real and so involves no angular frequency "shift" component. We then have

$$\frac{1}{\tau_{J_1}(0)} = \frac{1}{\tau_{J_S}(0)} + \frac{1}{\tau_{J_D}(0)} ,$$

where

$$\frac{1}{\tau_{J_D}(0)} = \frac{\mu^2}{I_1\omega_1^2} \langle \tfrac{1}{2} \sin^2\theta\, \Omega_J (\tilde{g}''(\Omega_J) - \tilde{g}''(-\Omega_J)) \rangle .$$

This can be expressed in terms of $\epsilon'(\Omega_J)$ and $\epsilon''(\Omega_J)$ using the results of Sec. III to give

$$\frac{1}{\tau_{J_D}(0)} = \frac{3\mu^2}{kTa^3} \left\langle \sin^2\theta \frac{\Omega_J\,\epsilon''(\Omega_J)}{(2\epsilon'(\Omega_J) + \epsilon_\infty)^2 + 4\epsilon''(\Omega_J)^2} \right\rangle , \qquad (48)$$

For the purpose of generality we may take the molecule of interest to be different from those forming the surrounding dielectric.

It will be noticed that the dielectric friction problem is closely similar to calculating the integrated absorption coefficient over the rotational absorption band of the solvent gas. This observation is now used to make some simplifications of the evaluation of the RHS of Eq. (48).

As is well known, the integrated absorption coefficient in gas phase is to a good approximation density independent and not dependent upon intermolecular collisions.[32] Although Eq. (48) differs in important respects, in particular through the weighting of $\Omega_J\,\epsilon''(\Omega_J)$ by $\sin^2\theta$, the additional factor depending upon $\epsilon'(\Omega_J)$ and $\epsilon''(\Omega_J)$, and the fact that the integration over all Ω_J is weighted by the rotational distribution function, the analogy with Gordon's sum rule suggests that as a first approximation Eq. (48) be evaluated using the complex permittivity of a gas of freely rotating molecules. We shall approximate the complex permittivity by

$$\epsilon(\omega) - \epsilon_\infty \cong \frac{\mu'^2}{kTb^3} \int_0^\infty -\dot{C}_{1\,\text{free}}(t)\, e^{-i\omega t}\, dt , \qquad (49)$$

where $C_{1\,\text{free}}(t)$ is the normalized dipole autocorrelation function. μ' is the dipole moment of the solvent molecules, and b is their respective Onsager cavity radius and is retained explicitly to bring out the symmetry that

exists between the solvent and solute molecules. Taking the personal volume condition $b^{-3} = 4\pi n/3$, for low densities we have as RHS coefficient of Eq. (49) the well-known result

$$\frac{4\pi n \mu'^2}{3kT} = \epsilon_0 - \epsilon_\infty , \qquad (50a)$$

and at the high densities of immediate interest here

$$\frac{4\pi n \mu'^2}{3kT} = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{3\epsilon_0} . \qquad (50b)$$

Equation (50b) is, of course, the Onsager equation, and its use in Eq. (49) corresponds to the nondispersive approximation[12,33] $\epsilon(\omega) \cong \epsilon_\infty$ to the Fatuzzo–Mason equation.[5,9] This approximation is useful in calculating the integrated absorption coefficient because it involves a frequency weighting towards the high frequency range of the absorption band.[33] This is precisely the case in the dielectric friction problem, firstly because of the Ω_J weight in Eq. (48), and secondly, an additional weighting towards high frequencies exists owing to the denominator function of $\epsilon'(\Omega_J)$ and $\epsilon''(\Omega_J)$. The nondispersive approximation works well when the strongest absorbing range is well separated from the main dispersion region and usually requires $\epsilon_0 \gg \epsilon_\infty$. For the compressed gas phase dielectric friction problem, however, with $\epsilon_0 \cong 2$ and $\epsilon_\infty \cong 1$ in the density region of interest, this assumption is not justified, but the error involved with the nondispersive approximation is not great because both ϵ_0 and ϵ_∞ are small and the change to Eq. (49) is no more than 20% even if the most extreme alternative $\epsilon'(\Omega_J) \cong \epsilon_0$ to the nondispersive approximation is made. Furthermore, $\epsilon'(\Omega_J) \cong \epsilon_0$ and $\epsilon''(\Omega_J) \cong 0$ on the bottom RHS of Eq. (48) produce a change of 25/9 compared with the usual nondispersive $\epsilon'(\Omega) \cong \epsilon_\infty$, $\epsilon''(\Omega_J) \cong 0$. Thus, use of the nondispersive approximation in evaluating Eq. (48) should be accurate to within a factor of approximately 2.

Applying Eq. (49) and the nondispersive approximation to Eq. (48) gives

$$\frac{1}{\tau_{J_D}(0)} \cong \frac{1}{3}\left(\frac{\mu^2}{\epsilon_\infty kTa^3}\right)\left(\frac{\mu'^2}{\epsilon_\infty kTb^3}\right)$$
$$\times \left\langle \sin^2\theta\, \Omega_J \int_0^\infty -\dot{C}_{1\,\text{free}}(t)\sin\Omega_J t\, dt \right\rangle$$
$$= \frac{1}{3}\left(\frac{\mu^2}{\epsilon_\infty kTa^3}\right)\left(\frac{\mu'^2}{\epsilon_\infty kTb^3}\right)$$
$$\times \left\langle \sin^2\theta\, \Omega_J^2 \int_0^\infty C_{1\,\text{free}}(t)\cos\Omega_J t\, dt \right\rangle . \qquad (51)$$

The time integral in this equation can be represented as[34]

$$\frac{1}{\pi}\int_0^\infty C_{1\,\text{free}}(t)\cos\Omega_J t\, dt = \langle \cos^2\phi\, \delta(\Omega_J) + \tfrac{1}{2}\sin^2\phi$$
$$\times (\delta(\Omega_J - \Omega'_J) + \delta(\Omega_J + \Omega'_J)) \rangle' , \qquad (52)$$

where ϕ is the angle between the solvent molecule symmetry axis and angular momentum and Ω'_J denotes the dummy angular velocity variable of the solvent molecules. $\langle\ \rangle'$ denotes the Boltzmann average over ϕ and

Ω'_J. The nonresonant component of Eq. (52) makes no contribution to Eq. (51). Incorporating Eq. (52) in Eq. (51), we find

$$\frac{1}{\tau_{J_D}(0)} \cong \frac{\pi}{6} \left(\frac{\mu^2}{\epsilon_\infty kT a^3} \right) \left(\frac{\mu'^2}{\epsilon_\infty kT b^3} \right)$$

$$\times \langle\langle \sin^2\theta \sin^2\phi \; \Omega_J^2 \; \delta(\Omega_J - \Omega'_J)'\rangle'\rangle \; . \tag{53}$$

The evaluation of the remaining averages over the solute and solvent distribution functions is described in the Appendix. The general result can be written in dimensionless form,

$$\frac{1}{\omega_\perp \tau_{J_D}(0)} \cong \frac{\pi^{1/2}}{3} \lambda^{3/2}(1+\lambda)^{-7/2}$$

$$\times \left(\frac{\mu^2}{\epsilon_\infty kT a^3} \right) \left(\frac{\mu'^2}{\epsilon_\infty kT b^3} \right) K(p,\, q,\, \lambda) J(p,\, q) \; ,$$
$$\tag{54}$$

where $\lambda = (I_\perp/I'_\perp)$. The values of p and q and the functions $K(p,\, q,\, \lambda)$ and $J(p,\, q)$ depend upon the signs of the quantities $\xi = (I_\perp/I_\parallel) - 1$ and $\xi' = (I'_\perp/I'_\parallel) - 1$. The results are summarized below.

(i) $\xi \geqslant 0, \; \xi' \geqslant 0$ or $\xi \leqslant 0, \; \xi' \leqslant 0$

$$q^2 = |\xi| \lambda(1+\lambda)^{-1}(1 + \xi\lambda(1+\lambda)^{-1})^{-1} \; , \tag{55a}$$

$$p^2 = |\xi'| (1+\lambda)^{-1} (1 + \xi'(1+\lambda)^{-1})^{-1} \; , \tag{55b}$$

$$K(p,\, q,\, \lambda) = (1 \pm \lambda p^2)^{1/2} (\lambda \pm q^2)^{1/2} \; , \tag{55c}$$

$$J(p,\, q) = \frac{1}{(pq)^2} \left[(3(pq)^2 \mp p^2 \mp q^2 + \tfrac{1}{2}) \frac{\arcsin(pq)}{pq} \right.$$

$$\left. - \tfrac{1}{2}(1 - (pq)^2)^{1/2}(1 \mp 2p^2 \mp 2q^2) \right] \; . \tag{56}$$

The upper signs apply when both ξ and ξ' are positive and the lower signs apply when both are negative.

(ii) $\xi \geqslant 0, \; \xi' \leqslant 0$ or $\xi \leqslant 0, \; \xi' \geqslant 0$

p^2 and q^2 are as defined in Eqs. (55a) and (55b):

$$K(p,\, q,\, \lambda) = (1 \mp \lambda p^2)^{1/2}(\lambda \pm q^2)^{1/2} \; , \tag{57}$$

$$J(p,\, q) = \frac{1}{(pq)^2} \left[(3(pq)^2 \pm q^2 \mp p^2 - \tfrac{1}{2}) \frac{\mathrm{arcsinh}(pq)}{pq} \right.$$

$$\left. + \tfrac{1}{2}(1 + (pq)^2)^{1/2}(1 \pm 2p^2 \mp 2q^2) \right] \; . \tag{58}$$

The upper signs apply to $\xi \geqslant 0, \; \xi' \leqslant 0$, and the lower signs apply to $\xi \leqslant 0, \; \xi' \geqslant 0$.

The simplest results are obtained for linear rotors $\xi = \infty$ and spherical tops $\xi = 0$. These two cases may be calculated from first principles using much simpler integrals than in the general case and serve as a useful check upon the above results. For a pure gas of rotors we find $\lambda = 1, \; q^2 = 1, \; p^2 = 1$, and

$$\frac{1}{\omega_\perp \tau_{J_D}(0)} \cong \frac{\pi(\pi/2)^{1/2}}{16} \left(\frac{\mu^2}{\epsilon_\infty kT a^3} \right)^2$$

$$= \frac{\pi(\pi/2)^{1/2}}{16} \left(\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{3\epsilon_0 \epsilon_\infty} \right)^2 \; . \tag{59a}$$

For a pure gas of spherical top molecules $\lambda = 1, \; q^2 \to 0, \; p^2 \to 0$, and

$$\frac{1}{\omega_\perp \tau_{J_D}(0)} \cong \frac{5(\pi/2)^{1/2}}{36} \left(\frac{\mu^2}{\epsilon_\infty kT a^3} \right)^2$$

$$= \frac{5(\pi/2)^{1/2}}{36} \left(\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{3\epsilon_0 \epsilon_\infty} \right)^2 \; . \tag{59b}$$

These equations exhibit a quadratic dependence of $1/\tau_{J_D}(0)$ upon the density, and this is representative of the many body nature of dielectric friction. Also, $1/\tau_{J_D}(0)$ is proportional to $\omega_\perp$, so that the dielectric friction effect is largest for small polar molecules of small moment of inertia $I_\perp$. The rate of electromagnetic work performed by a rotating molecule on its dielectric environment is greater for a faster rotating molecule. The critical fourth power dependence on μ indicates that a small factor of 2 in the value of μ changes $1/\tau_{J_D}(0)$ by a factor of 16. Finally, dielectric friction is greater by the factor $9\pi/20 \cong 1.41$ for rotors than for spherical tops of equal electric dipole moment. This is mainly because the whole of μ is effective in dielectric friction for rotors, whereas for spheres the part of μ parallel to Ω_J at any time is ineffective in dielectric friction.

The limiting validity of the theory is $\omega_\perp \tau_{J_\perp}(0) \cong 2\pi$. Taking $\omega_\perp \tau_{J_D} = 2\pi$, $\epsilon_\infty = 1$ in Eqs. (59a) and (59b) to provide a rough guide, we find under these conditions $\epsilon_0 = 1.96$ for rotors and $\epsilon_0 = 2.11$ for spherical top molecules. The number densities for highly polar molecules with $\mu = 1.5$ D are respectively 3.53×10^{21} cm^{-3} and 4.20×10^{21} cm^{-3} at 300 °K, which are typical of critical point number densities. The condition $\omega_\perp \tau_{J_S}(0) \cong 2\pi$ should occur in the same density range, suggesting that dielectric friction for highly compressed, strongly polar gases may be as important for rotational relaxation as intermolecular collisions. For example, measurements on compressed CF_4 where collision damping alone occurs gives at 273 °K and $n \cong 2.8 \times 10^{21}$ cm^{-3} the result $\omega_\perp \tau_{J_S} = 4.8$.[35] For CH_3D dissolved in CH_4 gas at 100 bar or $n \cong 2.7 \times 10^{21}$ cm^{-3} at 310 °K gives $\omega_\perp \tau_{J_S}(0) = 7.1$.[36] Dielectric friction should become well apparent in the rotational relaxation rate at $n \geqslant 2 \times 10^{21}$ cm^{-3} as a quadratic density dependence which varies with temperature as $(\omega_\perp \tau_{J_S}(0))^{-1} \propto T^{-2}$. Whereas the dielectric friction decreases with increasing temperature, the short range collisional contribution should increase with rising temperature.

Another conceivable approach towards distinguishing the dielectric friction and the short range collision contributions to the angular momentum relaxation rate is to compare two or more different isotopes with greatly different moments of inertia. Suitable candidates may be the hydrogen halides HX and the deuterated halides DX. These differ in $I_\perp$ by a factor near 2, and thus dielectric friction should be less in the deuterated case by a factor $\cong 0.707$.

A further approach is to compare mixtures of different isotopes. Consider for instance the highly polar rotors the hydrogen halides. Let X and Y denote the solute and solvent molecules, respectively. We denote $\tau_{J_D}(X,\, Y)$ as the dielectric friction relaxation time of molecules X in molecules Y acting as the solvent gas. We then get from Eqs. (54), (55c), and (56) for $p^2 = q^2 = 1$

$$\frac{1}{\omega_\perp(X)\,\tau_{J_D}(X,\,Y)} \cong \frac{\pi(\pi/2)^{1/2}}{16}\left(\frac{\mu^2}{\epsilon_\infty kT a^3}\right)^2 F(X,\,Y)\,,$$

(60a)

where

$$F(X,\,Y) = \frac{2^{5/2}\,\lambda(X,\,Y)}{(1+\lambda(X,\,Y))^{5/2}}\quad,$$

(60b)

and

$$\lambda(X,\,Y) = I_\perp(X)/I_\perp(Y)\,.$$

$F(X,\,X) = 1$, and so $F(X,\,Y)$ denotes the relative effect of isotope mixing.

As a specific example consider the highly polar molecules HF and DF with $\mu = 1.82$ D. We have $I_\perp(\text{HF}) = 1.362\times10^{-40}$ g cm^2 and $I_\perp(\text{DF}) = 2.577\times10^{-40}$ g cm^2.[37] Thus, $\lambda(\text{HF, HF}) = \lambda(\text{DF, DF}) = 1$, $\lambda(\text{HF, DF}) = 0.528$, $\lambda(\text{DF, HF}) = 1.893$, and we have from Eq. (60b), $F(\text{HF, HF}) = F(\text{DF, DF}) = 1$, $F(\text{HF, DF}) = 0.752$, and $F(\text{DF, HF}) = 1.035$. Thus HF in predominantly DF gas has a 25% smaller dielectric friction effect than in pure HF gas. Comparing DF in HF solvent with pure DF produces no significant change. Pure HF compared with pure DF has factor $\lambda^{1/2}(\text{DF, HF}) = 1.38$ more dielectric friction. To get some idea of the absolute values of $(\omega_\perp(X)\,\tau_{J_D}(X,\,Y))^{-1}$ we need to take a temperature larger than the critical temperature $T_c = 461\,^\circ$K and a suitable number density, say, 2×10^{21} cm^{-3}. Using $\epsilon_\infty = 1$, $\mu = 1.82$ D, $T = 473\,^\circ$K, we get $(\omega_\perp\text{HF})\,\tau_{J_D}(\text{HF, Y})^{-1} \cong 0.044\,F(\text{HF, Y})$. For Y = HF this is 30% of the limiting condition $(\omega_\perp(\text{HF}))\,\tau_{J_\perp}(\text{HF, HF}))^{-1} \cong (2\pi)^{-1} = 0.16$. In contrast, the slightly less polar molecule HCl with $\mu = 1.08$ D, $T = T_c = 325\,^\circ$K, and $n = 2\times10^{21}$ cm^{-3} gives $(\omega_\perp(\text{HCl})\,\tau_{J_D}(\text{HCl, Y})^{-1} \cong 0.012\,F(\text{HCl, Y})$, which is a large reduction by factor 0.27 relative to HF illustrating the critical dependence on the molecular dipole moment. To illustrate the importance of having small molecules of small collisional damping and small moments of inertia, consider fluorobenzene with $\mu = 1.60$ D and $I_\perp = 6.96\times10^{-38}$ g cm^2. At $T = 350\,^\circ$C and $n = 1.2\times10^{21}$ cm^{-3} it is found that $(\omega_\perp\tau_{J_\perp}(0))^{-1} \cong 0.29$,[38] which is reasonably close to but exceeds the $(2\pi)^{-1} \cong 0.16$ limit for our dielectric friction theory. Nevertheless we obtain $(\omega_\perp\tau_{J_D}(0))^{-1} \cong 0.004$ only and thus negligible dielectric friction in this case.

An interesting facet of the dielectric friction problem is the Eq. (60b) maximum of $F(X,\,Y)$ at $\lambda(X,\,Y) = 3/2$. This may be interpreted as a long range rotational resonance effect where the dielectric friction effect is greatest when the solute molecule's angular frequency is in near resonance with the absorption peak of the dielectric solvent. Molecular rotation significantly detuned either side of the solvent absorption peak has much less dielectric frictional damping.

VI. DISCUSSION

The major qualitative conclusion of this paper is that in general the first order approximation to dielectric friction is inadequate. For strongly hindered rotation such as in dense gases and in liquids, the first order theory is accurate at high frequencies but becomes progressively less accurate as the frequency is decreased. At the lowest frequencies this effort may be roughly represented as a deviation by the factor $\gamma(0)$ as dis-

cussed in Sec. IV. It is significant that the free rotation calculation at angluar frequency $\omega_\perp$ produces a much larger deviation from the first order theory than obtained using the factor $\gamma(0)$. This suggests that although the slow rotation approximation is not accurate with regard instantaneous dipole motion, it becomes more accurate owing to the effect of intermolecular interactions which slow down the net reorientation rate. This observation is important for the formulation of the theory of dipolar plasmons which employs the first order approximation. This theory appears to be supported experimentally by the results of Ascarelli,[39] although the results of Asfar, Chantry, Birch, and Kilp[40] are less clear support of the dipolar plasmon hypothesis.

The present uncertainties in the cavity theory of dielectric friction can only be cleared up by evaluating Eqs. (28) and (29c) for rotational relaxation theories with strong intermolecular interaction effects. Only with such developments will it be possible to check the accuracy of the first order theory for dipolar plasmons. Furthermore, to properly take into account dielectric friction effects over the whole frequency range of non-associative polar liquid absorption and dispersion, more general model solutions to the formal dielectric friction theory are required. The general inadequacy of the first order approximation may at least in part explain the failure to fit the generalized Nee–Zwanzig theories to the whole frequency range of some polar liquids.[31,41]

An interesting but complicating aspect of dielectric friction is its sensitivity to molecular reorientation models, at least for orders above the first order approximation. A very simple example of this can be given as follows. Suppose that we calculate the $\mu^{(k)}(t) \times \mu^{(k+1)}(t)$ required in the definition of the $\tilde{Y}_k(\omega)$ equation (12) for a model defined by

$$\mu_x(t) = \mu(\cos\alpha - A\sin\alpha\sin\omega_0 t)\,,$$

$$\mu_y(t) = \mu(\sin\alpha + A\cos\alpha\sin\omega_0 t)\,,$$

$$\mu_z(t) = 0\,.$$

This represents dipole oscillatory rotation in the xy plane together with dipole "stretching" according to the relation

$$\mu_x^2(t) + \mu_y^2(t) = \mu^2 + \mu^2 A^2\sin^2\omega_0 t\,.$$

The oscillation is about a symmetry direction S chosen at arbitrary angle α to the x axis. It is easily found that all $\mu^{(k)}$ for $k \geq 1$ are in the xy plane along the direction perpendicular to S. Thus $\mu^{(k)}\times\mu^{(k+1)} = 0$ for $k \geq 1$, and so only the first order term exists. Thus, no matter how rapid the dipole rms rotation, the first order theory is exact for this case. This contrasts with free dipole rotation with fixed $|\mu(t)|$, where the curvature of the rotational velocity path ensures that not all of the $\mu^{(k)}$ are collinear so that the higher order terms all contribute.

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APPENDIX

To evaluate $\langle\langle \sin^2\theta \sin^2\phi \, \Omega_J^2 \, \delta(\Omega_J - \Omega_J')\rangle'\rangle$ it is convenient to convert this to dimensionless terms by defining the variables $x = \Omega_J/\omega_\perp'$ and $y = \Omega_J'/\omega_\perp'$, where $\omega_\perp' = (2kT/I_\perp')^{1/2}$ is the rms value of $\Omega_\perp'$. It is also convenient to define the parameters $\xi = (I_\perp/I_\parallel) - 1$ and $\xi' = (I_\perp'/I_\parallel') - 1$, where $\perp$ and $\parallel$ denote principal axes of inertia perpendicular and parallel to the symmetry axes of the solute and solvent molecules all assumed to be symmetric tops. It is also useful to write $\lambda = \omega_\perp'^2/\omega_\perp^2$. The distribution functions are, for the solute and solvent molecules, respectively,

$$f(x, \theta) = 2\pi^{-1/2}\lambda^{3/2}(1 + \xi)^{1/2} x^2 \exp[-\lambda x^2(1 + \xi\cos^2\theta)] , \tag{A1a}$$

$$f'(y, \phi) = 2\pi^{-1/2}(1 + \xi')^{1/2} y^2 \exp[-y^2(1 + \xi'\cos^2\phi)] . \tag{A1b}$$

These are normalized according to

$$\int_0^\infty \int_0^\pi f(x, \theta) \sin\theta \, d\theta \, dx = 1 .$$

The required average may then be written as

$$\langle\langle \sin^2\theta \sin^2\phi \, \Omega_J^2 \, \delta(\Omega_J - \Omega_J')\rangle'\rangle = \omega_\perp \lambda^{1/2} \langle\langle \sin^2\theta \sin^2\phi \, x^2 \delta(x - y)\rangle'\rangle$$

$$= \omega_\perp 4\pi^{-1}\lambda^2(1 + \xi)^{1/2}(1 + \xi')^{1/2} \int_0^\pi \int_0^\pi \int_0^\infty \sin^3\theta \sin^3\phi \, x^6 \exp[-x^2(1 + \lambda + \xi'\cos^2\phi + \lambda\xi\cos^2\theta)] dx \, d\theta \, d\phi . \tag{A2}$$

The integral over x may be immediately carried out using the basic result

$$\int_0^\infty x^6 \exp[-\alpha^2 x^2] dx = \frac{15\pi^{1/2}}{16\alpha^7} .$$

Combining this and Eq. (A2) with Eq. (53) leads to

$$\frac{1}{\omega_\perp \tau_{J_D}(0)} \cong \frac{5\pi^{1/2}}{8}(1 + \xi)^{1/2}(1 + \xi')^{1/2}\lambda^2 \left(\frac{\mu^2}{\epsilon_\infty kT a^3}\right)\left(\frac{\mu'^2}{\epsilon_\infty kT b^3}\right) \int_0^\pi \int_0^\pi \frac{\sin^3\theta \sin^3\phi \, d\theta \, d\phi}{(1 + \lambda + \xi'\cos^2\phi + \lambda\xi\cos^2\theta)^{7/2}} \tag{A3}$$

$$= \frac{5\pi^{1/2}}{2}\lambda^2 \left(\frac{\mu^2}{\epsilon_\infty kT a^3}\right)\left(\frac{\mu'^2}{\epsilon_\infty kT b^3}\right) I(\xi, \xi', \lambda) ,$$

where the variable change $\cos\theta = v$, $\cos\phi = u$ gives

$$I(\xi, \xi', \lambda) = (1 + \xi)^{1/2}(1 + \xi')^{1/2} \int_0^1 \int_0^1 \frac{(1 - u^2)(1 - v^2) \, du \, dv}{(1 + \lambda + \xi'u^2 + \lambda\xi v^2)^{7/2}} . \tag{A4}$$

To evaluate Eq. (A4), one must take in turn each case of ξ and ξ' positive or negative. The procedure is illustrated here for both ξ and ξ' positive and the general approach and the results for other cases quoted. Set $\kappa = 1 + \lambda + \xi'u^2$ and $\beta = (\xi\lambda/\kappa)$. Then we have

$$I(\xi, \xi', \lambda) = (1 + \xi)^{1/2}(1 + \xi')^{1/2} \int_0^1 \frac{(1 - u^2) \, du}{\kappa^{7/2}} \int_0^1 \frac{(1 - v^2) \, dv}{(1 + \beta v^2)^{7/2}} ,$$

and using the substitution $\beta^{1/2} v = \tan\alpha$ this reduces to

$$I(\xi, \xi', \lambda) = \frac{2}{15}(1 + \xi)^{1/2}(1 + \xi')^{1/2} \int_0^1 \frac{(1 - u^2)}{\kappa^{7/2}} \left(\frac{1}{(1 + \beta)^{3/2}} + \frac{4}{(1 + \beta)^{1/2}}\right) du .$$

To proceed further we write

$$\kappa = (1 + \lambda)[1 + \xi'(1 + \lambda)^{-1}u^2] ,$$

$$\eta = \xi'(1 + \lambda)^{-1} , \qquad \eta^{1/2}u = \tan\alpha ,$$

$$\beta = \xi\lambda(1 + \lambda)^{-1}\cos^2\alpha .$$

Then we have

$$I(\xi, \xi', \lambda) = \frac{2}{15} \frac{(1 + \xi)^{1/2}(1 + \xi')^{1/2}}{(1 + \lambda)^{7/2}\eta^{1/2}} \int_0^{\arctan\eta^{1/2}} \cos^5\alpha(1 - \eta^{-1}\sin^2\alpha\sec^2\alpha) \left(\frac{1}{(1 + \beta)^{3/2}} + \frac{4}{(1 + \beta)^{1/2}}\right) d\alpha .$$

To reduce this further set

$$1 + \beta = (1 - q^2)^{-1}(1 - q^2\sin^2\alpha) ,$$

where

$$q^2 = \xi\lambda(1 + \lambda)^{-1}[1 + \xi\lambda(1 + \lambda)^{-1}]^{-1} .$$

Define also

$$p^2 = \eta(1 + \eta)^{-1} = \xi'(1 + \lambda)^{-1}[1 + \xi'(1 + \lambda)^{-1}]^{-1} ,$$

and the new dummy variable $x = \sin\alpha$. Then we have

$$I(\xi, \xi', \lambda) = \frac{2}{15} \frac{(1 + \lambda p^2)^{1/2}(\lambda + q^2)^{1/2}}{\lambda^{1/2}(1 + \lambda)^{7/2}} J(p, q) , \tag{A5a}$$

where

$$J(p, q) = \frac{1}{p} \int_0^p \left((1 - x^2)^2 - \frac{(1 - p^2)}{p^2} x^2(1 - x^2) \right) \left(\frac{(1 - q^2)}{(1 - q^2 x^2)^{3/2}} + \frac{4}{(1 - q^2 x^2)^{1/2}} \right) dx . \tag{A5b}$$

$J(p, q)$ can be expanded out as

$$J(p, q) = [(1 - q^2)A(0, 3) + 4A(0, 1) - (1 + p^{-2})(1 - q^2)A(1, 3) - 4(1 + p^{-2})A(1, 1) + p^{-2}(1 - q^2)A(2, 3) + 4p^{-2}A(2, 1)] ,$$

where

$$A(n, m) = \frac{1}{p} \int_0^p \frac{x^{2n} \, dx}{(1 - q^2 x^2)^{m/2}} \quad .$$

The $A(n, m)$ are evaluated using the substitution $qx = \sin\alpha$, giving

$$A(n, m) = \frac{1}{pq^{2n+1}} \int_0^{\arcsin(pq)} \frac{\sin^{2n}\alpha}{\cos^{m-1}\alpha} \, d\alpha .$$

The required values are

$$A(0, 1) = (pq)^{-1} \arcsin(pq) ,$$

$$A(0, 3) = (1 - (pq)^2)^{-1/2} ,$$

$$A(1, 1) = \tfrac{1}{2} q^{-2}[(pq)^{-1} \arcsin(pq) - (1 - (pq)^2)^{1/2}] ,$$

$$A(1, 3) = q^{-2}[(1 - (pq)^2)^{-1/2} - (pq)^{-1} \arcsin(pq)] ,$$

$$A(2, 3) = q^{-4}[(1 - (pq)^2)^{-1/2} + \tfrac{1}{2}(1 - (pq)^2)^{1/2} - \tfrac{3}{2}(pq)^{-1} \arcsin(pq)] ,$$

$$A(2, 1) = \tfrac{1}{2} q^{-4}[\tfrac{3}{4}(pq)^{-1} \arcsin(pq) - (1 - (pq)^2)^{1/2} + \tfrac{1}{4}(1 - (pq)^2)^{1/2}(1 - 2(pq)^2)] .$$

The result for $J(p, q)$ is found to be Eq. (56), and the final result for the dielectric friction contribution to the angular momentum relaxation rate equation (54) is obtained by substituting Eq. (A5a) into Eq. (A3).

If one or both of ξ and ξ' are negative, the above procedure is modified only slightly, where trigonometric substitutions are replaced by hyperbolic function substitutions. The results of these calculations are summarized in the main text of the paper.

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