Dipolar Solute Rotation in a Supercritical Polar Fluid

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ABSTRACT: Fluorescence anisotropy measurements reveal a non-monotonic density dependence for average rotation time \( \tau_R \) of a polar solute, coumarin 153 (C153) in polar supercritical fluoroform (CHF\(_3\)). The conventional Stokes–Einstein–Debye model, relating \( \tau_R \) to the solvent viscosity, fails to explain the observed density dependence, because the experimental viscosity increases monotonously with density for a fluid, in general. Here, the density-dependent \( \tau_R \) is calculated by incorporating the wave vector-dependent viscosity of the solvent and the solute–solvent interaction. A molecular hydrodynamic description is used for the wave vector-dependent viscosity which is verified by molecular dynamics (MD) simulation. A justification for the applicability of the present prescription is provided by reproducing the experimental viscosity of supercritical (SC) CHF\(_3\). Solute–solvent interaction has been included via the fluctuating torque acting on the rotating solute. Incorporation of wave vector-dependent viscosity leads to a qualitative description of the experimental density dependence of \( \tau_R \) which is further improved upon inclusion of solute–solvent interaction.

1. INTRODUCTION

A fluid phase slightly above the gas–liquid critical temperature is broadly regarded as a SC fluid.\(^1\) It is highly compressible, offering large tunability of density by mild pressure variations. Pedagogically, the solvent–density dependence of several non-equilibrium rate processes near room temperature can be studied in SC fluids like carbon dioxide, fluoroform, ethane, etc., having a critical temperature \( (T_c) \) close to room temperature.\(^2\) Specifically, rotational dynamics of aromatic solutes in a SC fluid can supply valuable information regarding the nature of solute–solvent coupling\(^3\)–\(^5\) and the local environment of the solute. For fluorescent solutes in different media, the rotational dynamics of the solute is usually followed by measuring the time-dependent fluorescence anisotropy\(^6\) \( r(t) \). In the case of large solutes, \( r(t) \) generally follows an exponential decay, with a characteristic time scale for the solute rotation. Sometimes there can be a multiplexponential decay. One then obtains via time integration of the scale for the solute rotation. In particular, the concept of dielectric friction\(^19\) has been invoked to address the change in the friction experienced by a rotating polar solute due to electrostatic interactions. However, none of the above works conclusively support this picture. Relatively recent work\(^17\) suggests that the additional friction due to solute–solvent interaction is attributable to a static ‘electrostriction’ effect. This is believed to originate from the enhanced solvent structure in the first solvation shell\(^20\).

Received: September 10, 2010
Revised: December 24, 2010
Published: January 21, 2011
The hydrodynamic viscosity \( \eta \) is replaced with the wave vector-dependent viscosity \( \eta(k\sigma) \) of the fluid which brings in \( S(k\sigma) \) directly into the picture. This is done based on molecular hydrodynamic arguments, leading to an analytical expression of \( \eta(k\sigma) \) which is verified via a MD simulation. We also show how to extract the experimental \( \eta \) for a SC fluid from \( \eta(k\sigma) \). This modification to the SED model captures quantitatively the experimentally observed nontrivial density dependence of \( \tau_R \) in SC CHF.

The effect of the solute–solvent interaction is included by considering the rotational relaxation of the excited solute in fluorescence depolarization experiments. In such experiments, anisotropy in depolarization is created by photo-exciting a dissolved solute. This anisotropy in polarization subsequently relaxes to a new equilibrium via rotational diffusion of the solute. Let us consider a small angular displacement of the solute dipole from its final solvent-equilibrated orientation in the background of the solvent dipoles (see Scheme 1). The solute dipole would then tend to relax back to its equilibrium orientation by rotational diffusion under the action of torque generated via the solute–solvent interaction.

2. WAVE VECTOR-DEPENDENT VISCOSITY

a. Case of a Normal Liquid. Let us first consider \( \eta(k\sigma) \) of a normal liquid. According to molecular hydrodynamics, the transverse current autocorrelation function \( C_{\perp}(k\sigma,t) \) is defined as

\[
C_{\perp}(k\sigma,t) = k^2 \langle \mathbf{j}_k(t) \cdot \mathbf{j}_k(0) \rangle,
\]

where \( \mathbf{j}_k(t) \) is the Fourier component of the transverse current. Now, \( C_{\perp}(k\sigma,t) \) is known to be related to the shear viscosity \( \eta \) of the fluid\(^{12} \)

\[
C_{\perp}(k\sigma,t) = \omega_0^2 e^{-\nu^2 t}
\]

where \( t \) denotes the time, \( \omega_0^2 = k^2 (k_B T/m) \), \( \nu = \eta/\rho m \), and \( m \) is the mass of a fluid molecule. Integrating both sides of eq 1 over the entire time range we get the wave vector-dependent viscosity given by\(^{28} \)

\[
\eta(k\sigma) = \frac{\rho \omega_0^2}{k^2} \left[ \int_0^\infty C_{\perp}(k\sigma,t) dt \right]^{-1}
\]

Fick’s law\(^{12} \) for diffusive motion states that the current

\[
\mathbf{j}(\mathbf{r},t) = -D \nabla \rho(\mathbf{r},t)
\]

where \( \rho(\mathbf{r},t) \) is the time-dependent microscopic solvent density at position \( \mathbf{r} \), \( D \) being the self-diffusion coefficient of the fluid. Now, eq 3 yields in the Fourier space for the transverse current, \( \mathbf{j}_k(t) = ik \cdot D \rho_k(t) \), \( k \perp \mathbf{r} \) being the transverse component of \( k \) (parallel to \( z \) axis). Multiplying both sides by \( k^2 \mathbf{j}_k(0) \) and taking the average over the initial conditions, we obtain

\[
\langle \mathbf{j}_k(t) \cdot \mathbf{j}_k(0) \rangle = k^2 D^2 \langle \rho_k(t) \rho_k(0) \rangle
\]

It is known\(^{12} \) that \( \rho_k(t) = \rho_k e^{-D k^2 t} \), \( \rho_k \) being the Fourier component of the microscopic solvent density. Inserting this in eq 4 leads to

\[
\langle \mathbf{j}_k(t) \cdot \mathbf{j}_k(0) \rangle = k^2 D^2 S(k\sigma) e^{-D k^2 t}
\]

where static structure factor \( S(k\sigma) = \langle \rho_k \rho_k \rangle \). Thus, we reach at a molecular hydrodynamic expression of \( C_{\perp}(k\sigma,t) \), following its definition\(^{12} \)

\[
C_{\perp}(k\sigma,t) = k^2 \langle \mathbf{j}_k(t) \cdot \mathbf{j}_k(0) \rangle = k^2 D^2 S(k\sigma) e^{-D k^2 t}
\]

Putting eq 5 in eq 2 and performing the integration one obtains

\[
\eta(k\sigma) = \frac{\rho_0 k_B T}{k^2 D S(k\sigma)}
\]
Figure 1. (a) $\eta(k)/\eta(k_{\text{min}})$ (filled circles with error bars) and $S(k_{\text{min}})/S(k)$ (open triangles, the solid line is drawn only as a guide to the eyes) as a function of $k$, both calculated from MD simulation, for LJ liquid for $\rho \sigma^2 = 0.8$ at 96 K. (Inset) $S(k)$ of the same system calculated from our simulation. (b) $S(k)$ as a function of $k$ for SC CHF$_3$ at 310 K at two densities: $\rho = 0.74$ (solid line) and 2.0 (the dotted line). (Inset) Scaled compressibility $\chi_T^2$ of SC CHF$_3$ at 310 K as a function of $k$.

We set $k_0^2 = 6\pi^2\rho\sigma$ (\rho being the bulk density and $\sigma$ the molecular radius of the fluid) to arrive at the final expression of wave vector-dependent viscosity

$$\eta(k) = \frac{k_b T}{6\pi D_0 S(k)}$$

(7)

We can also derive the weakly interacting limit of diffusion reported in ref 14 from the expression of $\eta(k)$: The isothermal compressibility of the fluid is given by $\chi_T = \lim_{k \to 0} k_0^2 (\rho/6\pi D_0) S(k)$. Thus, $\eta(k) \approx 0$ is given by $\rho k_0^2 (\rho/6\pi D_0) S(k) \approx 1/\rho (\rho/6\pi D_0) S(k)$. Rearranging this we get $D = \Gamma_d/\rho \chi_T$, where $\Gamma_d = \rho/6\pi D_0 \eta$, a density-dependent dissipative coefficient introduced in ref 14.

Note that eq 7 yields

$$\eta(k)/\eta(k') = S(k)/S(k')$$

(8)

for wave vectors $k$ and $k'$. In the long-wavelength $k \approx 0$ limit where $S(k)$ has a minimum\textsuperscript{12} (inset, Figure 1a), an expansion yields $\eta(k) \approx (1 - b\varepsilon^2 \sigma^2)$, where $b$ depends on the curvature of $S(k)$ near $k \approx 0$. Such small $k \sigma$ behavior of $\eta(k)$ has been reported earlier.\textsuperscript{28,29}

Both sides of eq 8 can be computed from molecular dynamics simulations which can provide a direct test of the wave vector-dependent viscosity. We consider to this end, for simplicity, a Lennard–Jones (LJ) system at normal liquid condition. The interaction potential between a pair of LJ liquid molecules at separation $r$ is given by $4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, $\varepsilon$ being the interaction strength parameter.\textsuperscript{12} Our simulation system involves 216 LJ particles using the argon units\textsuperscript{12} [\(\varepsilon = 120 K\) in $k_b$ unit, diameter $\sigma = 3.4$ A, and molecular mass 40 amu], adopting NVE ensemble.\textsuperscript{12} A simple cubic simulation box is used of side $L = 6.46 \sigma$ with the periodic boundary condition on all sides. The density of the system is taken at $\rho \sigma^3 = 0.8$ and the average temperature at $k_b T/\varepsilon \approx 0.8$ (96 K). The equations of motion are integrated using the Verlet algorithm,\textsuperscript{30} the time step for integration being 0.0215 ps.

We calculate $\eta(k)$ from the simulation by eq 2 where $C_L(k \sigma, t) = k^2 \langle \hat{J}_L(t) \hat{J}_L(0) \rangle$. The Fourier component of the current is given by $\hat{J}_L(t) = \sum_i \hat{v}_i(t) e^{-i k_0 z_i(t)}$, $\hat{v}_i(t)$ being the transverse component of the velocity of the $i$th particle at time $t$ and $z_i(t)$, its location at time $t$. Finally, we can write $C_L(k \sigma, t) = k^2 \langle \sum_i \hat{v}_i(t) e^{-i k_0 z_i(t)} \rangle$.

The minimum accessible wave vector in our simulation is $k_{\text{min}} = 2\pi \sigma/L$, $L$ being the side length of the simple cubic simulation box. The inset in Figure 1a shows $S(k)$ from the simulations. Figure 1a shows a comparison between $\eta(k)/\eta(k_{\text{min}})$ (circles with error bars) and $S(k_{\text{min}})/S(k)$ (open triangles), both computed from the simulations. Both plots are similar in appearance with almost the same rate of decrease from the minimum value of unity at the smallest wave vector, which is consistent with the low wave vector expansion. The discrepancy between the two plots is more pronounced for the low wave vector region, which could be due to finite size effects in the simulations.\textsuperscript{30}

**b. Extension to SC CHF$_3$.** As hydrodynamic results are insensitive to the detailed molecular interactions, we expect the hydrodynamic description of $\eta(k)$ to be valid for SC polar fluids also. To this end we locate the critical point\textsuperscript{31} of the polar fluid from the divergence of $\chi_T$ at the critical condition. We calculate $S(k)$ using the standard liquid-state theory\textsuperscript{12} and obtain its $k \sigma \approx 0$ limit as a theoretical estimate of $\chi_T$. Here, $S(k)$ is computed using the Ornstein–Zernike\textsuperscript{12,15} relation: $S(k) = [1 - \rho C(k)]^{-1}$, $C(k)$ being the Fourier transform (FT) of $C(r)$, the spatial direct correlation function of the fluid. In our calculation we assume that the solvent–solvent interaction consists of a hard-core part of diameter $\sigma$ and a longer ranged dipolar contribution due to a dipole moment of magnitude $\mu$ located at the center of a solvent molecule. $C(r)$ is expressed as a combination of the short-ranged and longer-ranged part for the polar fluid. For the former, we use the Percus–Yevick (PY)\textsuperscript{22,13} form $C_{\text{PY}}(r)$ for hard-sphere potential, while the latter $C_{\text{LR}}(r)$ is derived from the angle-averaged Mayer’s function\textsuperscript{12,13} based on the standard dipolar potential

$$C(r) = C_{\text{PY}}(r) + C_{\text{LR}}(r)$$

(9)

where

$$C_{\text{PY}}(r) = c_0 + c_1 (r/\sigma) + c_2 (r/\sigma)^3$$

for $r < \sigma$

$$= 0$$

for $r > \sigma$

and

$$C_{\text{LR}}(r) = 2\mu^4/9 (k_b T)^2 \rho^6$$

(11)

The three coefficients $c_0$, $c_1$, and $c_2$ in $C_{\text{PY}}(r)$ are functions of the packing fraction $\rho = (\pi/6) \rho \sigma^3$ and given by $c_0 = -(1 + 2 \rho)^4/(1 - \rho)^3$, $c_1 = 6 \rho (1 + 0.5 \rho)^4/(1 - \rho)^3$, and $c_2 = 0.5 \rho c_0$. The inset of Figure 1b shows $\chi_T^2(\pi k T/\sigma)$ for a typical isotherm. Our estimate for the critical point is $T_C = k_b T / \mu \approx 0.29$ and $\rho^* = 0.25$, which are in good agreement with the experimental numbers.\textsuperscript{11} The details of all these calculations are given in section I of the Supporting Information.
Subsequently, we perform calculations at a supercritical temperature.31 We show the calculated S(κτ) of SC CHF3 in Figure 1b at two densities above and below ρr. In general, two peaks can be observed in S(κτ): one around κτ ≈ 0 in a region dominated by fluid compressibility and another around κτ ≈ 2τ dictated by the molecular packing. For low ρr, the peak at κτ ≈ 0 predominates which gradually disappears with increasing ρr along with the concomitant enhancement of the packing-driven peak.

We use this S(κτ) and experimentally observed11 D to obtain η(κτ) for SC CHF3. It is found that the experimentally observed shear viscosity of SC CHF3 is well reproduced (see Figure 2) by an integration of η(κτ) over the entire range of wave vectors: η = (1/4π) ∫ η(κτ) dκ dτ/∫ dκ dτ, where the factor 1/4π takes care of the degeneracy of the choice of the transverse direction. Here, for numerical purposes, the integration range was taken from κτ = 0 to κτ = 10. We note that a larger upper limit does not alter the value of η. The experimentally observed viscosity is thus an average momentum transfer in a given layer of fluid over all length scales. This rationalizes the extension of the molecular hydrodynamic expression for η(κτ) for SC CHF3.

c. Rotation Time Scales in SC CHF3. Let us now consider the rotation of the SC solvent via replacement of η by η(κτ). Recalling the SED expression of η(κτ) = ηVp/kBT, we can define the rate of rotational relaxation as: τ = 1/τ = kBT/ηVp. Introducing η(κτ) we get the wave vector-dependent rate: Ω(κτ) = kBT/η(κτ)Vp. Now, the different peaks in S(κτ) for SC CHF3 both sharp and broad, appearing at different regions of wave vectors, create different wave vector windows for Ω(κτ). We average the Ω(κτ) over the wave vectors under a given structure factor peak to produce an average rate: Ωav = ∫ Ω(κτ) dκ dτ/∫ dκ dτ for the τth peak. The rotation time for the τth peak is then τR,τ = 1/Ωav. Here, each of the structure factor peaks (see Figure 1b) will give rise to a time scale implying an overall multiexponential rotational relaxation. For example, at the low-density region (ρr < 1), S(κτ) has a single prominent peak around κτ ≈ 0 but no such peak at larger wave vectors. This implies a single-exponential relaxation, τR being governed by the single peak. In the higher density region (ρr > 1), the relaxation would be biexponential with two time scales because of two peaks in S(κτ), τR being a weighted average of the two. However, the present formalism does not allow calculating the weights of these separate time scales.

Figure 3a shows both τR,1 and τR,2 of C153 in SC CHF3 at 310 K as a function of ρr, while the experimental data at two temperatures 302 and 310 K are shown in the inset. At very low densities, κτ ≈ 0 being the only peak of S(κτ), τR,1 is the only relevant time scale. Interestingly, it shows all the features of the experimental density dependence of rotation time with the maximum at ρr = 0.59, agreeing qualitatively with the experimental data. The appearance of this maximum can be explained by a minimum in compressibility (see inset of Figure 1b). Such a minimum also justifies the LDA becoming maximum near ρr = 0.6. τR,1 becomes a minimum at ρr = 1.03, with good agreement with the experimental finding. This minimum is explained by the maximum in compressibility at ρr = 1.03.

The packing-dominated peak appears for densities above ρr = 1, giving rise to τR,2 that increases linearly with ρr. In this regime the packing-dominated contribution of S(κτ) remains almost unchanged with density implying τR,2 ≈ 1/D. According to Eqs. 4 and 5, D ≈ 3/(8πρg(ρ))[(kBT/2m)]1/2 for a fluid where g(ρ) is the radial distribution function at contact, m being the mass of a molecule. As g(ρ) is weakly sensitive to ρr in this density regime, we get τR,2 ≈ 1/D ≈ ρr. Note that in the density range 0 < ρr < 1.6, τR,1 and τR,2 do not differ significantly from each other, although τR,1 < τR,2. However, τR,1 increases rapidly at very high densities (ρr > 1.6) where the fluid becomes highly incompressible. The experimental τR,2 in these densities does not show such rapid increase but rather is comparable in trend with τR,2.

3. SOLUTE–SOLVENT INTERACTION

Next we include the solute–solvent interaction. The torque on the solute dipole undergoing rotational relaxation, as shown in Scheme 1, is determined by the interaction energy, U(θ), of the rotating phototactic dipolar solute (with excited state dipole moment μr) as a function of its orientation θ (with respect to the laboratory frame z axis) due to the solvent dipoles (dipole
moment $\mu$) in the first solvation shell (see section II, Supporting Information). $U(\theta)$ depends on two factors:

1. The solute–solvent dipolar interaction potential and
2. the solvent orientation distribution in the first solvation shell.

The solvent orientation is characterized by $\rho_0(t)$, the projection of the solvent orientation distribution for spherical harmonic $l = 1$. Since we are considering the perturbation from the final equilibrium orientation of the solute and relaxation back to the same equilibrium state, we use overdamped equation of motion for all the relevant dynamical variables. Note that the solvent orientation distribution undergoes relaxation as well, the rate being dictated by the solvent rotational diffusion $D_\theta$. The fluctuating torque is then given by $-\partial U(\theta)/\partial \theta$, where $U(\theta) = -\omega_0\rho_0(t)\rho_0 \cos \theta$ (see section II, Supporting Information), where $\rho_0 = 1/4\pi$, the bulk value of the orientation profile. The overdamped equation of motion of the solute dipole: $\Gamma_{\rho_0}(\theta) = -\partial U(\theta)/\partial \theta$, where $\Gamma_{\rho_0}$ is the rotational frictional coefficient. For small angular displacement $\theta$ from the final equilibrium state and $t < R_1^2$, the solution is $\theta(t) = \theta(0)e^{-\omega t}$. Here $\omega = -\omega_0\rho_0(0)/\Gamma_{\rho_0}$, the angular frequency of rotation which is the relaxation rate of the orientational correlation function. Hence, we identify $R_{\rho_0} = 1/\omega = \eta V_\rho M/k_b T$, where $M = \pi(6k_b T/\mu_d)^{1/2}(1-2\mu_p/9k_b T)$, $R$ being the solute–solvent interaction length in the first solvation shell (see section II, Supporting Information). This expression is similar to the SED model, in its conventional form, can qualitatively reproduce the experimental data, shown in the inset of Figure 3b.

We expect that a more explicit treatment of the solute–solvent interaction would yield a better agreement to the experimental rotation times. Even though we restrict our discussion to rotation of C153 in SC fluoroform for the availability of experimental data, the present theoretical framework is applicable to rotation of a polar solute in a polar solvent in general. Moreover, such framework can be used to find the rotation time in other systems having different solute–solvent interactions and different solvent structures, like electrolytes and ionic liquids to name only a few.

### 4. CONCLUSION

We developed a straightforward understanding of the rotational relaxation for large polar solutes in polar SC solvents incorporating the solvent structure via wave vector-dependent shear viscosity and then the solute–solvent interaction. Here we extend the SED picture to incorporate the molecular interactions explicitly. The SED model, in its conventional form, can qualitatively produce the experimental data with the simple replacement of $\eta$ by $\eta(k\sigma)$. However, for a semiquantitative agreement one needs to include the solute–solvent interaction. Apart from extracting the time scales that compare well with the experimental data, the present theory explains the possible causes behind this remarkable density dependence of rotation of a polar solute in a SC polar fluid. In particular, the rotational relaxation of the solute at low solvent densities is essentially governed by fluid compressibility. We predict that at very high densities where the packing dominates the solvent structure, the time scales increase linearly.

Acknowledgment

A.D. thanks the Council of Scientific and Industrial Research, India, for a research fellowship. R.B. thanks M. Maroncelli for several useful suggestions.

### Supporting Information

Details of necessary derivations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Note that the total solute–solvent interaction contains an orientation-independent short-ranged component in addition to the asymmetric (dipolar) component. However, the short-ranged component does not contribute to the torque acting on the solute because the latter (torque) is determined by the angle-dependent interaction alone.

(34) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry*; W. H. Freeman: New York, 1980; Part II.


(36) Here, an obvious restriction arises, out of the mean field approximations we imposed in our formulation, to allow only positive values of the factor $M$ that $2\mu^2\rho/9k_B T < 1$. 


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