Re-entrant Behavior of Relaxation Time with Viscosity at Varying Composition in Binary Mixtures

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Abstract

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 inter-species interaction is more attractive than that between the pure components, while the reverse is true for model II. Simulations and also mode coupling theory calculations reveal that the models can capture a wide variety of behavior observed in experiments, most interesting among them are the non-monotonic variation of diffusion and viscosity with the composition and the re-entrant viscosity dependence of the relaxation time.

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

$$ P = x_1 P_1 + x_2 P_2 $$

(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 extremum!) in the composition dependence of excess viscosity and the re-entrant type behavior of the relaxation time when plotted against viscosity are certainly the most remarkable. The latter shows, in

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a dramatic fashion, that *viscosity is not a unique determinant of relaxation in binary mixtures*. 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 MD simulations of Lennard-Jones binary mixtures by using both the microcanonical (N V E) and canonical (N V T) ensemble methods to study the partial properties of transport coefficients in the inert gas medium 7. The non-ideality 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, 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 \((6 - 12)\) Lennard-Jones potential,

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

where \(i\) and \(j\) denote any two different particles. We set the diameter ($\sigma$) and mass ($m$) of both the solute and the solvent molecule 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". Note that both \(A\) and \(B\) have the same diameter. We believe that these simple models can serve as starting points to understand the many baffling properties of binary mixtures.

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

$$\eta(t) = (V k_B T)^{-1} \langle \sigma^{xz}(0) \sigma^{xz}(t) \rangle$$

(3)

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

$$\sigma^{xz} = \sum_{j=1}^{N_1} [(p_j^x p_j^z / m) + F_j^z x_j] + \sum_{j=N_1+1}^{N} [(p_j^x p_j^z / m) + F_j^z x_j]$$

(4)

Here, $F_j^z$ is the z-component of the force acting on the $j$-th particle and the corresponding X-coordinate is $x_j$, $p_j^z$ is the z-component of the momentum $p_j$ of $j$-th particle, $m$ being the mass of the particle. Amongst total $N$ particles, $N_1$ solvent particles are labelled 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 figures 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 non-monotonicity. These calculations have been carried out by using well-established expressions\textsuperscript{8–12}. 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 the MCT equations require accurate input of the short time dynamics. For a given transport property $P$, MCT formalism\textsuperscript{8–12} assumes the following separation into the short time, binary collision controlled, contribution $P^{(bin)}(t)$ 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 \textsuperscript{8},

$$P(t) = P^{(bin)}(t) + P^{(\rho\rho)}(t)$$

(5)

The binary part of both viscosity and the friction are assumed to be Gaussian, \textsuperscript{8–10}

$$P^{(bin)}(t) = P(t = 0) exp(-t^2 / \tau_P^2).$$

(6)
For viscosity, $P(t = 0)$ is the high frequency shear modulus $G_\infty$ of a binary mixture given by,\textsuperscript{15}

$$G_\infty = (\rho_1 + \rho_2)k_BT + \frac{2\pi}{15}\sum_{i,j=1}^{2} \rho_i \rho_j \int_0^\infty dr g_{ij}(r) \frac{d}{dr} \left[r^4 \frac{dv_{ij}(r)}{dr}\right]$$

(7)

here, $i,j = 1$ indicate solvent particles and $i,j = 2$ denote solute particles. $\rho_1$ and $\rho_2$ are the corresponding number densities for the solvent and solute particles. $g_{ij}(r)$ is the partial radial distribution function of the particles labelled $i$ and $j$. In the present calculation, $g_{ij}(r)$ is obtained from Ornstein-Zernike equations with SMSA closure\textsuperscript{14}, which provides a reasonable, although not perfect, agreement with the simulation results.

The characteristic relaxation time $\tau_\eta$ for viscosity can be determined by the second derivative of $\eta(t)$. The resulting expression of $\tau_\eta$ for a binary mixture is rather complex and is given elsewhere\textsuperscript{15}. The mode coupling contribution to viscosity is assumed to be given by the binary product of the density terms\textsuperscript{8,9}. In the present case, one derives contribution from four such density terms and total MCT term $\eta^{(\rho\rho)}$ is given by the simple addition of four $\eta^{(\rho_i\rho_j)}$ terms. The frequency dependent diffusion coefficients $D_i(z)$ are related to the respective frequency dependent frictions according to Einstein relation,

$$D_i(z) = C_{vi}(z) = \frac{k_BT}{m_i(z + \zeta_i(z))}$$

(8)

For friction, $\zeta_i(t = 0)$ is the Einstein frequency of the $i$-th component in the mixture and is determined by the static correlation functions. The initial short time part of time dependent friction is assumed to be Gaussian with characteristic time $\tau_\zeta$ which is calculated using the short time expansion of the force-force time correlation function\textsuperscript{8–10}. The expression for the mode coupling term has already been given by Bosse et al\textsuperscript{11} and need not be presented here. The dynamical input parameters for MCT calculation are the wavenumber ($q$) dependent and time ($t$) dependent partial intermediate scattering functions, $F_{ij}(q,t)$ and the self-dynamic structure factors, $F_{si}(q,t)$. The expressions of dynamic structure factors $F_{ij}(q,z)$ are obtained by solving four coupled equations obtained from time dependent density functional theory\textsuperscript{13}. This method requires the value of the frequency dependent self-diffusion coefficient of both the species. We have used the bare value of the diffusion coefficient here, calculated from Eq. 8 by using the binary part of the frequency dependent friction. We approximate $F_{si}(q,t)$ by $F_{si}(q,t) = exp(-q^2\langle \Delta r_i^2(t) \rangle/6)$ where

$$\langle \Delta r_i^2(t) \rangle = 2 \int_0^t C_{vi}(\tau)(t - \tau)d\tau$$

(9)

$C_{vi}(t)$ in Eq. 9 is obtained from the numerical inverse Laplace transform of $C_v(z)$.
Figure 1 shows the remarkable re-entrant 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 $\tau_i = \sigma^2 / D_i$. Thus, the relaxation time is inversely proportional to diffusion constant. We believe that a similar behavior will be observed for rotational relaxation as well. The simulation points 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 diffusion coefficients obtained from both theory and simulation, for model I. Figure 3 shows the same for model II. Note the non-monotonic composition dependence. Diffusion of $A$ and $B$ show differing behavior, in all the cases. 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 test 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 decoupling of diffusion from viscosity in binary mixtures, when the viscosity is changed by varying the composition. This decoupling is most dramatically manifested in the re-entrant type behavior depicted in Fig. 1. This shows that viscosity is not a unique determinant of relaxation in binary mixtures.

(2) Models I and II seem to reproduce the behavior observed in large number of systems. We believe that this is the first time a microscopic model captures the strong non-ideality 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 relaxation. The opposite has also been observed for model II which has the structure breaking interactions.

(3) What is also remarkable is that the non-ideality manifests itself in nearly opposite ways for the two models. This has been observed for all the transport properties and hence reflected in the re-entrance behavior also.

(4) The theoretical calculations reveal that the main reason for the anomalous composition dependence of viscosity lies in the variation of the mean square stress...
fluctuation (MSSF) with the composition of the mixture. Similarly, for friction, it is the Einstein frequency which shows non-monotonic behavior. It is thus fair to say that the anomalies have both a structural and a dynamic origin.

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**Figure Captions**

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

**Figure 2** The 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 3** The 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. $T^* = 1.24$, $\rho^* = 0.85$.

**Figure 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.
Relaxation time ($\tau_i$) vs. viscosity ($\eta$)

Viscosity values: 1.5, 2, 2.5, 3, 3.5, 4

Relaxation times: 10, 15, 20, 25, 30

The graph shows a trend where relaxation time increases with increasing viscosity.
Diffusion coefficient vs. solute composition ($X_B$)
Diffusion coefficient vs. solute composition ($X_B$)
Viscosity ($\eta$) vs. Solute Composition ($X_B$)