

# Anomalous orientational relaxation of solute probes in binary mixtures

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The orientation of a solute probe in a binary mixture often exhibits *multiple* relaxation times at the *same* solvent viscosity but different compositions [Beddard *et al.*, *Nature (London)* **294**, 145 (1981)]. In order to understand this interesting observation, we have carried out (*NPT*) molecular dynamics simulation study of rotation of prolate ellipsoids in binary mixtures. The simulations show that for a broad range of model parameters the experimental behavior can be reproduced. The plot of orientational relaxation time versus the solvent viscosity, the latter changed by varying the composition, shows a nonmonotonic viscosity dependence. The nature of the plot is found to depend on the system parameters, especially on the solute–solvent interactions. A mode coupling theoretical analysis of this complex dependence of the rotational relaxation time  $\tau_R$  on the binary viscosity  $\eta$  is presented. The theory can qualitatively explain the origin of the multiple relaxation time at the same viscosity.

## I. INTRODUCTION

Multicomponent systems are ubiquitous in nature. Among them, the binary mixtures are particularly relevant to solution chemistry since the properties of the solvent can be tuned by varying the composition. This is why the properties of binary mixtures are intensely investigated both experimentally and theoretically. Although the static and dynamical properties of many mixtures are well characterized, a general theoretical framework especially to understand the dynamical properties is still lacking.

While the elegant theory of Buff and Kirkwood can be used to explain many aspects of static properties,<sup>1</sup> such a theory is not available for the dynamical properties. This is somewhat surprising given the fact that the dynamical properties in a binary mixture show exotic features which pose interesting challenges to theoreticians. Among them, the extrema observed in the composition dependence of excess viscosity<sup>2</sup> and the anomalous viscosity dependence of the orientational relaxation time<sup>3,4</sup> are certainly the most important ones. Although the nonideality in the composition dependence of the viscosity has been addressed recently,<sup>5</sup> the anomalous behavior of the orientational dynamics is yet to be explained from theoretical or computer simulation studies.

In a binary mixture there exist three different potential interactions, two length scales, and two different masses. A combination of all these different parameters gives rise to several microscopic time scales in the system. Thus, the equilibrium and dynamical properties in these systems are considerably different from those of one-component fluids. In fact, very little understanding of a binary mixture can be obtained by studying a one-component system. In particular, the orientational relaxation of a solute in a binary mixture poses interesting questions which cannot be addressed by the study of a one-component solvent.

Conventionally the rotational diffusion ( $D_R$ ) for a spherical rotor is given by the well-known Debye–Stokes–Einstein (DSE) relation

$$D_R = \frac{k_B T}{C_R \eta v_s}, \quad (1)$$

where  $k_B T$  is the Boltzmann constant times the temperature ( $T$ ),  $\eta$  is the viscosity of the liquid medium,  $v_s$  is the specific volume of the molecule, and  $C_R$  is a constant which is equal to 3 in DSE theory but often left as a fitting parameter. According to the slip boundary condition, for a spherical rotor  $C_R=0$ , which seems unrealistic. This paradoxical result was resolved by Hu and Zwanzig,<sup>6</sup> who have shown that a reasonable value for  $D_R$  is obtained if the solute is approximated by a spheroid.

Experimentally one usually measures the orientational time correlation function,  $C_l(t)$  ( $l$  is the rank of the spherical harmonic coefficients). Now, if the Debye rotational diffusion model is assumed, then the relaxation time ( $\tau_{lR}$ ) is given by

$$\tau_{lR} = [l(l+1)D_R]^{-1}. \quad (2)$$

Although some experimental results can be explained using the DSE relation, there are many which show deviation from the DSE behavior. Beddard *et al.*<sup>3,4</sup> have used the picosecond fluorescence depolarization technique to study the rotational relaxation time of dye cresyl violet in alcohol–water mixture by varying the alcohol composition. They have reported different rotational relaxation times in solutions at the same viscosity but different compositions. They have also mentioned that this effect depends on the specific interactions.

Although the role of specific interaction in the orientational dynamics has often been discussed and the effect has been included in the DSE relation by changing the boundary

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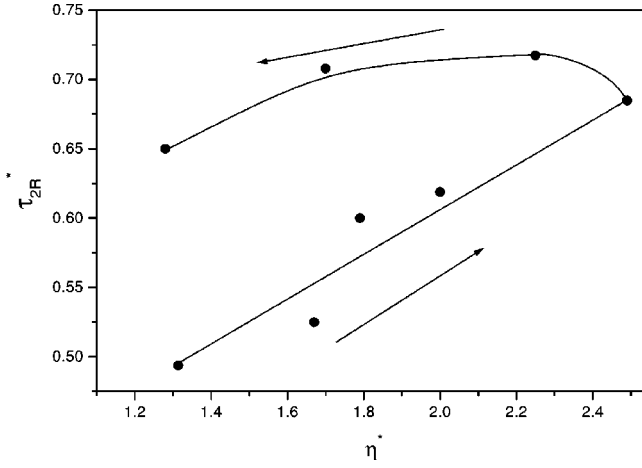


FIG. 1. The reduced orientational relaxation time,  $\tau_{2R}^*$ , plotted against the reduced viscosity of the binary mixture,  $\eta^*$ , is shown by the filled circles.  $\tau_{2R}^*$  shows a re-entrance. The solid line is a guide to the eye. The compositions of the A particles are 0.04, 0.08, 0.15, 0.2, 0.4, 0.6, 0.8, and 1.0, where the direction of the arrows shows the increasing composition of A particles. The study is performed at  $T^*=1.0$  and  $P^*=1.0$ , for model II.  $\tau_{2R}^* = \tau_{2R} \sqrt{(\epsilon_{BB}/m_A \sigma_A^2)}$  and  $\eta^* = \eta \sigma_A^2 / \sqrt{m_A \epsilon_{BB}}$ .

condition,<sup>7,8</sup> a detailed study of the rotational dynamics in a binary mixture has not been carried out yet to the best of our knowledge.

In the work reported here, extensive MD simulations [constant pressure ( $P$ ), temperature ( $T$ ), and total number of molecules ( $N$ )<sup>9,10</sup>] of isolated prolate ellipsoids have been carried out in several binary mixtures. The primary goal of this study is to understand the anomalous viscosity dependence of the orientational relaxation time ( $\tau_{2R}$ ). From our study of several systems we propose a set of model systems where the orientational relaxation time of the ellipsoid is found to be different in the solution at the same viscosity but different compositions. When plotted against viscosity (by varying the composition), the orientational relaxation time shows a re-entrance. In a binary mixture the viscosity itself is known to have a nonideal composition dependence.<sup>2,5</sup> But, it is found that this nonideality in viscosity alone cannot explain this re-entrance of  $\tau_{2R}$ . The nature of the re-entrance is found to depend on the system parameters, especially on the specific interaction of the solute with the solvents. If the solute has different interactions with the two species (present in a binary mixture), then the macroscopic properties (for example the viscosity) of the solvent are not the unique determinant of the solute dynamics. A plot of the rotational relaxation time against the solvent viscosity for a system which shows a typical re-entrant behavior is given in Fig. 1.

The results obtained from the simulations are explained from a mode coupling theoretical analysis. It is been shown that, unlike in one-component system, the inverse proportionality of the rotational diffusion of a solute and the solvent viscosity (as given by the DSE) is absent in a binary mixture. This is because in a binary mixture the expressions of both the rotational diffusion and viscosity are quite complex and involve different time and length scales.

The organization of the rest of the article is as follows. In the next section we discuss the simulation details and

present the potentials and the systems used in this study. In Sec. III the simulation results and discussions are presented. The mode coupling theoretical analysis is given in Sec. IV. The article concludes with a few remarks in Sec V.

## II. SYSTEMS AND SIMULATION DETAILS

A series of molecular dynamics simulations [constant pressure ( $P$ ), temperature ( $T$ ), and constant total number of particles ( $N$ )] of isolated prolate ellipsoids in binary mixtures has been carried out. Pressure is kept constant by Andersen's piston method,<sup>9</sup> while in the case of temperature a damped oscillator method has been adopted which keeps temperature constant at each and every step.<sup>10</sup> The piston mass involved here is  $0.0027(m_A/\sigma_A^4)$ , which is regarded as optimum.<sup>10,11</sup>

In the binary mixture let us denote the two species as "A" and "B." The composition ( $\chi$ ) of the binary mixture is varied, where composition of A and B particles is denoted as  $\chi_A$  and  $\chi_B$ , respectively. The total number of molecules in the system is 504, where there are 4 ellipsoids which are placed far from each other and 500 solvents which include both A and B types of molecules.

The interaction between the particles is modeled by different potentials. The interaction between the spheres in the binary mixture is given by the Lennard-Jones (LJ)

$$U_{ij} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right], \quad (3)$$

where "i" and "j" denotes two different particles which can both be A or both B or one A and the other B.

The interaction between two ellipsoids with arbitrary orientations is assumed to be given by the Gay-Berne (GB) potential<sup>12</sup>

$$U_{GB} = 4\epsilon(\hat{r}, \hat{u}_1, \hat{u}_2) \left[ \left( \frac{1}{r - \sigma(\hat{r}, \hat{u}_1, \hat{u}_2) + 1} \right)^{12} - \left( \frac{1}{r - \sigma(\hat{r}, \hat{u}_1, \hat{u}_2) + 1} \right)^6 \right], \quad (4)$$

where  $\hat{u}_1$   $\hat{u}_2$  are the axial vectors of the ellipsoids 1 and 2.  $\hat{r}$  is the vector along the intermolecular vector  $r = r_2 - r_1$ , where  $r_1$  and  $r_2$  denote the centers of mass of ellipsoids 1 and 2, respectively.  $\sigma(\hat{r}, \hat{u}_1, \hat{u}_2)$  and  $\epsilon(\hat{r}, \hat{u}_1, \hat{u}_2)$  are the orientation-dependent range and strength parameters, respectively.  $\sigma$  and  $\epsilon$  depend on the aspect ratio  $\kappa$ . Finally, the interaction between a sphere and an ellipsoid is accounted for by a modified GB-LJ potential given below<sup>13,14</sup>

$$U_{Ei} = 4\epsilon_{Ei} \left[ \left( \frac{\sigma(\theta)_{Ei}}{r} \right)^{12} - \left( \frac{\sigma(\theta)_{Ei}}{r} \right)^6 \right], \quad (5)$$

where "E" denotes the ellipsoids and "i" can be A or B.

$$\sigma(\theta)_{Ei} = \frac{(b/2 + R_i)}{\sqrt{1 - X^2 \cos^2 \theta}}, \quad (6)$$

TABLE I. The reduced mass, size, and interaction energies for solvent A and B and also for the ellipsoid E for models I, II, and III. The mass is scaled by  $m_A$ , size by  $\sigma_A$ , and interaction energy parameter by  $\epsilon_{BB}$ .

Parameters	Model I	Model II	Model III
$\sigma_A$	1.0	1.0	1.0
$\sigma_B$	1.0	0.66	0.66
$\epsilon_{AA}$	0.5	0.7	0.7
$\epsilon_{BB}$	1.0	1.0	1.0
$\epsilon_{AB}$	1.5	1.5	1.5
$m_A$	1.0	1.0	1.0
$m_B$	1.0	0.33	0.33
$L$	2.0	2.0	3.0
$a$	1.0	1.0	1.0
$\epsilon_{EA}$	1.2	1.4	1.3
$\epsilon_{EB}$	1.0	0.3	0.6
$m_E$	1.0	1.0	1.0

where  $\theta$  is the angle between the major axis of the ellipsoid and the vector joining the centers of the sphere and the ellipsoid.

$$R_i = \sigma_i/2, \quad (7)$$

$$X = \sqrt{\frac{\bar{a}^2 - b^2/4}{\bar{a}^2 + R_i^2}}, \quad (8)$$

and

$$\bar{a} = \sqrt{(b^2 + R_i^2) \left( \frac{L/2 + R_i}{b/2 + R_i} \right)^2 - R_i^2}, \quad (9)$$

where  $L$  is the major axis of the ellipsoid and  $b$  is the minor axis of the ellipsoid.

All the quantities in the simulation were scaled to appropriate units, the density by  $\sigma_A^{-3}$ , the temperature by  $\epsilon_{BB}/k_B$ , and the time by  $\sqrt{(m_A \sigma_A^2 / \epsilon_{BB})}$ —the scaled quantities are denoted by  $\rho^*$ ,  $T^*$ , and  $t^*$ , respectively.

In this article, simulations of three different systems, referred to as model I, model II, and model III are reported. The models differ in the values of the mass, size, and specific interactions of A, B, and E. The specific values for the models are presented in Table I. All the simulations were carried out at  $P^* = 1.0$  and  $T^* = 1.0$ , where the pressure is scaled by  $(\epsilon_{BB}/\sigma_A^3)$ .

The time step  $\Delta t$  used to simulate model I is 0.001 and that for models II and III is 0.0005. The system was equilibrated for  $1.5 \times 10^5$  time steps and after that the averages were obtained over another  $2 \times 10^5$  time steps. In each case we ran at least five independent simulations and took the averages.

To study the orientational correlation time,  $\tau_{lR}$ , we have calculated the single particle orientational correlation function, defined by

$$C_l^s(t) = \frac{\langle P_l(\hat{u}_i(0)\hat{u}_i(t)) \rangle}{\langle P_l(\hat{u}_i(0)\hat{u}_i(0)) \rangle}, \quad (10)$$

for  $l=2$ .  $P_l$  is the  $l$ th-order Legendre polynomial.  $\tau_{2R}$  is obtained by integrating over  $C_2^s(t)$ .

The viscosity is calculated from the simulations using the microscopic expression for the time-dependent shear viscosity, which is formulated in terms of stress autocorrelation function and is given by<sup>15,16</sup>

$$\eta(t) = (Vk_B T)^{-1} \langle \sigma^{xz}(0) \sigma^{xz}(t) \rangle, \quad (11)$$

where  $\sigma^{xz}$  is the off-diagonal element of the stress tensor

$$\sigma^{xz} = \sum_{j=1}^N [(p_j^x p_j^z / m_j) + F_j^z x_j]. \quad (12)$$

Here,  $F_j^z$  is the  $z$  component of the force acting on the  $j$ th particle and the corresponding position of the  $j$ th particle is  $x_j$ .  $p_j^z$  is the  $z$  component of the momentum of the  $j$ th particle and  $m_j$  is its mass. The summation  $j$  includes all the solvents. The viscosity is scaled by  $\sqrt{m_A \epsilon_{BB} / \sigma_A^2}$ .

### III. RESULTS AND DISCUSSIONS

In this section we will present the simulation results and discuss their interpretations.

#### A. Re-entrance of orientational correlation time

The re-entrance behavior is shown in Fig. 1. Here, the rotational relaxation time is plotted against the viscosity by varying the composition. The system in this study is described by model II (see Table I). The maximum of viscosity is obtained at composition  $\chi_A = 0.4$ , where its value is 2.66 times the value at  $\chi_A = 0.0$ . The rotational relaxation time varies by a factor of 1.5. The essence of re-entrance is nicely captured in Fig. 1.

Note that although Fig. 1 has the same qualitative feature as the experimental plot,<sup>3</sup> there exists some differences in the details. These details of the plot are sensitive to the interaction parameters, in agreement with the observations of Beddard *et al.*<sup>3</sup>

#### B. Sensitivity of re-entrance to mass, size, and specific interactions

To understand the role of specific solute–solvent interactions in this anomalous behavior of  $\tau_{2R}$ , we have performed a study by keeping the mass and the size of the two species in the binary mixture the same. The mass of the ellipsoid is also kept the same and its minor axis is kept equal to the radius of the spheres (model I). The results obtained for this system are plotted in Fig. 2. It is clear from the figure that this model, too, can exhibit the re-entrant behavior of the orientational relaxation time when plotted against solvent viscosity. Although the mass and the size do change the values of the  $\tau_{2R}$  and  $\eta$ , and thus the details of the plot, the specific interactions of the ellipsoids with the solvents A and B play the key role in this anomalous behavior of  $\tau_{2R}$ . In this system the maximum of viscosity is obtained at composition  $\chi_A = 0.2$ , where its value is 1.67 times that at  $\chi_A = 0$ . The orientational relaxation time varies by a factor of 1.28. The composition in this plot is varied from 0–0.6.

In Fig. 3 we plot the orientational relaxation time against the viscosity for an ellipsoid with aspect ratio,  $\kappa = 3$  (model III). Here, the binary mixture is the same as in model II. The plot shows a sharp re-entrance. This can be attributed to two

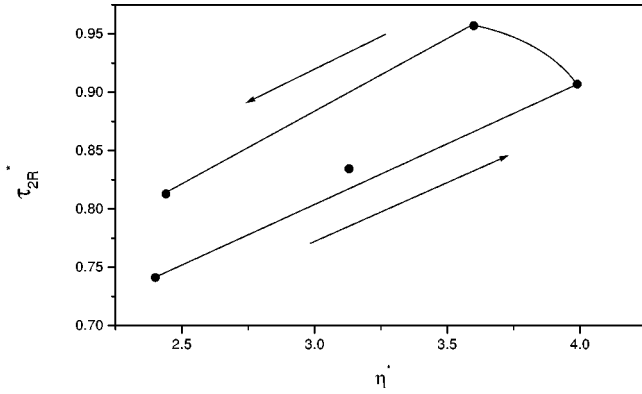


FIG. 2. The reduced orientational relaxation time,  $\tau_{2R}^*$ , plotted against the reduced viscosity of the binary mixture,  $\eta^*$ , is shown by the filled circles.  $\tau_{2R}$  shows a re-entrance. The solid line is a guide to the eye. The compositions of the A particles are 0, 0.08, 0.2, 0.4, and 0.6, where the direction of the arrows shows the increasing composition of A particles. The study is performed at  $T^*=1.0$  and  $P^*=1.0$ , for model I.  $\tau_{2R}^* = \tau_{2R} \sqrt{(\epsilon_{BB}/m_A \sigma_A^2)}$  and  $\eta^* = \eta \sigma_A^2 / \sqrt{m_A \epsilon_{BB}}$ .

different reasons. First, the difference in interactions of the ellipsoid with molecules A and B is less than that in model II. Second, for a larger ellipsoid the time scale of rotation is comparable to that of the dynamics of the solvent. Thus, it probes a more average solvent dynamics.

### C. Can nonideality in viscosity alone explain the re-entrance?

In Fig. 4 we plot the simulated viscosity against the composition. The viscosity shows a nonideal behavior. The ideal behavior is given by the dotted line. This nonideality in the composition dependence of the viscosity has been discussed at length by Srinivas *et al.*<sup>5</sup>

We next investigate whether the nonideality in viscosity alone can reproduce the observed anomalous behavior of the orientational relaxation time. In Fig. 5 we have shown the ratio of  $\tau_{2R}(\chi_A)/\tau_{2R}(\chi_A=0.04)$  against the ratio

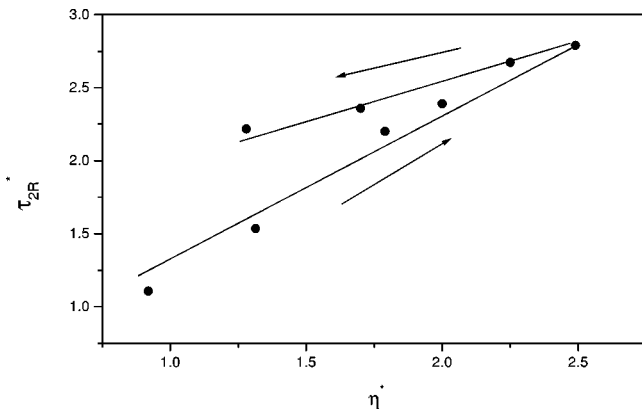


FIG. 3. The reduced orientational relaxation time,  $\tau_{2R}^*$ , plotted against the reduced viscosity of the binary mixture,  $\eta^*$ , is shown by the filled circles.  $\tau_{2R}$  shows a sharp re-entrance. The solid line is a guide to the eye. The compositions of the A particles are 0, 0.04, 0.15, 0.2, 0.4, 0.6, 0.8, and 1.0, where the direction of the arrows shows the increasing composition of A particles. The study is performed at  $T^*=1.0$  and  $P^*=1.0$ , for model III.  $\tau_{2R}^* = \tau_{2R} \sqrt{(\epsilon_{BB}/m_A \sigma_A^2)}$  and  $\eta^* = \eta \sigma_A^2 / \sqrt{m_A \epsilon_{BB}}$ .

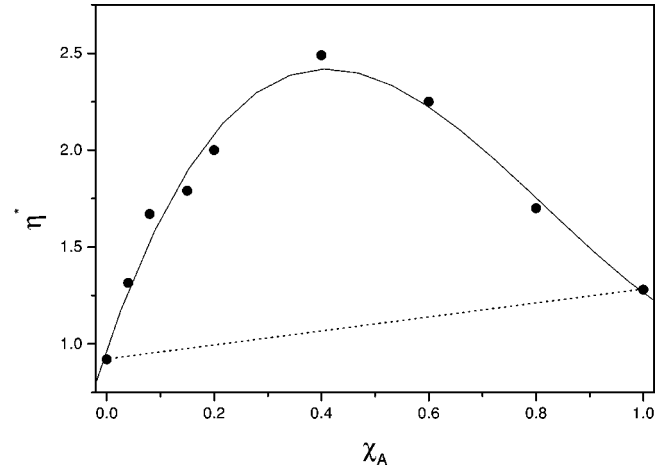


FIG. 4. The composition dependence of the reduced viscosity is shown by the filled circles. The solid line is a guide to the eye. The dashed line shows the ideal behavior of viscosity in a binary mixture. The study is performed at  $T^*=1.0$  and  $P^*=1.0$ , for model II.  $\eta^* = \eta \sigma_A^2 / \sqrt{m_A \epsilon_{BB}}$ .

$\eta(\chi_A)/\eta(\chi_A=0.04)$ . The dashed line is the result obtained from the DSE relation where  $\tau_{2R}$  is calculated from Eq. (1) and Eq. (2) by using the viscosities plotted in Fig. 4. From this figure it is obvious that *the nonideality in viscosity in a binary mixture cannot alone explain the re-entrance.*

The study here shows that, in a system where the solute interacts with the two different species in a binary mixture in a different manner, the rotational relaxation of the solute will depend more on the composition than on the viscosity of the binary mixture. Thus, the re-entrant type behavior is strongly dependent on the interactions of the solute with the two different species in the solvent.

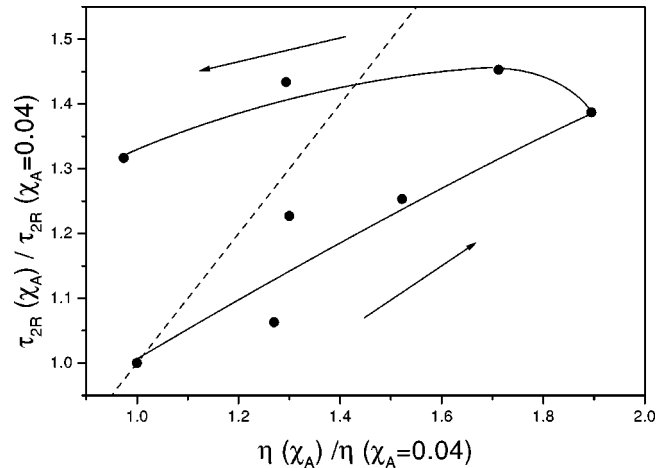


FIG. 5. The ratio  $\tau_{2R}(\chi_A)/\tau_{2R}(\chi_A=0.04)$  against the ratio  $\eta(\chi_A)/\eta(\chi_A=0.04)$  is shown by the filled circle. The solid line is a guide to the eye. The dashed line shows the plot of the same, but here  $\tau_{2R}(\chi_A)$  is calculated from Eqs. (1) and (2) of the text using the simulated viscosities. The compositions of the solvent are the same as in Fig. 1 and the direction of the arrows shows the increasing composition of A particles. The study is performed at  $T^*=1.0$  and  $P^*=1.0$ , for model II.

#### IV. MODE COUPLING THEORY ANALYSIS OF THE NONHYDRODYNAMIC BEHAVIOR

The inverse proportionality between orientational diffusion of a tagged particle and the liquid viscosity can be rationalized either from Navier–Stokes hydrodynamics or from microscopic mode-coupling theory. The former prescription does not change in going from single component to binary mixture and thus fails to account for the multiple values of the rotational correlation time at a fixed viscosity. The mode coupling theory (MCT), on the other hand, suggests a completely different scenario and is more in agreement with the results observed in present simulations. Although quantitative calculation of the correlation time of an ellipsoid in binary mixture (or even in a one-component liquid) has not been carried out yet, we can draw some general conclusions from the structure of the equations.

Thus, we present here an analysis of the nonhydrodynamic behavior of the rotational relaxation time/rotational diffusion, within the mode coupling theoretical framework. The analysis is qualitative, the aim here is to show that the logic behind the validity of the hydrodynamic theory in a one-component system cannot be extended to a binary mixture.

Let us assume that  $\rho_E(\mathbf{r}_E, \mathbf{\Omega}_E, t)$  denotes the position  $\mathbf{r}_E$ , orientation  $\mathbf{\Omega}_E$ , and time-dependent number density of the ellipsoid E at time  $t$ .  $\rho_j(\mathbf{r}_j, t)$  is the position- and time-dependent density of the solvent  $j$ , where  $j$  represents both A- and B-type of solvents.  $\mathbf{N}(\mathbf{r}_E, \mathbf{\Omega}_E, t)$  is the torque on a tagged ellipsoid at  $(\mathbf{r}_E, \mathbf{\Omega}_E, t)$ . The expression of the torque is given by<sup>17</sup>

$$\mathbf{N}_E(\mathbf{r}_E, \mathbf{\Omega}_E, t) = k_B T \nabla_{\mathbf{\Omega}_E} \sum_j \int d\mathbf{r}'_j \times C^{Ej}(\mathbf{r}_E - \mathbf{r}'_j, \mathbf{\Omega}_E) \delta\rho_j(\mathbf{r}'_j, t), \quad (13)$$

$C^{Ej}(\mathbf{r}_E - \mathbf{r}'_j, \mathbf{\Omega}_E)$  is the angular direct correlation function between the ellipsoid E and the solvent  $j$ .

The orientational friction can now be given by Kirkwood's formula, which expresses the friction as an integral over the torque–torque time correlation function<sup>17</sup>

$$\zeta_{R,\rho\rho} = \frac{1}{2k_B T} \int_0^\infty dt \frac{1}{4\pi V} \int d\mathbf{r}_E d\mathbf{\Omega}_E \langle \mathbf{N}_E(\mathbf{r}_E, \mathbf{\Omega}_E, 0) \cdot \mathbf{N}_E(\mathbf{r}_E, \mathbf{\Omega}_E, t) \rangle, \quad (14)$$

where  $\langle \dots \rangle$  involves averaging over the initial solvent configurations and also solvent dynamics when the position and the orientation of the solute probe are held fixed.

In the subsequent steps one writes the integral in the wave vector ( $\mathbf{k}$ ) space and expands the direct correlation function in the spherical harmonics (in the framework where  $\mathbf{k}$  is taken parallel to the  $z$  axis). Straightforward algebra leads to the following expression of the torque:

$$\mathbf{N}_E(\mathbf{r}_E, \mathbf{\Omega}_E, t) = \frac{1}{(2\pi)^3} \sum_{lm} (\nabla_{\mathbf{\Omega}_E} Y_{lm}(\mathbf{\Omega}_E)) \times \sum_j \int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}_E} C_{lm}^{Ej}(k) \delta\rho_j(\mathbf{k}, t), \quad (15)$$

where  $\delta\rho_j(\mathbf{k}, t)$  is the Fourier transform of  $\delta\rho_j(\mathbf{r}_j, t) = \rho_j(\mathbf{r}_j, t) - \rho_{0j}$ , where  $\rho_{0j}$  is the average density of the solvent  $j$ .  $C_{lm}^{Ej}(k)$  is the  $lm$ th coefficient in the spherical harmonic expansion of the direct correlation function  $C^{Ej}(k, \mathbf{\Omega}_E)$  term, which is the Fourier transform of  $C(\mathbf{r}_E - \mathbf{r}'_j, \mathbf{\Omega}_E)$ . The above expression of torque is now substituted in Eq. (14) to obtain the following expression for the time-dependent friction:

$$\zeta_{R,\rho\rho}(t) = \frac{k_B T \rho_s}{16\pi^3} \sum_{i,j} \int_0^\infty dk k^2 \sum_{lm} l(l+1) \times C_{lm}^{Ei}(k) C_{lm}^{Ej}(k) \sqrt{\chi_i \chi_j} F_{ij}(k, t). \quad (16)$$

In the above expression  $F_{i,j}(k, t)$  is the dynamic structure factor or the intermediate scattering function of the liquid,  $\rho_s$  is the density of the solvent, and  $\chi_i$  is the mole fraction of species  $i$ . We believe that the above expression of rotational friction in a binary mixture is presented for the first time over here.

A similar expression for the mode coupling part of the viscosity in a binary mixture can also be written as<sup>5</sup>

$$\eta_{\rho\rho} = \frac{k_B T}{60\pi^2} \sum_{i,j} \int_0^\infty dq q^4 \frac{S'_{ii}(q) S'_{jj}(q)}{S_{ii}^2(q) S_{jj}^2(q)} \int_{\tau_\eta}^\infty dt F_{ij}^2(k, t), \quad (17)$$

where  $S_{ii}(q)$  and  $S'_{ii}(q)$  are the static structure factor and its derivative, respectively.  $\tau_\eta$  is the characteristic time for the Gaussian decay of the binary viscosity.

The above two expressions take simpler forms in a one-component system.<sup>18,19</sup> An analysis of the recovery of the hydrodynamic condition for a one-component system has been presented recently.<sup>18</sup> In a dense liquid, most of the contribution to the wave vector integration comes from the intermediate regime where the static structure factor of the liquid,  $S(q)$ , has a sharp peak. In this region, the dynamic structure factor or the intermediate scattering function,  $F(k, t)$ , of a neat liquid is diffusive in nature and can be given by the following simple expression:

$$F(k, t) = S(k) \exp(-D_0 k^2 t / S(k)). \quad (18)$$

This equation, when substituted in the expression of rotational friction,  $\zeta_R$ , for a one-component liquid yields the following expression for the friction:

$$\zeta_{R,\rho\rho} = \frac{k_B T \rho_s}{16\pi^3 D_0} \int_0^\infty dk S(k) \sum_{lm} l(l+1) C_{lm}^2(k). \quad (19)$$

This equation can be recast in the following form:

$$\tau_R D_0 = \frac{\rho_s}{32\pi^3} \int_0^\infty dk S(k) \sum_{lm} l(l+1) C_{lm}^2(k). \quad (20)$$

This expression has the nice feature that the terms on the right-hand side are purely static and determined by local correlations. Here,  $D_0$  is the translational diffusion of the solvent molecules.

With the same diffusive assumption for the dynamic structure factor, one can show that the collective part of viscosity is related to translational diffusion by the following relation:

$$D_0 \eta = \frac{k_B T}{120 \pi^2} \int_0^\infty dk k^2 [S'(k)/S(k)]^2 S(k). \quad (21)$$

From Eqs. (20) and (21),  $D_0$  can be eliminated and the inverse proportionality between  $\tau_R$  and  $\eta$  can be established.

A similar analysis for the binary system needs the expressions for the  $F_{ij}(k, t)$ . Approximate expressions for the dynamic structure factors are available. Even these approximate expressions have complex dependence on  $D_A$  and  $D_B$ . Thus, the product  $\tau_R \eta$  cannot be expressed in terms of static quantities alone. Moreover, diverse length and time scale are present in Eqs. (16) and (17). Given the diversity of the system, it is naive to expect the presence of such simple proportionality between  $\tau_R$  and  $\eta$ .

A one-loop calculation of the binary viscosity within the mode coupling theoretical framework already exists.<sup>5</sup> These calculations could explain the nonideal composition dependence of the viscosity. A similar full MCT calculation of the rotational friction should be able to explain the re-entrance. This is a nontrivial calculation and remains an exercise to be addressed in the future. Our aim here was to show that, just from the expressions of rotational friction and viscosity in binary mixture, it can be argued that there exists no simple proportionality between  $\tau_R$  and  $\eta$  as predicted by hydrodynamics.

## V. CONCLUSION

In this article we presented computer simulation studies and mode coupling theoretical analysis of the orientational relaxations in binary mixtures, with an aim to understand the re-entrant type behavior observed by Beddard *et al.*<sup>3</sup> when the orientational correlation function is plotted against viscosity. As we noted earlier, this interesting problem has drawn surprisingly little attention from theoreticians. As correctly discussed by Beddard *et al.*<sup>3</sup> and emphasized by Fleming,<sup>4</sup> the orientation relaxation of a solute probe in a binary mixture is determined by many factors and viscosity ceases to be the unique determinant.

We have performed isothermal–isobaric (*NPT*) MD simulations of isolated Gay–Berne ellipsoids in binary Lennard–Jones mixtures. From this study, we have proposed different model systems which show the anomalous viscosity dependence of orientational relaxation time, similar to that observed in the experiments.<sup>3,4</sup>  $\tau_{2R}$ , when plotted against  $\eta$  by varying the composition of the solvent, shows a re-entrance. Our study suggests that this re-entrant type behavior could be a general feature of orientational relaxations in binary mixtures. The three different models presented here are examples of the kind of systems where the  $\tau_{2R}$  of the ellipsoid when plotted against  $\eta$  will show such re-entrant type behavior. This anomalous viscosity dependence of the

rotational relaxation time cannot be explained only in terms of the nonideality in viscosity. The solute–solvent interactions play a key role. If the difference in the interactions of the solute with the two species in the solvent is not large, then the re-entrance will be sharp (as shown in Fig. 5) and similar interactions of the solute with the two different species will lead to DSE type behavior.

A qualitative mode coupling theoretical analysis of the nonhydrodynamic behavior has also been presented. We have argued that because of the complex structure of the rotational relaxation time and the viscosity, in a binary mixture, a simple proportionality between them does not exist.

Further, note that the response of a binary mixture to an external probe is sensitive to the composition fluctuation, particularly when the solute–solvent interaction is different for the two species. Thus, the spatial and dynamical correlations of such fluctuations could be of importance. Our preliminary study shows that in a neat binary mixture the correlation length of composition fluctuation is less than  $3\sigma$ . Dynamical correlation of a binary mixture at short length scale is yet to be studied in detail. In the mode coupling theory these static and dynamical correlations of the composition fluctuation are taken into account through the wave number and frequency-dependent dynamic structure factor.

Here, we would like to mention an interesting phenomenon observed in the study of the orientational relaxation. The orientational correlation function for ellipsoids with aspect ratio 2, at  $\chi_A = 0$  and even for  $\epsilon_{EB} = 0.7$ , was found to be oscillatory with an initial Gaussian part. This free-rotor-like behavior is usually expected in the gas phase but not in a liquid at reduced density 0.8 (which is typical of normal liquids). To analyze this surprising phenomenon we have simulated the radial distribution function,  $g_{EB}(r)$  and found that it does not have any structure. It starts from zero, then slowly rises, and eventually at large “ $r$ ” saturates at 1. Due to the absence of any solvent structure around the solute, the density contribution to the friction is small, although the density is above 0.8. The binary contribution to the friction is even smaller because of a combined effect of this radial distribution function and small value of the specific interaction. Thus, the small friction at short and intermediate time leads to the free-rotor-like behavior.

The relevance of the study of orientational dynamics in binary mixtures goes beyond the observed re-entrance. Orientational relaxation in a binary mixture is particularly relevant when one or both of the constituents are dipolar. Binary mixtures are also known to be potential glass formers. The orientational dynamics of the solute can be used as a probe to study the heterogeneous dynamics in supercooled binary mixture. This is an interesting problem and work in this direction is in progress.

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