

# Atypical violation of the Stokes–Einstein relation in a dense binary Lennard–Jones mixture<sup>1)</sup>

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We study the dynamics of particles in binary mixtures near the freezing transition using molecular dynamics simulations. The particles are considered to interact via a Lennard–Jones potential, and the impact of varying their size-ratio on their dynamics is examined. By calculating the mean-squared displacements and the self-intermediate scattering function of the particles, we find that introducing size disparity in an equimolar mixture at a constant packing fraction hinders particle movement, leading to a decrease in the self-diffusion coefficient. Additionally, as the size disparity increases, the local cage relaxation time becomes longer. Interestingly, the increase in the system’s viscosity does not correspond to an expected decrease in self-diffusion, resulting in an unusual violation of the Stokes–Einstein relation. Unlike typical glass-forming mixtures, where this violation parameter increases as temperature decreases, we observe the opposite behaviour.

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The macroscopic behavior of fluids is fundamentally influenced by the properties of their constituent particles and the interactions between them. The transport properties such as diffusion and viscosity, which are critical to processes like heat and mass transfer and fluid dynamics, depend heavily on the shape, size, and mass of the particles, as well as the interaction potentials that govern the forces they exert on one another [1]. The self-diffusion coefficient and the shear viscosity of fluids are often coupled via the Stokes–Einstein (SE) relation,  $D = k_B T / c \pi \mu R$ , where  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $c$  is a numerical constant depending on the boundary condition,  $\mu$  is the shear viscosity and  $R$  is the radius of the constituent particles. However, deviations from this relationship are observed in dense mixtures under certain conditions. These deviations, commonly attributed to dynamic heterogeneities, become more pronounced in systems near phase transitions or in the presence of structural constraints [1–3]. Binary Lennard–Jones (LJ) mixtures provide an ideal model for studying the dynamics of fluids near the freezing transition, particularly the effects of size asymmetry on transport properties such as diffusion and viscosity. The current work investigates a two-dimensional binary LJ system consisting of equal concentrations of two particle types interacting via a truncated and shifted LJ

potential. The size-ratio ( $\alpha = \sigma_B / \sigma_A$ ) is varied between 0.8 and 1.0, while the packing fraction is maintained at 0.707. The mass of all the particles is considered to be unity. Using molecular dynamics simulations, the system in a two-dimensional box is equilibrated at a high temperature and then quenched to temperature  $T = 0$  with a cooling rate of  $10^{-3} / \tau_{LJ}$ , where  $\tau_{LJ}$  is the characteristic LJ time unit. We determine the liquid-solid transition temperature  $T^*$  of these mixtures by roughly estimating the temperature at which the specific heat at constant volume diverges, which is estimated by computing the dependence of average potential energy on temperature. Our results indicate that reducing the size-ratio leads to a decrease in the liquid-solid phase transition temperature due to enhanced configurational entropy and the disruption of crystallinity by smaller particles occupying interstitial spaces [4].

Once the transition temperature is estimated, we measure the dynamical quantities, the mean-squared displacement (MSD) and the self-intermediate scattering function (SISF) at temperatures close to the transition temperature for mixtures with different size-ratios. Further, the self-diffusion coefficients of these mixtures are estimated using the late-time slopes of the MSD plots. We analyze the self-diffusion coefficients as a function of temperature and obtain the usual Arrhenius behavior at high temperatures while deviations from Arrhenius behavior is observed at temperatures close to  $T = T^*$  [5]. Moreover, both large and small particles exhibit decreased self-diffusion coefficients as  $\alpha$

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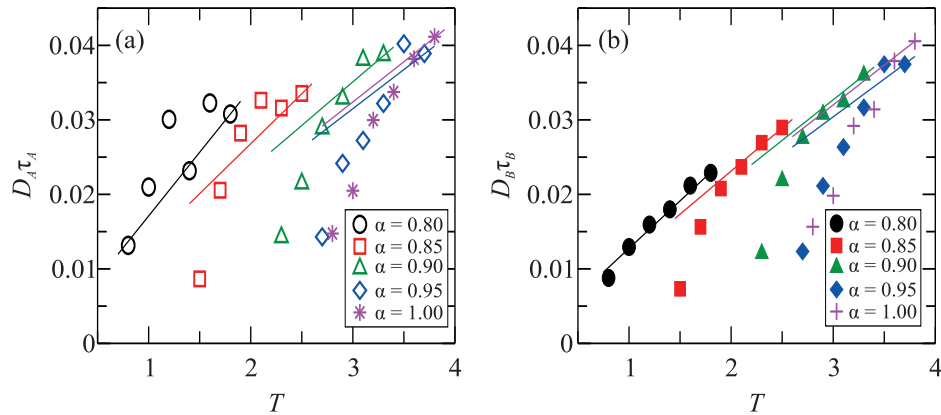


Fig. 1. (Color online) The product of diffusion coefficient and relaxation time: (a) –  $D_A \tau_A$  vs.  $T$  and (b) –  $D_B \tau_B$  vs.  $T$  for different size-ratios. Here, the solid lines represent the SE relation assuming it holds for the highest temperature and the dashed lines are the linear fit to the data points for each  $\alpha$

decreases, while their average mobilities remain comparable. The relaxation times in these mixtures, defined as the time at which the SISF decays to  $1/e$  of its value, increase significantly with decrease in size-ratios, demonstrating slower dynamics for mixtures with larger size-disparity. Furthermore, the fragility parameter determined through Vogel–Fulcher–Tammann (VFT) fitting increases with size disparity, indicating enhanced fragility in mixtures with greater asymmetry [6]. Interestingly, the late time relaxation of SISF displays a non-monotonic dependence on size-ratio of the mixtures with  $\alpha = 0.85$  undergoing the slowest relaxation.

Finally, we investigate the validity of the SE relation near the freezing transition by plotting  $D_A \tau_A$  and  $D_B \tau_B$  versus temperature in Figs. 1a and b. The SE relation holds when  $D_S \tau_S$ , where  $S \in (A, B)$ , exhibits a constant slope with  $T$ , assuming a constant particle radius. It is to be noted that here we use the relaxation time  $\tau$  instead of shear viscosity  $\mu$  to test SE relation as it has been shown recently that the relaxation time shows a linear dependence on the shear viscosity of a fluid [7]. The solid lines in Fig. 1 represent the expected SE behaviour. The observed  $D_S \tau_S$  values are lower than expected, indicating dynamical heterogeneity. Notably, this deviation decreases with increasing size disparity, which contrasts with typical behaviour in glasses and one-component fluids, where  $D_S \tau_S$  increases as temperature decreases [8]. Overall, the present work provides new insights into the complex interplay between diffusion, relaxation, and viscosity in dense binary LJ mix-

tures. The intuitive results demonstrate how size disparity can influence the transport properties and dynamic heterogeneities of these systems, offering potential implications for glass formation and other phase transition phenomena. The findings challenge conventional interpretations of the SE relation and underscore the need for further exploration of cooperative motion and structural relaxation in systems with high particle density and size asymmetry.

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