

# Mass dependence of shear viscosity in a binary fluid mixture: Mode-coupling theory

Sk. Musharaf Ali,<sup>1</sup> Alok Samanta,<sup>2</sup> Niharendu Choudhury,<sup>2</sup> and Swapan K. Ghosh<sup>2,\*</sup>

<sup>1</sup>Chemical Engineering Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

<sup>2</sup>Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400 085, India

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An expression for the shear viscosity of a binary fluid mixture is derived using mode-coupling theory in order to study the mass dependence. The calculated results on shear viscosity for a binary isotopic Lennard-Jones fluid mixture show good agreement with results from molecular dynamics simulation carried out over a wide range of mass ratio at different composition. Also proposed is a new generalized Stokes-Einstein relation connecting the individual diffusivities to shear viscosity.

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## I. INTRODUCTION

Diffusivity and viscosity [1–6] of fluid mixtures play an important role in various disciplines and have been investigated over decades through different theoretical tools such as hydrodynamics, kinetic theory, and more recently the mode coupling theory (MCT). Each of these theories has been successful in different regimes of mass and size of the diffusing particle and the density of the fluid mixture. For a massive and large tagged particle, the diffusivity  $D$  is related to the solvent viscosity  $\eta$  through the well known Stokes-Einstein (SE) relation of hydrodynamics, viz.  $D = Ck_B T / \eta \sigma_{\alpha\beta}$ , where  $C$  is a constant determined by the nature of hydrodynamic boundary condition,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\sigma_{\alpha\beta}$  is the arithmetic mean of the solute and solvent sizes (diameters)  $\sigma_{\beta\beta}$  and  $\sigma_{\alpha\alpha}$ , respectively. The SE expression for diffusivity has an explicit size dependence, but predicts a mass-independent diffusivity, although simulation studies [7,8] have shown that the product  $D\eta$  does not remain constant with variation of mass of the solute particle. The failure of SE theory is attributed to the fact that although the variation of mass of the tracer particle does not affect the viscosity  $\eta$ , it does affect the diffusivity  $D$ . However, in a binary fluid mixture of finite concentration of each of the components, both these quantities are affected by the variation of mass and hence one may expect a relation similar to the SE theory to hold good. There also exists a linear model [9] for the evaluation of shear viscosity of a binary isotopic fluid mixture where  $\eta$  is expressed as a sum of the corresponding mole fraction averaged component viscosities. For an isotopic mixture, it can be expressed as

$$\eta_{ideal} = x_\alpha \eta_\alpha^0 + x_\beta \eta_\beta^0, \quad (1)$$

where  $\eta_\alpha^0$  and  $\eta_\beta^0$  are the shear viscosities of the  $\alpha$  and  $\beta$  components in pure form. Since the viscosity of a pure fluid is proportional to the square root of the mass of its particles, Eq. (1) can be rewritten as

$$\frac{\eta}{\eta_\alpha^0} = x_\alpha + x_\beta \left( \frac{m_\beta}{m_\alpha} \right)^{1/2}. \quad (2)$$

\*Author to whom correspondence should be addressed. Email address: [skghosh@magnum.barc.ernet.in](mailto:skghosh@magnum.barc.ernet.in)

Equations (1) and (2) correspond to the assumption of an ideal solution model and the deviation from ideality is linked with the interparticle correlation. The best tool for understanding this nonideality should therefore consist of a microscopic theory which can incorporate the correlation effects and predict a proper mass dependent viscosity. In the recent past, MCT has established [6,10–14] itself as a successful microscopic theory for the study of diffusivity in fluids and fluid mixtures. We have also derived simple universal scaling laws of diffusivity, viscosity, and Kolmogorov entropy [15–17] which connect these dynamical quantities with entropy calculated from equilibrium properties alone. Although attempts have been made to understand different aspects of viscosity using MCT, no attention has been drawn to the effect of mass on viscosity and time-dependent viscosity. It is thus of interest to understand through MCT the nature as well as the origin of the mass dependence of shear viscosity of a mixture. Kushal and Tankeswar [18] have studied the effect of mass on shear viscosity for isotopic systems using the expression of only short time expansion of time-dependent shear viscosity  $\eta(t)$ . However,  $\eta(t)$  is contributed by the short time as well as the long time dynamics of the fluid particle which can be included in the microscopic theory of MCT. Also they have not compared their results with those of simulation. Hence our objective here is to understand the effect of mass on the shear viscosity and time-dependent shear viscosity of a fluid mixture using MCT as well as computer simulation study [19,20]. To the best of our knowledge, such a systematic study of mass dependence has not been addressed so far. The rest of the paper is organized as follows. The theoretical formalism is presented in Sec. II. In Sec. III, we discuss the models and simulation methodology while the numerical results obtained through theoretical calculation and simulation are presented in Sec. IV. The work is finally concluded in Sec. V.

## II. THEORETICAL FORMALISM

The system of interest here is a binary fluid mixture consisting of two components  $\alpha$  and  $\beta$  with  $N_\alpha$  and  $N_\beta$  number of particles, respectively. The expression for the time-dependent shear viscosity of this  $N(=N_\alpha+N_\beta)$  particle system of volume  $V$  is given by the Green-Kubo formula

$$\eta(t) = \frac{1}{k_B TV} \langle \sigma^{xz}(0) \sigma^{xz}(t) \rangle, \quad (3)$$

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

$$\sigma^{xz}(t) = \sum_{i=1}^N (m_i v_{ix} v_{iz} + x_i F_{iz}) \quad (4)$$

with  $m_i, v_{ix}$ , and  $x_i$  denoting respectively the mass and  $x$  components of velocity and position of the  $i$ th particle while  $v_{iz}$  and  $F_{iz}$  are the  $z$  components of the velocity and the force acting on the  $i$ th particle. The shear stress thus consists of two terms representing the kinetic and potential energy contributions, respectively. At higher density of the liquid, the contribution of the second term is more prominent than the first one.

In MCT, [6,10] the total time-dependent shear viscosity can be decomposed into two parts, viz.

$$\eta(t) = \eta_{bin}(t) + \eta_{mct}(t), \quad (5)$$

where  $\eta_{bin}(t)$  represents the short time contribution and  $\eta_{mct}(t)$  is the long time collective mode-coupling contribution. The short time binary contribution  $\eta_{bin}(t)$  can be obtained through the well known Gaussian expression [6,10] as

$$\eta_{bin}(t) = \eta(0) \exp(-t^2/\tau_\eta^2), \quad (6)$$

where  $\eta(0)$ , representing the zero time shear viscosity, is defined as

$$\eta(0) = \frac{1}{k_B TV} \langle \sigma^{xz}(0) \sigma^{xz}(0) \rangle, \quad (7)$$

which can be expressed as

$$\eta(0) = \left[ \rho k_B T + \frac{2\pi}{15} \sum_{\mu,\nu} \rho_\mu \rho_\nu \int_0^\infty dr g_{\mu\nu}(r) \frac{d}{dr} \left\{ r^A \frac{d\phi_{\mu\nu}(r)}{dr} \right\} \right]. \quad (8)$$

Here,  $\rho (= \sum_\mu \rho_\mu)$  is the bulk density representing the sum of the two component densities  $\rho_\alpha$  and  $\rho_\beta$ ,  $g_{\mu\nu}(r)$  is the partial radial distribution function, and  $\phi_{\mu\nu}(r)$  is the interparticle interaction potential. The value of  $\tau_\eta$  can be obtained from the time derivative of  $\eta(t)$  using Eq. (6) as

$$\tau_\eta = [-2\eta(0)/\ddot{\eta}(0)]^{1/2}. \quad (9)$$

The integrated shear viscosity  $\eta$  can be obtained as  $\eta = \eta_{bin} + \eta_{mct}$ , where  $\eta_{bin} = \int_0^\tau dt \eta_{bin}(t)$  and  $\eta_{mct} = \int_\tau^\infty dt \eta_{mct}(t)$ .

From Eqs. (3) and (4), it is clear that there are three distinct contributions (kinetic, kinetic-potential, and potential) to the time-dependent viscosity. The major contribution, however, comes from the potential part as has been clear from the study of Balucani *et al.* [21] in a one component dense fluid. Thus the expression for the time-dependent viscosity  $\eta(t)$  can be well approximated by the expression

$$\eta(t) = \frac{1}{k_B TV} \left\langle \left( \sum_{i=1}^N x_i F_{iz} \right) \left( \sum_{j=1}^N x_j F_{jz} \right) \right\rangle. \quad (10)$$

The second derivative of the total short time  $\eta(t)$ , which involves contributions from two- and three-particle correlation terms since the four-particle correlation term  $\ddot{\eta}_4(0)$  is exactly zero [21], can be expressed as

$$\ddot{\eta}(0) = \ddot{\eta}_2(0) + \ddot{\eta}_3(0). \quad (11)$$

The contributions from the two- and three-particle correlation terms  $\ddot{\eta}_2(0)$  and  $\ddot{\eta}_3(0)$ , respectively, can be expressed as

$$\begin{aligned} \ddot{\eta}_2(0) = & -\frac{4\pi}{15} \left[ \sum_{\mu,\nu=\alpha,\beta} \frac{\rho_\mu \rho_\nu}{m_\mu} \int_0^\infty dr r^2 [7\phi'_{\mu\nu}(r)^2 \right. \\ & \left. + 2r\phi'_{\mu\nu}(r)\phi''_{\mu\nu}(r) + r^2\phi''_{\mu\nu}(r)^2] g_{\mu\nu}(r) \right] \end{aligned} \quad (12)$$

and

$$\begin{aligned} \ddot{\eta}_3(0) = & -\frac{8\pi}{75} \left[ \sum_{\mu,\nu,\gamma=\alpha,\beta} \frac{\rho_\mu \rho_\nu \rho_\gamma}{m_\mu} \int dk k^2 h_{\nu\gamma}(k) \right. \\ & \left. \times [3I_3^{\mu\nu}(k)I_3^{\mu\gamma}(k) + 2I_1^{\mu\nu}(k)I_1^{\mu\gamma}(k)] \right] \end{aligned} \quad (13)$$

where  $h_{\nu\gamma}(k)$  is the Fourier transform of the pair correlation function and  $m_\mu$  is the mass of a particle of the  $\mu$ th component. Here the integrals  $I_3^{\mu\nu}(k)$  and  $I_1^{\mu\nu}(k)$  are defined as

$$I_3^{\mu\nu}(k) = \int_0^\infty dr r^2 J_3(kr) [r\phi''_{\mu\nu}(r) - \phi'_{\mu\nu}(r)] g_{\mu\nu}(r) \quad (14)$$

and

$$I_1^{\mu\nu}(k) = \int_0^\infty dr r^2 J_1(kr) [r\phi''_{\mu\nu}(r) + 4\phi'_{\mu\nu}(r)] g_{\mu\nu}(r), \quad (15)$$

where  $J_1(kr)$  and  $J_3(kr)$  are the spherical Bessel functions and  $\phi'_{\mu\nu}(r)$  and  $\phi''_{\mu\nu}(r)$  denote the first and second derivatives of  $\phi_{\mu\nu}(r)$ . Using Eqs. (6), (8), (9), and (11), one thus has a route to the calculation of the binary contribution to the shear viscosity.

The mode-coupling contribution  $\eta_{mct}(t)$  to the shear viscosity of the fluid mixture can be evaluated by using the general approach initiated by Bosse *et al.* [22] and Gestzi [23] for the one component system. In an MCT framework, where the first step involves a choice of suitable bilinear modes in terms of which one defines the projection operator  $P$  as

$$P = \sum_{\mathbf{k}} |A\rangle \langle AA\rangle^{-1} \langle A|, \quad (16)$$

with  $|A\rangle$  denoting the column matrix represented by the product of the component density modes as

$$|A\rangle = \begin{pmatrix} \rho_\alpha(\mathbf{k})\rho_\alpha^*(\mathbf{k}) \\ \rho_\alpha(\mathbf{k})\rho_\beta^*(\mathbf{k}) \\ \rho_\beta(\mathbf{k})\rho_\beta^*(\mathbf{k}) \end{pmatrix}. \quad (17)$$

Also, for a binary mixture, there are two density components  $\rho_\alpha(\mathbf{k})$  and  $\rho_\beta(\mathbf{k})$  defined as

$$\rho_\alpha(\mathbf{k}) = \sum_{j=1}^{N_\alpha} \exp(-i\mathbf{k} \cdot \mathbf{r}_j^\alpha), \quad (18)$$

$$\rho_\beta(\mathbf{k}) = \sum_{j=1}^{N_\beta} \exp(-i\mathbf{k} \cdot \mathbf{r}_j^\beta). \quad (19)$$

The next step is to extract the dominant slow variable contributions by introducing the projection operator  $P$  which projects any variable onto the subspace spanned by the bilinear density products. As a result, the quantity  $\eta_{mct}(t)$  predicted by MCT turns out to be

$$\eta_{mct}(t) = \lim_{k \rightarrow 0} \frac{1}{k^2 V} [J^x(k) P | \exp(iLt) | P J^x(k)], \quad (20)$$

where the momentum density  $J^x(k)$  for simple dense liquids is given by

$$J^x(k) = \frac{1}{N^{1/2}} \sum_{\mu=\alpha,\beta} \sum_{j=1}^{N_\mu} m_\mu \mathbf{v}_j^\mu(0) \exp[i\mathbf{k} \cdot \mathbf{r}_j^\mu(0)], \quad (21)$$

with  $\mathbf{v}_j^\mu(0)$  and  $\mathbf{r}_j^\mu(0)$  as the velocity and position of the  $j$ th particle belonging to the  $\mu$ th component. Equation (20) is further simplified by using Gaussian approximation, along with the translational invariance properties of the correlation function and also the change of summation over  $k$  to an integral, to obtain the final expression

$$\eta_{mct}(t) = \frac{k_B T}{60\pi^2} \int_0^\infty dk k^4 \sum_{\mu,\nu} \sum_{\mu',\nu'} c'_{\mu,\nu}(k) c'_{\mu',\nu'}(k) \times F_{\mu\mu'}(k,t) F_{\nu\nu'}(k,t), \quad (22)$$

where  $c'_{\mu,\nu}(k)$  is the first derivative of the direct correlation function  $c_{\mu,\nu}(k)$ . Here  $F_{\mu\nu}(k,t)$  is the partial dynamic structure factor which can be evaluated using time-dependent density functional theory, the details of which are given elsewhere [12]. We present here the final expression given by

$$F_{\mu\nu}(k,t) = \frac{S_{\mu\nu}(k)}{(\phi_- - \phi_+)} [A_{\mu\nu}(k, \phi_-) \exp(\phi_- t) - A_{\mu\nu}(k, \phi_+) \exp(\phi_+ t)], \quad (23)$$

where

$$A_{\mu\nu}(k, \phi_\pm) = \left( \phi_\pm + D_\nu k^2 [1 - \rho_\nu c_{\nu\nu}(k)] + D_\mu k^2 \rho_\nu c_{\mu\nu}(k) \sum_{\nu' \neq \mu} S_{\nu'\nu}(k) \right), \quad (24)$$

with

$$\phi_\pm = -\frac{(\lambda_1 + \lambda_2) \pm \sqrt{(\lambda_1 - \lambda_2)^2 + 4\lambda_3}}{2},$$

$$\lambda_1 = D_\alpha k^2 [1 - \rho_\alpha c_{\alpha\alpha}(k)],$$

$$\lambda_2 = D_\beta k^2 [1 - \rho_\beta c_{\beta\beta}(k)],$$

$$\lambda_3 = D_\alpha D_\beta \rho_\alpha \rho_\beta c_{\alpha\beta}^2(k),$$

and  $S_{\mu\nu}(k)$  representing the partial static structure factor. It is interesting to note that the expression given by Eq. (22), which is obtained here through MCT is identical to the results obtained using fluctuating hydrodynamics [24,25]. It is clear from Eqs. (22) and (23) that the time-dependent shear viscosity  $\eta(t)$  depends on the static quantities, viz. the partial static structure factor  $S_{\mu\nu}(k)$ , direct correlation function  $c_{\mu\nu}(k)$ , and the self-diffusivities  $D_\alpha, D_\beta$ .

Another approach which connects the shear viscosity  $\eta$  with the diffusivity  $D$  for a pure fluid uses the generalized SE relation [26,27] given by

$$D^* = A/\eta^{\gamma}, \quad (25)$$

where the scaled diffusivity  $D^* = D/(k_B T \sigma^2/m)^{1/2}$  and scaled viscosity  $\eta^* = \eta/(mk_B T/\sigma^4)^{1/2}$ . Here  $A$  and  $\gamma$  depend on the system parameters. However, in a binary fluid mixture, there are two component diffusivities and a similar relation is not known yet. We propose here a general SE relation for a binary fluid mixture as

$$D_\mu^* = A_\mu/\eta^{\gamma_\mu}, \quad \mu = \alpha, \beta, \quad (26)$$

where  $A_\mu$  and  $\gamma_\mu$  are empirical constants to be determined by best fitting. Here the component diffusivity  $D_\mu^*$  has been scaled by  $(k_B T \sigma_{\alpha\alpha}^2/m_\alpha)^{1/2}$ . Therefore, the above equation provides a direct route to calculate the shear viscosity in binary fluid mixture from a knowledge of the individual diffusivity parameters.

### III. MODELS AND SIMULATION METHODS

The system considered here consists of two kinds of particles ( $\alpha$  and  $\beta$ ) of mass ( $m_\alpha$  and  $m_\beta$ ), interacting with each other through the pair potential, given by the Lennard-Jones (LJ) form, viz.

$$\phi_{\mu\nu}(r) = 4\epsilon_{\mu\nu} \left[ \left( \frac{\sigma_{\mu\nu}}{r} \right)^{12} - \left( \frac{\sigma_{\mu\nu}}{r} \right)^6 \right], \quad (27)$$

where  $\sigma_{\mu\nu}$  and  $\epsilon_{\mu\nu}$  denote the LJ parameters for the pair of particles of types  $\mu$  and  $\nu$ . For dissimilar particles, the parameters are obtained from those for similar particles by using the Lorentz-Berthelot mixing rules, viz.

$$\sigma_{\mu\nu} = (\sigma_{\mu\mu} + \sigma_{\nu\nu})/2, \quad \epsilon_{\mu\nu} = (\epsilon_{\mu\mu}\epsilon_{\nu\nu})^{1/2}. \quad (28)$$

The mass  $m_\beta$  of the  $\beta$  component has been varied by keeping the mass of the  $\alpha$  component fixed. We consider here only a model system with the size and potential remaining unchanged with variation of mass, as is the standard practice for investigating the effect of only one property, viz.

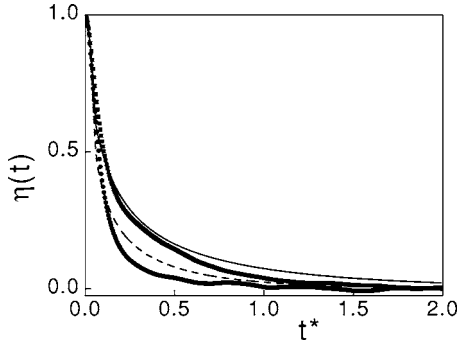


FIG. 1. Plot of the normalized  $\eta(t)$  vs time  $t^*$  of isotopic LJ fluid mixtures at different values of the dimensionless relative mass  $m_\beta^*$  for the  $\beta$  component. The size and interaction potential of both the components are taken as identical and the density, temperature, and composition parameters used are  $\rho^*=0.85$ ,  $T^*=0.965$ , and  $x_\beta=0.5$ . The solid and dashed lines represent the present MCT based results for  $\eta(t)$  for  $m_\beta^*=2$  and 16, respectively, whereas the symbols (filled squares and circles) represent the corresponding simulation results.

the mass here. Thus we have used  $\sigma_{\alpha\alpha}=\sigma_{\beta\beta}$  and  $\epsilon_{\alpha\alpha}=\epsilon_{\beta\beta}$ . We have truncated the potential at a cutoff distance of  $2.5\sigma_{\alpha\alpha}$ . Also, the LJ model parameters used here for the isotopic system considered correspond to Ar.

We have carried out molecular dynamics (MD) simulation of LJ fluid mixture in micro-canonical (NVE) ensembles and calculated the diffusivity and shear viscosity. We have considered a total number of particles  $N=500$  placed in a cubic box with periodic boundary conditions. We have used the reduced LJ units (based on the parameters for species  $\alpha$ ), viz. reduced density  $\rho^*=\rho\sigma_{\alpha\alpha}^3$ , reduced temperature  $T^*=T(k_B/\epsilon_{\alpha\alpha})$ , reduced time  $t^*=t(m_\alpha\sigma_{\alpha\alpha}^2/\epsilon_{\alpha\alpha})^{1/2}$ , reduced self-diffusivity  $D_\mu^*=D_\mu(\epsilon_{\alpha\alpha}\sigma_{\alpha\alpha}^2/m_\alpha)^{1/2}$ , and reduced shear viscosity  $\eta^*=\eta(m_\alpha\epsilon_{\alpha\alpha})^{1/2}/\sigma_{\alpha\alpha}^2$ . The equations of motion are integrated using the velocity Verlet algorithm [19] with a time step of  $\Delta t^*=0.005$ . Starting from a fcc lattice configuration, the system was equilibrated for  $5 \times 10^5$  MD steps. In order to allow a target temperature  $T^*$ , velocities were scaled at every time step during equilibration and this constraint was removed during a production run of  $5 \times 10^5$  MD steps. All the

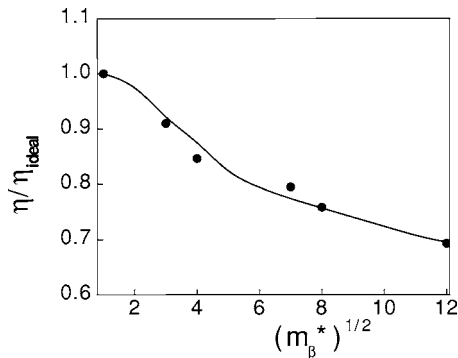


FIG. 2. Plot of the scaled shear viscosity ( $\eta/\eta_{ideal}$ ) vs square root of the dimensionless relative mass  $(m_\beta^*)^{1/2}$  of isotopic LJ fluid mixtures for the parameters  $\rho^*=0.85$ ,  $T^*=0.965$ , and  $x_\beta=0.5$ . The MD simulation results are shown by filled circle whereas the MCT results are represented by the solid line.

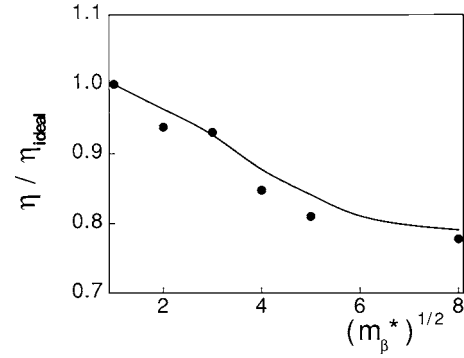


FIG. 3. Plot of the scaled shear viscosity ( $\eta/\eta_{ideal}$ ) vs square root of the dimensionless relative mass  $(m_\beta^*)^{1/2}$  of isotopic LJ fluid mixtures for the parameters same as in Fig. 2 except  $x_\beta=0.75$ . The key is same as in Fig. 2.

coordinates, velocities, and pressure tensors were stored at every time step during the production run for further analysis. The self-diffusivity and shear viscosity have been calculated using a Green-Kubo relation for velocity autocorrelation function and stress-stress autocorrelation function, respectively.

Due to the oscillating nature of the stress-stress correlation function at long time, the integrand in Eq. (3) has been multiplied with  $\exp(-\alpha t^*)$  to evaluate the integral with the value of  $\alpha$  needed for convergence found [28] to be 0.001.

#### IV. RESULTS AND DISCUSSION

The input parameters such as the radial distribution function, pair correlation function, direct correlation function, and static structure factor needed for the calculation of shear viscosity using the MCT approach discussed here have been obtained through the integral equation theory by adopting the procedure of Duh and Henderson [29]. The self-diffusivity values for both the components have been obtained from our simulation results.

We have used the present theory to calculate the shear viscosity  $\eta$  of a LJ isotopic binary mixture for the physical parameters:  $\rho^*=0.85$  and  $T^*=0.965$  at different compositions. The particle mass for the  $\alpha$  component has been kept

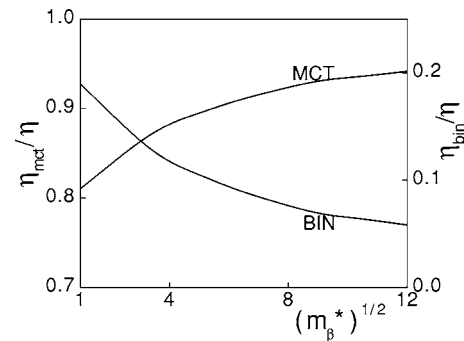


FIG. 4. Plot of  $(\eta_{mct}/\eta)$  and  $(\eta_{bin}/\eta)$  vs square root of the dimensionless relative mass  $(m_\beta^*)^{1/2}$  of isotopic LJ fluid mixtures for the parameters same as in Fig. 2. The key is same as in Fig. 2.

constant whereas the same for the  $\beta$  component is varied covering a wide range. For convenience, the mass of the particles of the  $\beta$  component is expressed in dimensionless form as  $m_\beta^* = [m_\beta/m_\alpha]$ , in units of that of the  $\alpha$  component. We have plotted in Fig. 1 the time-dependent shear viscosity  $\eta(t)$  (MCT based as well as simulation results) versus time at different values of  $m_\beta^*$  for the composition  $x_\beta=0.5$ . It is observed that decay of  $\eta(t)$  slows down with increase in  $m_\beta^*$ , leading to an increase in the value of the integrated quantity  $\eta$ . With increase in  $m_\beta^*$ , the MCT contribution to viscosity,  $\eta_{\text{MCT}}(t)$ , slows down due to slow relaxation of the collective dynamic structure factor  $F_{\mu\nu}(k,t)$ . It is clear from Eq. (23) that for a particular isotopic composition, the relaxation of  $F_{\mu\nu}(k,t)$  mainly depends on the component diffusivities  $D_\alpha$  and  $D_\beta$ , both of which decrease with increase in  $m_\beta^*$ , leading to a slow relaxation of  $F_{\mu\nu}(k,t)$ . Although  $\eta$  increases with an increase in the mass of the  $\beta$  component, what is more interesting is its deviation from the ideal behavior, for which we have plotted the quantity  $\eta/\eta_{\text{ideal}}$  for a wide range of values of the mass  $m_\beta^*$  in Figs. 2 and 3 for the composition  $x_\beta=0.5$  and  $x_\beta=0.75$ , respectively. Also plotted in the same figures are our simulation results for the shear viscosity and a good agreement between the calculated and the simulation results is observed. It is clear from these figures that the nonideal behavior of  $\eta$  depends rather strongly on the mass ratio especially at higher values. In order to understand the relative contributions of the binary and mode-coupling components to the total viscosity, we have plotted these quantities in Fig. 4. It is clear from the figure that the relative binary contribution to the total viscosity gradually decreases, whereas the relative mode-coupling contribution gradually increases with increase in the mass  $m_\beta^*$ . The decrease in the binary contribution to the total viscosity with increase in mass can easily be understood from Eqs. (9), (12), and (13), while the increase in the relative MCT contribution can be attributed to slow relaxation of the collective modes.

Using the present simulation results of the component diffusivities  $D_\alpha, D_\beta$  and shear viscosity  $\eta$ , we have obtained the best fitted values for  $A_\mu$  and  $\gamma_\mu$  as  $\ln A_\alpha = -1.94$ ,  $\ln A_\beta = -1.66$ ,  $\gamma_\alpha = 1.05$ , and  $\gamma_\beta = 1.30$  in Eq. (26) for the composition  $x_\beta=0.5$ . Using these constants in Eq. (26), we have plotted  $D_\mu$  vs  $\eta$  for the composition  $x_\beta=0.5$  in Fig. 5 along with the simulation results. An excellent agreement with the simulation results justifies the proposed equation (26). It is interesting to note that while an increase in mass of the heavier particle does affect the diffusivity of both the components, the data for the lighter particle obey the Stoke-

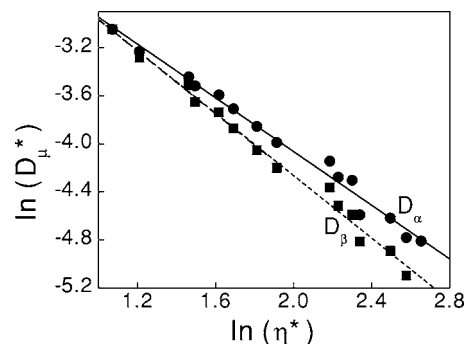


FIG. 5. Plot of the scaled self-diffusivities ( $D_\alpha^*$ ) and ( $D_\beta^*$ ) vs the scaled shear viscosity ( $\eta^*$ ) at different values of the dimensionless relative mass  $m_\beta^*$  for an isotopic LJ fluid mixture for the same parameters as in Fig. 2. The solid circles and squares are the results of simulation while the solid and dotted lines are the best linear fit for  $\alpha$  and  $\beta$  components, respectively.

Einstein relation rather well as is clear from the value of  $\gamma_\alpha$  being quite close to unity whereas for the heavier  $\beta$  particle, the deviation is significant.

## V. CONCLUSION

In this work, we have studied the effect of mass on the shear viscosity of a binary fluid mixture using the microscopic MCT as well as molecular dynamics simulation. The calculated results based on the present MCT formalism are in good agreement with our simulation results. The shear viscosity increases with increase in the mass of the heavier component, due to slowing down of the relaxation of the collective dynamic structure factor. Earlier theoretical [12] as well as simulation studies [30] have shown that the diffusivity depends only weakly on mass whereas the present study shows that the shear viscosity has a much stronger mass dependence than diffusivity. We have also proposed a Stokes-Einstein like relation for a binary fluid mixture and the calculated results using this relation are in excellent agreement with the simulation results.

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