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Solute rotation in polar liquids: Microscopic basis for the Stokes-Einstein-Debye model

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Here, we develop a framework for a molecular level understanding of the celebrated Stokes-Einstein-Debye (SED) formula. In particular, we explore reasons behind the surprising success of the SED model in describing dipolar solute rotation in complex polar media. Relative importance of solvent viscosity and solute-solvent dipolar interaction is quantified via a self-consistent treatment for the total friction on a rotating solute where the hydrodynamic contribution is modified by the friction arising from the longer ranged solute-solvent dipolar interaction. Although the solute-solvent dipolar coupling is obtained via the Mori-Zwanzig formalism, the inclusion of solvent structure via the wave vector dependent viscosity in the hydrodynamic contribution incorporates solvent molecularity in the present theory. This approach satisfactorily describes the experimental rotation times measured using a dipolar solute, coumarin 153 (C153), in protic and aprotic polar liquids, and more importantly, provides microscopic explanation for insignificant contribution of electrical interactions on solute rotation, in contrast to the substantial role played by the translational dielectric friction in the context of ionic mobility. It is also discussed on how the present theory can be suitably extended to study the rotation of a realistic solute in media other than dipolar solvents. © 2012 American Institute of Physics. [doi:10.1063/1.3672508]

I. INTRODUCTION

Solute rotation, obtained via time-resolved fluorescence anisotropy¹ experiments, supplies information on the structure and dynamics of the environment surrounding a solute in a given medium.^{2–5} The average rotation time (τ_R) of a solute that describes the overall relaxation of the solute orientation, is conventionally understood by the Stokes-Einstein-Debye (SED) model.^{6,7} According to this model under the stick boundary condition, τ_R for a spherical rotor with volume V_p in a medium of viscosity η is given by $\tau_R = 1/6D_R = \Gamma_{rot}^{hyd}/6k_B T$, where D_R is the rotational diffusion coefficient, and $k_B T$, the Boltzmann constant (k_B) times the absolute temperature. The hydrodynamic rotational friction,^{8,9} $\Gamma_{rot}^{hyd} = 6\eta V_p$. A modified version of the original SED expression,^{6,7} $\tau_R = \eta V_p C f / k_B T$, is also used to account for the variations in solute shape (f) and the consequent changes in solute-solvent coupling (C).

Even though the conventional SED model and its variant has received enormous success in describing solute rotation in polar solvents,⁷ electrolyte solutions⁴ and for biologically relevant moieties,⁵ it completely breaks down while explaining the non-monotonic density dependence of τ_R measured using coumarin 153 (C153) in a supercritical (SC) polar medium, such as fluoroform (CHF₃) at different temperatures.¹⁰ Our recent work,¹¹ incorporating the solvent structural effects in

the friction experienced by the rotating solute rather satisfactorily describes the above density-dependence in molecular terms within the SED-framework. In that approach,¹¹ for a given fluid with molecular diameter σ we have used a generalized expression of the hydrodynamic friction: $\Gamma_{rot}^{hyd}(k\sigma) = 6\eta(k\sigma)V_p$, where $\eta(k\sigma)$ is the wave vector (k)-dependent viscosity. Here, we find that $\eta(k\sigma)$ contains the molecular information of the solvent in the friction via the solvent static structure factor $S(k\sigma)$.^{12–14} The validity of this description of $\eta(k\sigma)$ has been verified by molecular dynamics simulations¹¹ on normal liquids and reproduction of the experimental viscosity of SC CHF₃ by numerical calculations.

The success of the above generalization of the SED model then naturally raises the following question: Why does the simple and purely hydrodynamic SED model work so well for complex media? We address this question here through a rigorous microscopic description of solute rotation in a dipolar liquid medium. Note that the generalized molecular hydrodynamic friction $\Gamma_{rot}^{hyd}(k\sigma)$ takes into account the solvent-solvent interactions. However, the solute-solvent interactions are accounted for only via V_p , the excluded volume of the solvent due to the presence of the solute. Since the friction arises due to the solute-solvent coupling at the molecular level, the rotational friction Γ_{rot} should contain the effects from all the solute-solvent and solvent-solvent microscopic interactions.

The solute-solvent long-ranged electrostatic interactions become operational when the solute and the solvent are charged or having permanent electrical moment. Nee and Zwanzig¹⁵ explored, within a continuum model description, the connection between the rotational friction and the dielectric response of a liquid. When a polar solute rotates in a

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polar medium, there is a redistribution of the polarization field generated by the solute in its surrounding solvent. This redistribution is not instantaneous, rather takes time, thus imparting a friction on the solute against the motion, termed as the “dielectric friction.” The early theoretical approaches,^{15–20} addressing dielectric friction, included the solvent effects through continuum dielectric constant and relaxation time.

The solute in all these theories has been a point dipole in a spherical cavity. Alavi and Waldeck²¹ carried out a significant development of dielectric friction introducing extended charge distribution model where a solute molecule is treated so that the constituent atoms with individual partial charges are distributed in an asymmetric ellipsoidal cavity. The solute rotation in this anisotropic model is considered in different directions rendering it much more realistic compared to the earlier theories. The model has been able to qualitatively explain the differences in observed experimental rotation times of ionic and neutral fluorescent phenoxazine dyes of similar size in a common solvent.^{22–24} In case of anionic resorufin, the agreement is quantitative. However, the estimated times are far less than the experimental data for the neutral resorufamine and cationic oxazine and thionine. Later simulation studies^{22,25} show that the neutral and cationic solutes participate in complexation with the solvent leading to enhancement of the effective volume of the rotating body and hence larger rotation times. In spite of realistic elements, this model received limited applications for two principal reasons: the high sensitivity on the cavity radius²¹ and the somewhat arbitrary truncation of the number of terms used in the expression of dielectric friction.^{21,26} Both these factors are highly system specific, varying for different solute-solvent combinations. Moreover, the solvent is still considered as a dielectric continuum without any microscopic details.

Although the concept of dielectric friction has been a key to understand ion-transport^{27–32} and other non-equilibrium phenomena in polar media; in general,²⁰ its role in solute rotation are still a matter of considerable debate.^{7,20,33–35} Fluorescence anisotropy measurements of C153 in various polar liquids show⁷ that τ_R increases linearly with the solvation time and consequently, viscosity of the solvent. τ_R in a polar medium is observed to be slightly larger than that in a non-polar medium of similar viscosity. It is tempting to interpret the additional slowing down of τ_R in terms of extra dielectric friction operating in the system. The conventional van der Zwan and Hynes (VZH) theory,¹⁸ used widely to estimate the dielectric contributions towards the rotational friction, shows that the dielectric friction depends linearly on the solvation time. Calculations for C153 in the aprotic solvents reported in Ref. 7 using this model, yield dielectric contributions around 10–20% of the total friction. Similar estimation for the monohydroxy alcohols indicates even larger contributions of dielectric friction due to larger average solvation times for the alcohols compared to those for the aprotic solvents of similar polarity. However, the enhancement of experimental τ_R is not as large as predicted by the existing dielectric friction theories.^{15,18} Such discrepancy calls for a proper microscopic theory of the dielectric friction on solute rotation.

Recent computer simulation studies^{20,34} reveal that the enhancement of the friction can be attributed to a static

“electrostriction” effect, originated from an enhanced solvent structure in the first solvation shell around the solute due to solute-solvent electrostatic interactions. In this work, we develop a theoretical formalism for the modification of the rotational friction due to increased solvent ordering around the solute via the longer-ranged solute-solvent interactions. The microscopic solvent-solvent interaction has been taken into account via wave vector dependent viscosity. We derive an expression for the rotation time of a dipolar solute in a dipolar solvent, where the relevant parameters have been obtained from microscopic considerations. Both the solute and the solvent are treated as point dipoles embedded in the center of hard spheres to keep the calculation analytically tractable. Our main finding is that the solute-solvent electrical interactions have marginal effects on solute rotation, allowing an overwhelming dominance of hydrodynamic friction on the average rotation times. In this way, we provide a molecular level explanation for the validity of the well-known SED description for solute rotation in polar solvents.

II. MOLECULAR HYDRODYNAMIC FRICTION

Let us first calculate the rotation time for a polar solute in a polar liquid from the molecular hydrodynamic friction $\Gamma_{rot}^{hyd}(k\sigma)$. Consider the case of C153 in acetonitrile at ambient condition as a representative example. The wave vector dependent viscosity for a liquid solvent¹¹ in the limit of slip boundary condition,¹⁴ appropriate for normal liquids, is $\eta(k\sigma) = k_B T / 4\pi r_0 D S(k\sigma)$, r_0 and D being the radius and the translational self-diffusion coefficient of the solvent, respectively. Here, we model acetonitrile as a fluid consisting of hard spheres of diameter σ with central point dipole, of dipole moment $\mu = 3.5D$.³⁶ Calculated $S(k\sigma)$, shown in Figure 1, reveals the only peak (nearest neighbor) around the wave vector $k\sigma \approx 2\pi$ which according to molecular hydrodynamics, represents the governing wave vector modes for shear waves in a liquid.^{37–39} Therefore, the average viscosity is given by,¹¹ $\bar{\eta} = \int \eta(k\sigma) d\mathbf{k}\sigma / \int d\mathbf{k}\sigma$, integrating over the wave vectors spanning the nearest neighbor peak. Using the values of r_0 and D for acetonitrile,^{7,40} we find $\bar{\eta} = 0.29$ cP at 300 K, which is close to the experimental shear viscosity,⁷ 0.34 cP. Now, we introduce the wave vector dependent rate of rotational relaxation:¹¹ $\tilde{\omega}(k\sigma) = k_B T / \eta(k\sigma) V_p$, obtained with $\eta(k\sigma)$ replacing η in the SED expression. An average rate of rotational relaxation is defined by integrating over the wave vectors under the $k\sigma \approx 2\pi$ peak of $S(k\sigma)$: $\tilde{\omega}_{av} = \int \tilde{\omega}(k\sigma) d\mathbf{k}\sigma / \int d\mathbf{k}\sigma$. The average rotation time can then be identified as⁴¹ $\tau_R^{hyd} = 1/\tilde{\omega}_{av} \approx \bar{\eta} V_p / k_B T$. Using $V_p = 246 \text{ \AA}^3$,³⁶ we find $\tau_R^{hyd} = 17$ ps for C153, which is faster by $\sim 20\%$ from that measured (22 ps) in experiments.⁷

III. FRICTION DUE TO LONG-RANGED INTERACTION

Let us now include the longer ranged solute-solvent interactions in the total rotational friction. The torque acting on a rotating dipolar solute can then be written as $f(t) = -\partial U(\theta) / \partial \theta$, where θ is the time-dependent solute-orientation with respect to the laboratory frame z -axis, $U(\theta)$

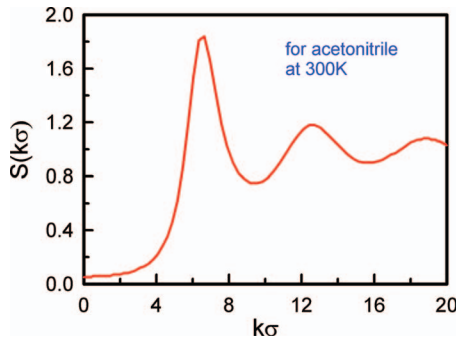


FIG. 1. Static structure factor of acetonitrile at 300 K, as a function of wave vectors. The details of this calculation have been given in our earlier work.¹¹

being the solvent-orientation averaged solute-solvent dipolar interaction potential energy.¹¹ For simplicity, consider first the solvent molecules that are immediate neighbors to the dissolved solute. The interaction potential between the dipolar solute and a polar solvent molecule, $V_{dip}(R_s, \theta, \theta')$, integrated over all possible solvent orientation θ' , weighted by the solvent orientational density $\rho(\theta', t)$ in the first solvation shell, provides an estimate of $U(\theta)$,

$$U(\theta) = \int V_{dip}(R_s, \theta, \theta') \rho(\theta', t) d(\cos \theta'), \quad (1)$$

where $R_s = r_0 + R_0$, the solute-solvent separation in the first solvation shell, R_0 being the solute radius. Note, $U(\theta)$ has got implicit time dependence via the time-dependent solvent density $\rho(\theta', t)$. $V_{dip}(R_s, \theta, \theta')$, for the photo-excited solute dipole and a solvent dipole, can be written as¹¹

$$V_{dip}(R_s, \theta, \theta') = -u_0 \cos \theta \cos \theta', \quad (2)$$

where $u_0 = \mu_0 \mu / R_s^3$, the solute-solvent interaction strength. The normalized projection of $\rho(\theta', t)$ for spherical harmonics $l = 1$ and $m = 0$ is given by

$$\rho_{10}(t) = \int d(\cos \theta') Y_1^0(\cos \theta') \rho(\theta', t) / \rho_0, \quad (3)$$

where $\rho_0 = 1/4\pi$, the bulk orientational solvent density. Here, $\rho_{10}(t)$ approximately determines the solvent response towards the photo-excitation of the solute dipole, which is proportional to the solvent polarization. Using Eqs. (1)–(3), one obtains

$$U(\theta) = -u_0 \rho_{10}(t) \rho_0 \cos \theta. \quad (4)$$

The microscopic expression for the time-dependent total torque, in the limit of small angular displacements, then becomes

$$f(t) = u_0 \rho_{10}(t) \rho_0 \sin \theta \approx u_0 \rho_{10}(t) \rho_0 \theta. \quad (5)$$

Rotational friction due to the long-ranged solute-solvent interaction, $\delta \Gamma_{rot}$ is subsequently determined by the memory function^{14,42} $M(t)$, the auto-correlation function of the time-dependent fluctuating torque which is the orthogonal projection^{14,42} of the total torque $f(t)$. $M(t)$ is related to the auto-correlation function of the total torque, $\phi(t) = \langle f(t)f(0) \rangle / I^2 \langle \dot{\theta}(0)\dot{\theta}(0) \rangle$, by the Mori-Zwanzig

formalism^{14,42}

$$\frac{1}{\tilde{M}(s)} = \frac{1}{\tilde{\phi}(s)} + \frac{1}{s}, \quad (6)$$

where $\tilde{M}(s)$ and $\tilde{\phi}(s)$ denote the Laplace transforms of $M(t)$ and $\phi(t)$, respectively, at a complex frequency s . Here, I denotes the moment of inertia of the rotating body about the axis of rotation. Using the equipartition theorem, we obtain

$$\phi(t) = \frac{\langle f(t)f(0) \rangle}{Ik_B T}, \quad (7)$$

which, after using Eq. (5), takes the following form

$$\phi(t) = \frac{u_0^2 \rho_0^2}{Ik_B T} \langle \rho_{10}(t) \rho_{10}(0) \theta(t) \theta(0) \rangle. \quad (8)$$

Note that $\phi(t)$ has coupling between the fast mode $\rho_{10}(t)$, describing the orientational relaxation of the solvent and slow mode $\theta(t)$, describing the rotational motion of the solute. For rotation of a massive and large polar solute in fast polar solvents, the relaxation time scales of $\rho_{10}(t)$ and $\theta(t)$ are widely separated. Hence, under decoupling approximation⁴³ one can write

$$\phi(t) \approx \frac{u_0^2 \rho_0^2}{Ik_B T} \langle \rho_{10}(t) \rho_{10}(0) \rangle \langle \theta(t) \theta(0) \rangle. \quad (9)$$

Now, the lag in solvent response towards solute rotation can be linked to the solvent reorganization time via the following approximate relation: $\rho_{10}(t) = \rho_{10}(0)e^{-t/\tau_s}$, τ_s being the average solvation time. For the auto-correlation function of the slow angular variable, we consider the equation of motion of the solute,

$$\Gamma_{rot} \dot{\theta} = -\frac{\partial U(\theta)}{\partial \theta} + \xi(t), \quad (10)$$

where $\xi(t)$ denotes the fluctuating torque arising out of all possible sources including short-ranged and long-ranged forces and the terms non-linear in θ . Here, $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(0) \rangle = 2\Gamma_{rot} k_B T \delta(t)$.^{12,14} Considering the initial equilibrium distribution of the solvent around the rotating solute, we can write Eq. (10) in Fourier space,

$$i\omega \Gamma_{rot} \theta(\omega) = u_0 \rho_{10}(0) \rho_0 \theta(\omega) + \xi(\omega), \quad (11)$$

and subsequently

$$\langle \theta(\omega) \theta(-\omega) \rangle = \frac{2k_B T}{\Gamma_{rot} [\omega^2 + (u_0 \rho_0 \rho_{10}(0) / \Gamma_{rot})^2]}, \quad (12)$$

which, upon inverse Fourier transformation, becomes

$$\langle \theta(t) \theta(0) \rangle = \frac{k_B T}{u_0 \rho_0 \rho_{10}(0)} \exp \left[-\frac{u_0 \rho_0 \rho_{10}(0)}{\Gamma_{rot}} t \right]. \quad (13)$$

Therefore, the normalized profile for orientational correlation function for solute,

$$\frac{\langle \theta(t) \theta(0) \rangle}{\langle \theta(0) \theta(0) \rangle} = \exp \left[-\frac{u_0 \rho_0 \rho_{10}(0)}{\Gamma_{rot}} t \right]. \quad (14)$$

Using this normalized profile in Eq. (9), we get

$$\phi(t) = B e^{-\lambda t}, \quad (15)$$

where $B = u_0^2 \rho_0^2 \rho_{10}(0)^2 / Ik_B T$ and $\lambda = ((u_0 \rho_0 \rho_{10}(0) / \Gamma_{rot}) + (1/\tau_s))$.

Now, the Laplace transform of Eq. (15) is $\tilde{\phi}(s) = B/(s - \lambda)$. Insertion of this in Eq. (6) leads to

$$\tilde{M}(s) = \frac{Bs}{(s - \lambda)s + B}, \quad (16)$$

which can further be expressed as

$$\tilde{M}(s) = \frac{B}{\sqrt{\lambda^2 - 4B}} \left[\frac{s_+}{s - s_+} - \frac{s_-}{s - s_-} \right], \quad (17)$$

s_+ and s_- being the roots of the equation, $s^2 - \lambda s + B = 0$, given by $s_{\pm} = (\lambda \pm \sqrt{\lambda^2 - 4B})/2$. Here s_- gives a divergent exponential in $t \rightarrow \infty$ limit, implying an unphysical situation. Therefore, integrating around the pole at s_+ , we have the inverse Laplace transform

$$M(t) = \frac{B}{\sqrt{\lambda^2 - 4B}} s_+ e^{-s_+ t}. \quad (18)$$

Now, we calculate $\delta\Gamma_{rot}$ by the time-integral of the memory function $M(t)$,

$$\delta\Gamma_{rot} = \frac{I}{2} \int_0^\infty M(t) dt, \quad (19)$$

providing

$$\delta\Gamma_{rot} = \frac{I}{2} \frac{B}{\sqrt{\lambda^2 - 4B}}. \quad (20)$$

In the limit of weak solute-solvent coupling (i.e., $\lambda^2 > B$), insertion of the expressions of B and λ in Eq. (20) produces

$$\delta\Gamma_{rot} = \frac{[u_0 \rho_0 \rho_{10}(0)]^2}{2k_B T} \left(\frac{u_0 \rho_0 \rho_{10}(0)}{\Gamma_{rot}} + \frac{1}{\tau_s} \right)^{-1}. \quad (21)$$

Equation (21) is a self-consistent expression for $\delta\Gamma_{rot}$ since $\Gamma_{rot} = \Gamma_{rot}^{hyd} + \delta\Gamma_{rot}$. The solution to Eq. (21) is given by

$$\delta\Gamma_{rot} = \frac{\frac{[u_0 \rho_0 \rho_{10}(0)]^2}{2k_B T} \Gamma_{rot}^{hyd} \tau_s}{u_0 \rho_0 \rho_{10}(0) \tau_s + \Gamma_{rot}^{hyd} - \frac{[u_0 \rho_0 \rho_{10}(0)]^2}{2k_B T} \tau_s}. \quad (22)$$

Note Eq. (22) connects $\delta\Gamma_{rot}$ to the orientational static solvent structure around the solute, ρ_{10} and the average solvation time, τ_s . The total friction now becomes

$$\Gamma_{rot} = \Gamma_{rot}^{hyd} \left[1 - \frac{(u_0 \rho_0 \rho_{10}(0))^2 \tau_s}{2k_B T (\Gamma_{rot}^{hyd} + u_0 \rho_0 \rho_{10}(0) \tau_s)} \right]^{-1}. \quad (23)$$

Expansion of Eq. (23) in the weak solute-solvent coupling limit produces the following first order term:

$$\Gamma_{rot} = \Gamma_{rot}^{hyd} \left[1 + \frac{(u_0 \rho_0 \rho_{10}(0))^2 \tau_s}{2k_B T (\Gamma_{rot}^{hyd} + u_0 \rho_0 \rho_{10}(0) \tau_s)} \right], \quad (24)$$

where $\rho_{10}(0) = \frac{2u_0/3k_B T}{1 - 2\mu^2 \rho_b / 9k_B T}$, obtained¹¹ from equilibrium density functional theory (DFT) for the classical systems, ρ_b being the bulk solvent density. Now, we write down Eq. (24) as

$$\Gamma_{rot} = \Gamma_{rot}^{hyd} [1 + J], \quad (25)$$

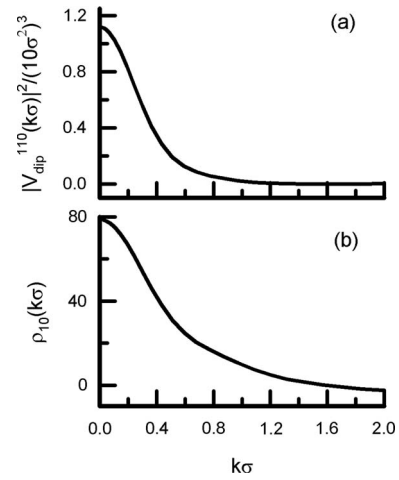


FIG. 2. (a) $|V_{dip}^{110}(k\sigma)|^2$, the dominant angular part of the solute-solvent interaction potential and (b) the relevant angular component of the microscopic solvent density $\rho_{10}(k\sigma)$ around the solute. Here, we show both these quantities for C153 in acetonitrile, at different wave vectors.

where $J = \frac{(u_0 \rho_0 \rho_{10}(0))^2 \tau_s}{2k_B T (\Gamma_{rot}^{hyd} + u_0 \rho_0 \rho_{10}(0) \tau_s)}$, the solute-solvent dipolar coupling factor. Note that, J is essentially the ratio $\delta\Gamma_{rot}/\Gamma_{rot}^{hyd}$, diminishing with increasing hydrodynamic friction.

Next, we extend our calculations to take into account the effects of solvent molecules beyond the first solvation shell around the solute. We find the expression of the coupling factor (Appendix A): $J = 3\rho_b I_R \tau_s / 8\pi k_B T [\Gamma_{rot}^{hyd} + U_0(0)\tau_s]$, where $I_R = (2\pi)^{-6} \int d\mathbf{k} |V_{dip}^{110}(\mathbf{k})|^2 |\rho_{10}(\mathbf{k}, 0)|^2$ and $U_0(t) = -\sqrt{3/4\pi} (2\pi)^{-3} \int V_{dip}^{110}(\mathbf{k}) \rho_{10}(\mathbf{k}, t) d\mathbf{k}$. Here, $V_{dip}^{110}(\mathbf{k})$ and $\rho_{10}(\mathbf{k}, t)$ denotes the Fourier components of the solute-solvent dipolar interaction potential and the normalized solvent density distribution around the solute, respectively. We calculate $\rho_{10}(\mathbf{k}, 0)$ by using the DFT treatment (Appendix B).

In Figure 2, we illustrate the behaviors of $V_{dip}^{110}(\mathbf{k})$ and $\rho_{10}(\mathbf{k}, 0)$. These two quantities govern the interaction terms $U_0(0)$ and I_R to decide the values of J . We consider the case of C153 in acetonitrile, using the excited state dipole moment of C153 to be³⁶ $\mu_0 = 14\text{D}$ and van der Waals radius³⁶ $R_0 = 3.9\text{\AA}$. Figure 2(a) shows the plot of $|V_{dip}^{110}(\mathbf{k})|^2$ at different wave vectors. It decays from maximum near $k\sigma \approx 0$ mode. We show in Figure 2(b), the profile of $\rho_{10}(\mathbf{k})$ for the same system exhibiting a similar behavior to $|V_{dip}^{110}(\mathbf{k})|^2$. From the nature of these two at different wave vectors, it is quite clear that the dominant electrical contributions towards the friction come from the long wavelength, i.e., $k\sigma \approx 0$ mode. This actually reflects the long-ranged nature of the solute-solvent interaction.

The details of estimated dielectric friction for C153 in various polar liquids, both aprotic and the alcohols are presented in Figure 3. Here, the solvent parameters we use in our calculations are: the liquid self-diffusion coefficients,^{40,44–48} dipole moments,^{36,49–51} static dielectric constants,³⁶ van der Waals radii,⁷ and the average solvation times.⁷ For these calculations, we replace Γ_{rot}^{hyd} in Eq. (25) by that averaged over the wave vector window around the nearest neighbor modes. Figure 3(a) shows the dielectric part of the total friction, $\delta\Gamma_{rot}$ as a function of average solvation time while the hydrodynamic part Γ_{rot}^{hyd} is shown in Figure 3(b). Note the difference

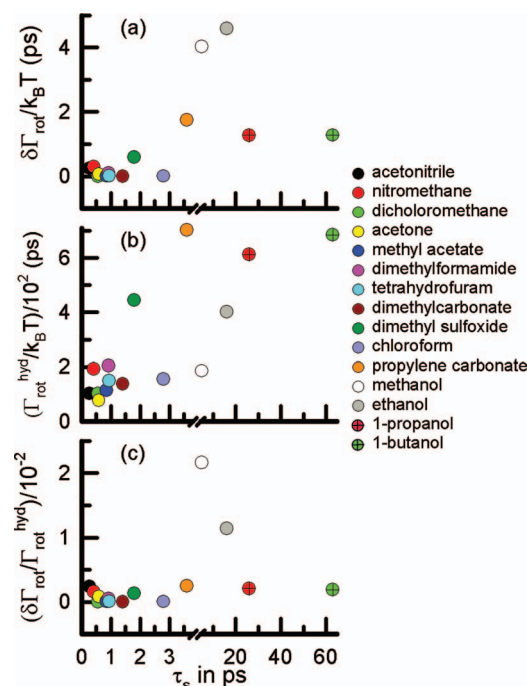


FIG. 3. (a) The dielectric contribution $\delta\Gamma_{rot}$ and (b) the hydrodynamic contribution Γ_{rot}^{hyd} towards the total rotational friction, and (c) the ratio of those two: $\delta\Gamma_{rot}/\Gamma_{rot}^{hyd}$, all as functions of average experimental solvation times for C153 in aprotic polar liquids and in alcohol solvents. The solvation times have been taken from Ref. 7.

in scales of the vertical axes in these two panels. We find that for most of the aprotic solvents the dielectric part is nearly zero barring the cases of dimethyl sulfoxide and propylene carbonate both of which have dipole moments larger than 4D. The alcohols also exhibit comparatively larger dielectric contributions. In Figure 3(c), we show the ratio $\delta\Gamma_{rot}/\Gamma_{rot}^{hyd}$, i.e., the coupling factor J which turn out to be too small in all the cases to generate any considerable dielectric contribution. This coupling factor accounts for at most $\sim 1\%$ – 2% of the total friction, even for solvents like the alcohols supporting observations of Ref. 7. A closer inspection reveals that the hydrodynamic friction Γ_{rot}^{hyd} is always very large compared to the product $I_R\tau_s$ in the numerator of J , rendering it small.

IV. ROTATION TIMES

Let us now discuss about the rotation times. We can rewrite Eq. (25) as

$$\tau_R = \tau_R^{hyd} [1 + J]. \quad (26)$$

Figure 4 shows the experimental (circles) and calculated (triangles) average rotation times⁷ of C153 in the polar liquids depicted in Figure 3, as a function of experimental average solvation times. From the data in Figure 4, it is clear that the calculated rotation times agree reasonably well with the experimental values. The deviations observed in some of the cases are purely due to the limitation of the model parameters used. For instance, 10% reductions in the molecular radius⁷ of acetone (2.5 Å) and its self-diffusion coefficient⁴⁵ ($4.77 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), enhances the estimated τ_R by about 30%, in better agreement to the experimental time.⁷ Further, Figure 4

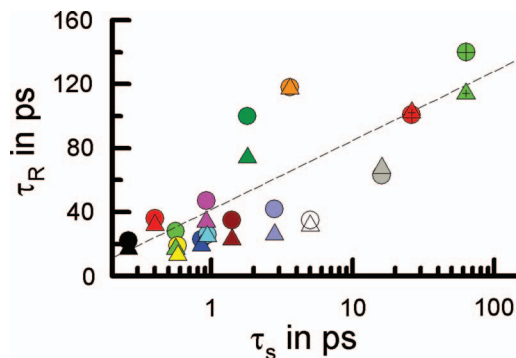


FIG. 4. The experimental (circles) and calculated (triangles) rotation times of C153 in aprotic polar solvents and alcohols, as a function of experimental average solvation times. The experimental rotation times are taken from Ref. 7. Note, the color codes used in this figure are identical to that of Figure 3. We also show here the best linear fit through the experimental points by the dotted straight line.

indicates a more or less linear dependence^{52–54} between τ_R and τ_s , shown by the best fit line through the experimental data. Such behavior can be rationalized by noting that in general we have $\Gamma_{rot}^{hyd} \gg U_0(0)\tau_s$, true for all the liquids we study here. Under these circumstances, Eq. (26) can be approximated as

$$\tau_R = \tau_R^{hyd} + \frac{3\rho_b I_R}{48\pi(k_B T)^2} \tau_s, \quad (27)$$

showing a linear dependence between τ_R and τ_s . Typically in polar solvents, τ_s is proportional to solvent viscosity η . So the linear dependence in Eq. (27) implies that τ_R is also proportional to η which is observed in experiments. In most of the polar solvents, the pre-factor of the term containing τ_s is too small to contribute significantly to τ_R . However, if the pre-factor is large due to large solute-solvent coupling this additional dependence could be observed.

V. DISCUSSION AND CONCLUSION

In summary, we have developed a microscopic theory that systematically includes the effects of solute-solvent dipole-dipole interactions and solvent structure on average rotation time of a polar solute in a polar solvent. We find that the rotational relaxation of a dipolar solute in a polar medium is governed by the hydrodynamics, having little dependence on the long-ranged solute-solvent interaction. We thus provide a molecular basis for the SED model which has been obtained from purely hydrodynamic consideration.

As far as the magnitudes are concerned, our estimated values of dielectric friction are smaller than those obtained from the VZH theory. The differences between the VZH and our results are more significant for the alcohol solvents. Interestingly, a common point of both the frameworks lies in the inclusion of the solute-solvent interaction and the solvation time to determine the dielectric friction. In the VZH approach, the solute-solvent interaction is incorporated in terms of experimentally observed fluorescence Stokes shift.³⁶ It has been experimentally observed that C153 exhibits larger solvation times in alcohol solvents compared to the same in aprotic solvents of equivalent polarity, probably due to

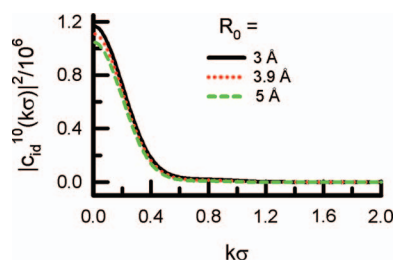


FIG. 5. The longitudinal component of solute-solvent direct correlation function, $|c_{id}^{10}(k\sigma)|^2$ as a function of wave vector $k\sigma$, for ionic solutes in acetonitrile. The solute here is modeled as a hard-sphere with a unit positive charge embedded at the center. We show the data for three values of the solute radius with insignificant dependence for solutes larger than solvents.

solute-solvent specific interactions and/or solvent-solvent interactions. It is to be mentioned here that computer simulation studies⁵⁵ have indicated presence of such interactions, even though effects of these interactions have not been reflected strongly in the solvatochromic shift³⁶ of C153 in protic polar solvents. Therefore, the VZH description, based directly on the Stokes shift values and solvation times, predicts larger friction for alcohols than aprotic solvents. In the present theory, the solute-solvent interactions are considered using a microscopic model of the interactions where in principle the Stokes shift values can also be used. It is indeed true that, in common to the VZH approach, the dielectric friction in the present theory is related to the average solvation time. However, the difference here is that the dependence on the average solvation times is non-linear and enters through a self-consistent manner (Eq. (22)). This non-linear dependence on average solvation time reduces the magnitude of dielectric friction significantly compared to that predicted by the VZH approach. Even in the linearized version (Eq. (27)), the pre-factor of τ_s for these solute-solvent systems is rather small.

Similar self-consistent treatment of dielectric friction, as in our calculation, done in the context of ion-transport in a polar medium to obtain the dielectric friction^{27–32} shows substantial contribution of the long-ranged forces. The solute-solvent longer ranged interaction in those cases is of ion-dipole type, much stronger compared to the dipole-dipole interaction. Figure 5 shows the longitudinal component of wave vector dependent direct correlation function, $c_{id}^{10}(k\sigma)$ (Refs. 32 and 56) plotted for an ionic solute placed in acetonitrile. For a univalent cationic solute of size comparable to C153, the value of $|c_{id}^{10}(k\sigma)|^2$ is about 1000 times larger than $|V_{dip}^{110}(k\sigma)|^2$ (Figure 2(a)) at $k\sigma \approx 0$. Since the principal electrical contribution to friction arises from the $k\sigma \approx 0$ mode, clearly the dielectric friction would be important for ion translation but not so significant for solute rotation in a polar solvent.

Finally, the present approach can be extended to rotation of more realistic solute in variety of solvents. One needs to this end, a proper description of the solvent static structure factor to calculate the wave vector dependent viscosity and an appropriate solute-solvent interaction model. One can consider in that case, the solute-solvent interaction in a general way: $V(|\mathbf{r} - \mathbf{R}|, \theta, \theta') = \sum_{l_1, l_2, m} V^{l_1 l_2 m}(|\mathbf{r} - \mathbf{R}|) Y_{l_1}^m(\cos \theta) Y_{l_2}^m(\cos \theta')$. Inclusion of

the higher harmonics ($l_1, l_2 > 1$) will take care of the contributions from the finite charge distributions over the solute and the solvent molecules systematically. Similar expressions can be written for the fluctuating solvent density and the solvent-solvent static correlations. This kind of modeling would be very similar to the extended charge distribution model²¹ considered earlier. Note that the coupling parameter J depends on a competition between Γ_{rot}^{hyd} and the product $U_0(0)\tau_s$. The modified treatment will affect the solute-solvent interaction strength $U_0(0)$, resulting in very different value of the dielectric friction. However, the calculation scheme will be numerically quite intensive, losing analytical simplicity of the present one. The scenario could be simplified for an uncharged multipolar solute in a non-dipolar solvent having only higher multipole moments. The solute-solvent interaction term $V^{l_1 l_2 m}(|\mathbf{r} - \mathbf{R}|)$ will then fall off quite fast as a function of $|\mathbf{r} - \mathbf{R}|$. In such cases,⁵⁷ the rotational friction will be dominated by the packing of the solvent around the solute, as indicated by the data in Ref. 7.

Furthermore, it would be interesting to investigate different cases where the dielectric contributions to net friction may be appreciable. If, for a certain solute-solvent combination, $U_0(0)\tau_s$ becomes comparable to Γ_{rot}^{hyd} , the corresponding dielectric contribution may be significant. For instance, the solute-solvent coupling and the average solvation times for similar fluorescent solutes are reported to be very large in room temperature ionic liquids.^{3,53,54,58–61} We shall report on some of these systems in future papers.

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APPENDIX A: CALCULATION OF THE SOLUTE-SOLVENT DIPOLAR COUPLING FACTOR J INCLUDING THE EFFECTS OF SOLVENT MOLECULES BEYOND THE FIRST SOLVATION SHELL AROUND THE POLAR SOLUTE

Here, we calculate the coupling factor after considering the solvent molecules in the immediate neighborhood and beyond. To this end, we write the average dipolar solute-solvent interaction energy as

$$U(\theta) = \int V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta, \theta') \rho(\mathbf{r}, \theta', t) d\mathbf{r} d(\cos \theta'), \quad (\text{A1})$$

where $V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta, \theta')$ is space-dependent form of dipolar interaction potential between the photo-excited solute dipole and a solvent dipole, with a separation $|\mathbf{r} - \mathbf{R}|$. $\rho(\mathbf{r}, \theta', t)$ denotes the time-dependent solvent density distribution. Here, \mathbf{r} and \mathbf{R} are the position vectors of the solvent molecule and the solute molecule, respectively. Now, $V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta, \theta')$ can be written as¹¹

$$V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta, \theta') = -\frac{\mu_0 \mu}{|\mathbf{r} - \mathbf{R}|^3} \cos \theta \cos \theta'. \quad (\text{A2})$$

One can expand $V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta, \theta')$ as a function of spherical harmonics,⁶²

$$V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta, \theta') = \sum_{l_1, l_2, m} V_{dip}^{l_1 l_2 m}(|\mathbf{r} - \mathbf{R}|) Y_{l_1}^m(\cos \theta) Y_{l_2}^m(\cos \theta') \quad (\text{A3})$$

where

$$V_{dip}^{l_1 l_2 m}(|\mathbf{r} - \mathbf{R}|) = \int V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta, \theta') Y_{l_1}^m(\cos \theta) Y_{l_2}^m(\cos \theta') \times d(\cos \theta) d(\cos \theta'). \quad (\text{A4})$$

As it turns out, $V_{dip}^{110}(|\mathbf{r} - \mathbf{R}|)$ is the leading component of $V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta, \theta')$ that couples with $\rho_{10}(\mathbf{r}, t)$. Therefore, we obtain for the interaction energy,

$$U(\theta) = \sqrt{3/4\pi} \cos \theta \int V_{dip}^{110}(|\mathbf{r} - \mathbf{R}|) \rho_{10}(\mathbf{r}, t) d\mathbf{r}, \quad (\text{A5})$$

using⁶² $Y_1^0(\cos \theta) = \sqrt{3/4\pi} \cos \theta$. Setting $|\mathbf{R}| = 0$, implying the solute being located at the origin, we can write Eq. (A5) in Fourier space using the Parseval's relation,⁶²

$$U(\theta) = \sqrt{3/4\pi} (2\pi)^{-3} \cos \theta \int V_{dip}^{110}(\mathbf{k}) \rho_{10}(\mathbf{k}, t) d\mathbf{k} \quad (\text{A6})$$

Equation (A6) can be rewritten as

$$U(\theta) = -U_0(t) \cos \theta, \quad (\text{A7})$$

where

$$U_0(t) = -\sqrt{3/4\pi} (2\pi)^{-3} \int V_{dip}^{110}(\mathbf{k}) \rho_{10}(\mathbf{k}, t) d\mathbf{k}, \quad (\text{A8})$$

the solute-solvent interaction strength, weighted by the solvent distribution. Therefore, the torque on the rotating solute becomes

$$f(t) \approx U_0(t) \theta(t), \quad (\text{A9})$$

in small θ limit. The autocorrelation function of $f(t)$, under the decoupling approximation

$$\phi(t) = \frac{3\rho_b}{4\pi I k_B T} (2\pi)^{-6} \int d\mathbf{k} |V_{dip}^{110}(\mathbf{k})|^2 \langle \rho_{10}(\mathbf{k}, t) \times \rho_{10}(-\mathbf{k}, 0) \rangle \langle \theta(t) \theta(0) \rangle. \quad (\text{A10})$$

Here, for the solvent density modes we use $\rho_{10}(\mathbf{k}, t) = \rho_{10}(\mathbf{k}, 0) e^{-t/\tau_s}$. For the autocorrelation of the angular variable, through analysis of the equation of motion as described in Sec. III of the manuscript, we get

$$\frac{\langle \theta(t) \theta(0) \rangle}{\langle \theta(t) \theta(0) \rangle} = \exp \left[-\frac{U_0(0)}{\Gamma_{rot}} t \right], \quad (\text{A11})$$

where $U_0(0) = -\sqrt{3/4\pi} (2\pi)^{-3} \int V_{dip}^{110}(\mathbf{k}) \rho_{10}(\mathbf{k}, 0) d\mathbf{k}$. Using this normalized profile in Eq. (A10), we arrive at

$$\phi(t) = B e^{-\lambda t}, \quad (\text{A12})$$

where $B = \frac{3\rho_b}{4\pi I k_B T} (2\pi)^{-6} \int d\mathbf{k} |V_{dip}^{110}(\mathbf{k})|^2 \langle \rho_{10}(\mathbf{k}, 0) \rangle^2$ and $\lambda = ((U_0(0)/\Gamma_{rot}) + (1/\tau_s))$. Finally, we calculate the memory function as described earlier, using Eq. (A12) and derive the

long-range part of the rotational friction:

$$\delta\Gamma_{rot} = \frac{3\rho_b}{8\pi k_B T} (2\pi)^{-6} \times \int d\mathbf{k} |V_{dip}^{110}(\mathbf{k})|^2 \langle \rho_{10}(\mathbf{k}, 0) \rangle^2 \left(\frac{U_0(0)}{\Gamma_{rot}} + \frac{1}{\tau_s} \right)^{-1}. \quad (\text{A13})$$

This leads to the following expression of total friction:

$$\Gamma_{rot} = \Gamma_{rot}^{hyd} \left[1 + \frac{3\rho_b I_R \tau_s}{8\pi k_B T (\Gamma_{rot}^{hyd} + U_0(0) \tau_s)} \right], \quad (\text{A14})$$

where $I_R = (2\pi)^{-6} \int d\mathbf{k} |V_{dip}^{110}(\mathbf{k})|^2 \langle \rho_{10}(\mathbf{k}, 0) \rangle^2$. Therefore, the modified dipolar coupling parameter J becomes

$$J = \frac{3\rho_b I_R \tau_s}{8\pi k_B T (\Gamma_{rot}^{hyd} + U_0(0) \tau_s)}. \quad (\text{A15})$$

APPENDIX B: CALCULATION OF $\rho_{10}(\mathbf{k})$ FOR A POLAR LIQUID AROUND THE DIPOLAR SOLUTE

To evaluate $\rho_{10}(\mathbf{k})$ we need $\rho_{10}(\mathbf{r})$. We evaluate it by minimizing the equilibrium density functional free energy¹⁴ $F[\rho(\mathbf{r}, \theta')]$, with respect to the equilibrium density $\rho(\mathbf{r}, \theta')$. $F[\rho(\mathbf{r}, \theta')]$, describing the equilibrium fluctuation in the solvent density distribution $\rho(\mathbf{r}, \theta')$ from its bulk value ρ_b , is given by

$$\begin{aligned} \beta F[\rho(\mathbf{r}, \theta')] &= \int d\mathbf{r} d(\cos \theta') \rho(\mathbf{r}, \theta') \left[\ln \left(\frac{\rho(\mathbf{r}, \theta')}{\rho_b/4\pi} \right) - 1 \right] \\ &\quad - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' d(\cos \theta') d(\cos \theta'') \\ &\quad \times C(|\mathbf{r} - \mathbf{r}'|, \theta', \theta'') [\rho(\mathbf{r}, \theta') - \rho_b/4\pi] [\rho(\mathbf{r}', \theta'') - \rho_b/4\pi] \\ &\quad + \beta \int d\mathbf{r} d(\cos \theta') \rho(\mathbf{r}, \theta') V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta = 0, \theta'), \end{aligned} \quad (\text{B1})$$

where $\beta = 1/k_B T$ and $C(|\mathbf{r} - \mathbf{r}'|, \theta', \theta'')$ are the two-particle direct correlation function (DCF) between solvent molecules at positions \mathbf{r} and \mathbf{r}' having orientations θ' and θ'' . Minimization of $F[\rho(\mathbf{r}, \theta')]$, with respect to the constraint for N solvent molecules,

$$\int d\mathbf{r} d(\cos \theta') \rho(\mathbf{r}, \theta') = N, \quad (\text{B2})$$

yields $\delta\beta F/\delta\rho + \lambda(\delta/\delta\rho) \int d\mathbf{r} d(\cos \theta') \rho(\mathbf{r}, \theta') = 0$, λ being the Lagrange's multiplier. The differentiations give

$$\begin{aligned} \ln \left(\frac{\rho(\mathbf{r}, \theta')}{\rho_b/4\pi} \right) &= \int d\mathbf{r}' d(\cos \theta'') C(|\mathbf{r} - \mathbf{r}'|, \theta', \theta'') \\ &\quad \times \{ \rho(\mathbf{r}, \theta'') - \rho_b/4\pi \} - \beta V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta') - \lambda. \end{aligned} \quad (\text{B3})$$

For $[\rho(\mathbf{r}, \theta') - \rho_b/4\pi]/(\rho_b/4\pi) = \delta\rho(\mathbf{r}, \theta')/(\rho_b/4\pi) \ll 1$ implicating small density fluctuations, we can expand the

logarithmic term in Eq. (B3) to get

$$\frac{\delta\rho(\mathbf{r}, \theta')}{\rho_b/4\pi} = \int d\mathbf{r}' d(\cos\theta'') C(|\mathbf{r} - \mathbf{r}'|, \theta', \theta'') \{ \rho(\mathbf{r}, \theta'') - \rho_b/4\pi \} - \beta V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta') - \lambda. \quad (\text{B4})$$

Multiplying both sides of Eq. (B4) by $Y_1^0(\cos\theta')$, integrating over $\cos\theta'$ and using the definition of $\rho_{10}(\mathbf{r})$, we obtain

$$\begin{aligned} \frac{\rho_{10}(\mathbf{r})\rho_0}{\rho_b/4\pi} &= \int d\mathbf{r}' d(\cos\theta') d(\cos\theta'') Y_1^0(\cos\theta') \\ &\times C(|\mathbf{r} - \mathbf{r}'|, \theta', \theta'') \delta\rho(\mathbf{r}, \theta'') \\ &- \beta \int d(\cos\theta') Y_1^0(\cos\theta') V_{dip}(|\mathbf{r} - \mathbf{R}|, \theta'). \end{aligned} \quad (\text{B5})$$

Again, multiplying both sides of Eq. (B5) by $e^{-i\mathbf{k}\cdot\mathbf{r}}$, integrating over \mathbf{r} and using the convolution theorem⁶²

$$\begin{aligned} \frac{\rho_{10}(\mathbf{k})\rho_0}{\rho_b/4\pi} &= \int d(\cos\theta') d(\cos\theta'') Y_1^0(\cos\theta') C(\mathbf{k}, \theta', \theta'') \rho(\mathbf{k}, \theta'') \\ &- \beta \int d(\cos\theta') Y_1^0(\cos\theta') V_{dip}(\mathbf{k}, \theta'). \end{aligned} \quad (\text{B6})$$

Here, the surviving component of the Fourier mode of the DCF, $C(\mathbf{k}, \theta', \theta'')$ is given by $C^{110}(\mathbf{k}) = \int C(\mathbf{r}, \theta', \theta'') e^{-i\mathbf{k}\cdot\mathbf{r}} Y_1^0(\cos\theta') Y_1^0(\cos\theta'') d\mathbf{r} d(\cos\theta') d(\cos\theta'')$. We can write within mean-field approximation:¹¹ $C(r, \theta', \theta'') = C^{\text{PY}}(r) + C^{\text{LR}}(r)$. Here, $C^{\text{PY}}(r)$ denotes the hard-sphere part, approximated by the Percus-Yevick form^{13,14}. $C^{\text{LR}}(r)$ is obtained by angle-averaging of $C^{\text{LR}}(r, \theta', \theta'') = (\beta\mu^2/r^3) \cos\theta' \cos\theta''$, denoting the long-ranged part.¹¹ Finally, we get from Eq. (B6),

$$\frac{\rho_{10}(\mathbf{k})\rho_0}{\rho_b/4\pi} = (\rho_0/2\pi) C^{110}(\mathbf{k}) \rho_{10}(\mathbf{k}) - \beta V_{dip}^{10}(\mathbf{k}), \quad (\text{B7})$$

where $V_{dip}^{10}(\mathbf{k}) = \sqrt{3\pi} V_{dip}^{110}(\mathbf{k})$. Rearrangement of Eq. (B7) leads to

$$\rho_{10}(\mathbf{k}) = \frac{-\rho_b \beta V_{dip}^{10}(\mathbf{k})}{1 - \rho_b C^{110}(\mathbf{k})/8\pi^2}. \quad (\text{B8})$$

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