

## Reentrant Behavior of Relaxation Time with Viscosity at Varying Composition in Binary Mixtures

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In order to understand the long known anomalies in the composition dependence of diffusion and viscosity of binary mixtures, we introduce here two new models and carry out extensive molecular dynamics simulations. In these models, the two molecular species ( $A$  and  $B$ ) have the same diameter and mass. In model I the interspecies interaction is more attractive than that between the pure components, while the reverse is true for model II. Simulations and mode coupling theory calculations reveal that the models can capture a wide variety of behavior observed in experiments, including the *reentrant* viscosity dependence of relaxation time.

Transport properties of binary mixtures often show strong and baffling dependencies on the composition which have not been understood or even adequately addressed in a molecular theory. The well-known Raoult's law of classical physical chemistry [1] predicts the following simple linear dependence on the composition for a given property  $P$ ,

$$P = x_1 P_1 + x_2 P_2, \quad (1)$$

where  $x_i$ s are the mole fractions and  $P_i$ s are the values of the property  $P$  of the pure (single component) liquids. More often than not, significant deviation from Eq. (1) is observed. Of many anomalies exhibited by binary mixtures, the existence of an extremum (sometimes even a double extrema) in the composition dependence of excess viscosity [2] and the reentrant type behavior of the relaxation time when plotted against viscosity [3] are certainly the most remarkable. The latter shows, in a dramatic fashion, that *viscosity is not a unique determinant of relaxation in binary mixtures* [3]. Several interesting theoretical and computer simulation studies on Lennard-Jones binary mixtures have been carried out recently [4–6], but these studies have concentrated mainly on the glass transition in binary mixtures and considered *only one particular composition* and a unique interaction strength. Earlier Heyes carried out the extensive equilibrium molecular dynamics (MD) simulations of Lennard-Jones binary mixtures to study the partial properties of transport coefficients in the inert gas medium [7], by using the Berthelot mixing rule and found only a weak nonideality. The nonideality in the case of inert gas mixtures is small, since their mutual interaction strength ( $\epsilon_{AB}$ ) follows the Berthelot mixing rule.

In order to understand the markedly nonlinear composition dependence of viscosity and diffusion, here we introduce and study two models (referred to as model I and model II) of binary mixtures in which the solute-solvent interaction strength is varied by keeping *all the other parameters* unchanged. In our models, all the three interactions (solute-solute, solvent-solvent, and solute-solvent) are described by the Lennard-Jones (12 – 6) potential,

$$U_{ij} = 4\epsilon_{ij} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], \quad (2)$$

where  $i$  and  $j$  denote any two different particles. We set the diameter ( $\sigma$ ) and mass ( $m$ ) of both the solute and the solvent molecules to unity, for simplicity. The solvent-solute interaction strength lies in the potential well depth  $\epsilon_{AB}$ , where  $A$  and  $B$  represent the solvent and solute particles, respectively. Throughout this study we keep the interaction strength  $\epsilon_{AA} = 1.0$  (solvent-solvent),  $\epsilon_{BB} = 0.5$  (solute-solute). In the two models we use two different solvent-solute interaction strength values, namely  $\epsilon_{AB} = 2.0$  in model I and  $\epsilon_{AB} = 0.3$  in model II. So, while model I is a “structure former” (between  $A$  and  $B$ ), model II is a “structure breaker.” Model I shows glass transition behavior similar to the Kob-Andersen model. One advantage of this model is that only the interaction energy is varied. These models can also capture the anomalous inverse correlation between excess viscosity and excess volume observed in many experiments. We believe that the models introduced here can serve as starting points to understand the many baffling properties of binary mixtures.

In addition to the self-diffusion coefficients ( $D_i^s$ ) and the viscosity, we also calculated the mutual (or the inter-) diffusion coefficients ( $D_{AB}$ ) of the binary mixture at various compositions. The latter is a subject of long-standing interest, although not much is known about the extent of its nonideality. The ideal value is given by ( $D_{AB}^0$ )

$$D_{AB}^0 = Q(x_B D_A^s + x_A D_B^s), \quad (3)$$

where  $x_i$  and  $D_i^s$  are the mole fraction and the self-diffusion coefficient of the  $i$ th species in the mixture, respectively, and  $Q$  is the well-known thermodynamic factor of binary mixing [8]. The simulations presented here shows a marked departure from Eq. (3), due to cross-velocity correlations. We believe that this is the first time that such pronounced nonideality in  $D_{AB}$  is established.

It is worthwhile to note that Enskog kinetic theory, which is applicable to hard sphere systems [9], attempts to

explain in a concise way the composition dependence of the transport properties in binary mixtures. But unfortunately this theory fails completely to explain the observed strong nonideality in the composition dependence of diffusion in binary mixture.

Extensive MD (microcanonical ensemble, with the usual periodic boundary condition) simulations have been carried out with a total of 500 particles for two types of models by varying the solute mole fraction (that is, of  $B$ ) from 0 to 1. The reduced temperature  $T^*(= k_B T/\epsilon)$  is set equal to unity in model I and 1.24 in model II, and the reduced density ( $\rho^* = \rho \sigma^3$ ) is 0.85 in both the models. After many trial runs to verify the existing results on viscosity [7] of one component liquids, we have selected a time step  $\Delta t^* = 0.002\tau$  for model I and  $\Delta t^* = 0.001\tau$  for model II, where  $\tau = \sigma\sqrt{m/\epsilon}$ . We have dealt with six different solute compositions, namely 0, 0.2, 0.4, 0.6, 0.8, and 1.0. For each solute composition we have equilibrated the system up to  $1.5 \times 10^5$  steps. Simulations carried out for another  $2.0 \times 10^5$  steps after the equilibration during which all the relevant quantities have been calculated. For each composition, we have run three independent simulations and have taken averages over them. We have checked all the three partial radial distribution functions to make sure no phase separation occurs during simulations (for model II). Viscosity values are obtained by integrating the stress time correlation function which defines the time dependent viscosity by the following relation:

$$\eta(t) = (Vk_B T)^{-1} \langle \sigma^{xz}(0) \sigma^{xz}(t) \rangle, \quad (4)$$

where the off-diagonal element of the stress tensor  $\sigma^{xz}$  for binary mixture is defined as

$$\sigma^{xz} = \sum_{j=1}^N [(p_j^x p_j^z / m) + F_j^z x_j]. \quad (5)$$

Here  $F_j^z$  is the  $z$  component of the force acting on the  $j$ th particle, the corresponding  $x$  coordinate is  $x_j$ , and  $p_j^z$  is the  $z$  component of the momentum of  $j$ th particle,  $m$  being the mass of the particle. Among total  $N$  particles, solvent particles are labeled from 1 to  $N_1$  and solute particles from  $(N_1 + 1)$  to  $N$ .

Diffusion coefficients are calculated both from the mean square displacement and velocity autocorrelation function via the Green-Kubo relation. The results of the simulation are given in Figs. 1–4. We shall discuss the results after we describe the mode coupling theory employed.

We have carried out mode coupling theory (MCT) calculations of diffusion and viscosity to understand the simulation results, especially the origin of nonmonotonicity. These calculations have been carried out by using well-established expressions [10–14]. Note that for binary mixtures at normal density and temperature, the short time dynamics of the relevant time correlation functions are important and, in fact, can contribute more than 50% of the total value, just as for one component liquids. Thus, any solution of MCT equation requires accurate input of the

short time dynamics. For a given transport property  $P$  [ $P$  can be viscosity ( $\eta$ ) or friction ( $\zeta$ )], MCT formalism [10–14] assumes the following separation into the short time, binary collision controlled, contribution  $P^{(\text{bin})}(t)$  and the contribution from the collective term, which in dense liquid is dominated by the density term,  $P^{(\rho\rho)}(t)$ . So the total dynamical quantity  $P(t)$  can be written as [10],

$$P(t) = P^{(\text{bin})}(t) + P^{(\rho\rho)}(t), \quad (6)$$

where the binary term is assumed to be Gaussian as  $P^{(\text{bin})} = P(t=0) \exp(-t^2/\tau_P^2)$ . The resulting expressions of the characteristic time  $\tau_P$  are complicated and given elsewhere [15].  $P(t=0)$  values are determined mainly by the static correlation like the radial distribution functions [ $g_{ij}(r)$ ] or the direct correlation functions [ $c_{ij}(r)$ ] which are obtained from Ornstein-Zernike equations with soft mean spherical approximation (SMSA) closure [16]. The mode coupling contribution to viscosity is assumed to be given by the binary product of the density terms. In case of binary mixture total MCT term  $\eta^{(\rho\rho)}$  can be expressed as the sum of four  $\eta^{(\rho_i\rho_j)}$  terms [15(a)]. The short time part of time dependent friction is calculated from short time expansion of force-force time correlation function [10–14] and the mode coupling expression follows Bosse *et al.* [13]. The frequency dependent diffusion coefficients [ $D_i^s(z)$ ] [which is the same as the Laplace transform of velocity autocorrelation function ( $C_{vi}(z)$ )] are related to the respective frequency dependent frictions [ $\zeta_i(z)$ ] according to Einstein relation,

$$D_i^s(z) = C_{vi}(z) = \frac{k_B T}{m_i [z + \zeta_i(z)]}. \quad (7)$$

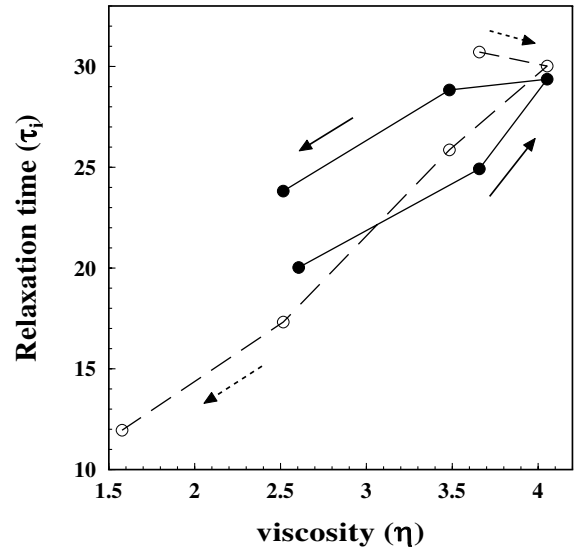


FIG. 1. The simulated values showing the reentrant behavior of the relaxation times  $\tau_i$  are plotted against simulated viscosity for model I. Filled circles represent  $\tau_A$ , while open circles represent  $\tau_B$ . The direction of the arrow shows the increasing solute ( $B$ ) composition in both the cases.  $T^* = 1.0$ ,  $\rho^* = 0.85$ .

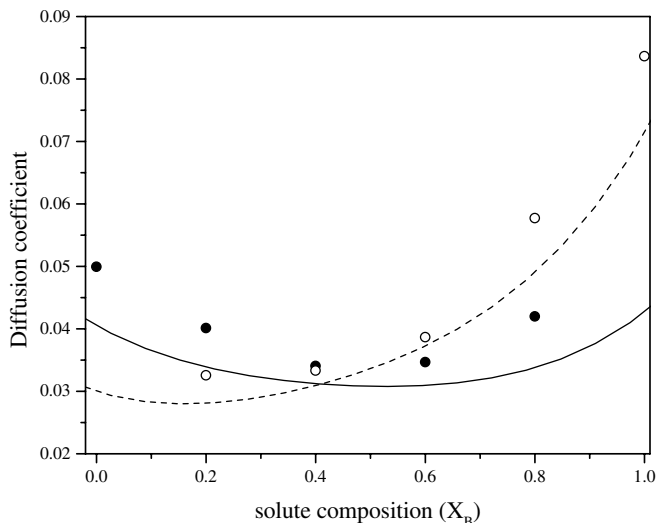


FIG. 2. The self-diffusion coefficients obtained from MD simulation and mode coupling theory are plotted for model I. Filled and open circles represent the solvent and solute diffusion coefficients obtained from simulations, respectively. Full and dashed lines show the MCT results.  $T^* = 1.0$ ,  $\rho^* = 0.85$ .

Figure 1 shows the remarkable reentrant behavior of the structural relaxation times ( $\tau_i$ ) when the viscosity is changed by varying the composition. The increase in composition is indicated by arrows. Here the relaxation time  $\tau_i$  is calculated by using  $\tau_i = \sigma^2/D_i^s$ . Thus, the relaxation time is inversely proportional to the diffusion constant. We believe that a similar behavior will be observed for rotational relaxation as well. The simulation results here are averages over three independent long runs; error bars are typically  $\pm 0.2$  for viscosity and  $\pm 1.5$  for the relaxation time (that is,  $\pm 0.002$  for diffusion coefficients). Note that in this figure we have shown only the simulation results, for clarity—theory shows a similar behavior.

Figure 2 shows the composition dependence of self-diffusion coefficients obtained from both theory and simulation, for model I. Figure 3 shows the same for model II. Note the nonmonotonic composition dependence. Diffusion of  $A$  and  $B$  shows differing behavior, in all the cases. This demonstrates the sensitivity of the transport properties to  $\epsilon_{AB}$ .

Mutual diffusion coefficients  $D_{AB}$  (sometimes called interdiffusion coefficients) are also calculated for model I

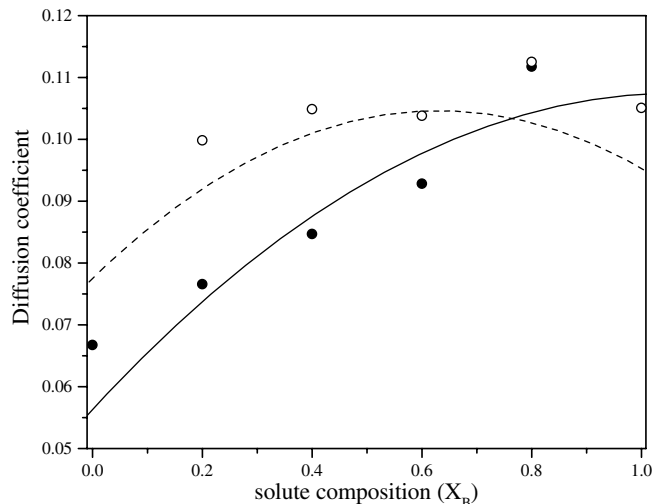


FIG. 3. The self-diffusion coefficients obtained from MD simulation and mode coupling theory are plotted for model II. Filled and open circles represent the solvent and solute diffusion coefficients obtained from simulations, respectively. Full and dashed lines show the MCT results.  $T^* = 1.24$ ,  $\rho^* = 0.85$ .

and model II for three different compositions (0.2, 0.4, and 0.8) following the scheme of Schoen *et al.* [8] and the results are given in Table I. The comparison between self and mutual diffusion coefficients clearly shows that cross correlations are NOT negligible in both the models introduced here. For model I, Enskog theory even fails to predict the qualitative trend.

Figure 4 depicts the nonideality of viscosity with respect to composition, for both the models. Though the agreement between theory and simulation is certainly not perfect, the trends are similar in both the calculations. Note that the theoretical calculation does not use *any* simulation data as input or *any adjustable parameter* either; thus the theory and the simulation provide independent tests of each other which is important for binary mixtures.

We conclude this Letter with the following comments.

(1) It is shown that the simple models can describe the differing behavior of diffusion and viscosity in binary mixtures, when the viscosity is changed by varying the composition. This nonmonotonicity of diffusion with viscosity is most dramatically manifested in the reentrant type behavior depicted in Fig. 1. This shows that *viscosity is not a unique determinant of relaxation in binary mixtures*.

TABLE I. The calculated thermodynamic factor for binary mixing ( $Q$ ), the ideal mutual diffusion coefficient ( $D_{AB}^0$ ), and the simulated mutual diffusion coefficient ( $D_{AB}$ ) are listed against the solute composition ( $X_B$ ) for both models I and II. (The definitions of all these quantities are adopted from Ref. [8].)

$X_B$	Model I			Model II		
	$Q$	$\frac{D_{AB}}{D_{AB}^0}$ (sim)	$\frac{D_{AB}}{D_{AB}^0}$ (Enskog)	$Q$	$\frac{D_{AB}}{D_{AB}^0}$ (sim)	$\frac{D_{AB}}{D_{AB}^0}$ (Enskog)
0.2	10.3702	0.4095	1.1642	0.2318	1.6491	1.0628
0.4	5.3465	0.1708	1.4315	0.0580	3.3832	1.2882
0.8	8.8987	0.3541	1.1334	0.2484	2.3353	1.0711

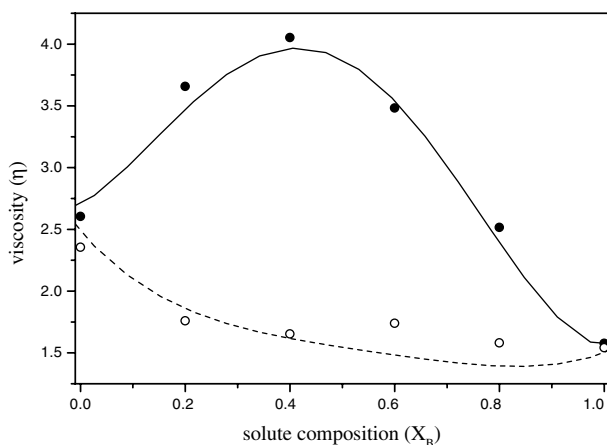


FIG. 4. The composition dependence of viscosity obtained from MD simulations (symbols) and mode coupling theory (lines) for both the models. Filled (open) circles give simulation results for model I (model II). The lines give the theories.

(2) Model I and model II seem to reproduce the behavior observed in a large number of systems. We believe that this is the first time a microscopic model captures the strong nonideality of diffusion and viscosity. The results agree with the age old wisdom that structure making interactions between the two constituents (here  $A$  and  $B$ ) lead to a slower stress relaxation. The opposite has also been observed for model II which has the structure breaking interactions.

(3) Both simulations and theoretical calculations reveal that the main reason for the anomalous composition dependence of viscosity lies in the variation of the mean square stress fluctuation with the composition of the mixture. Similarly, for friction, it is the Einstein frequency which shows nonmonotonic behavior. It is thus fair to say that the anomalies have both structural and dynamical origins.

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