

## Frequency-dependent Stokes-Einstein relation in supercooled liquids

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We investigate by molecular dynamics simulations the validity of the frequency-dependent Stokes-Einstein (SE) relation in supercooled liquids at different temperatures. The results indicate that the SE relation holds at intermediate frequencies that correspond to the  $\beta$ -relaxation and the onset of the  $\alpha$ -relaxation regimes. Large deviations, which increase as the temperature decreases, are observed at frequencies well below the frequency at which the non-Gaussian parameter  $\alpha_2$  is maximum. We argue that the breakdown of the SE relation in supercooled liquids arises from underestimation of the diffusion coefficient due to neglect of correlated motions.

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Transport of momentum in dense fluids is accomplished by collisions between particles. On the other hand, diffusion (transport of mass) is achieved by the displacement of particles and is, therefore, hindered by collision events. These opposing contributions of collisions are expressed in the Stokes-Einstein (SE) relation [1,2]

$$D\eta = \frac{k_B T}{c\pi a}, \quad (1)$$

which indicates that the product of the diffusion coefficient of tracer particles,  $D$ , and the shear viscosity of the solvent,  $\eta$ , depends only on the temperature and not on the system's density or pressure. The constant  $c$  is a result of the hydrodynamic boundary condition at the surface of the tracer particle and the parameter  $a$  is its effective radius. The SE relation is derived from macroscopic considerations for large massive particles, at infinite dilution, immersed in a bath of particles that are much smaller and lighter. Nevertheless, the relation holds remarkably well for a wide range of systems including pure simple liquids [3], molecular systems [4], and colloidal suspensions [5].

A key assumption in the derivation of the SE relation is that, over long times, particle trajectories are uncorrelated and stochastic. This allowed Einstein to use a statistical model (random walk) to relate the diffusion coefficient of a Brownian particle to the thermal energy and the friction coefficient [2]. The combination of this expression with Stokes' law, which relates the friction coefficient to the viscosity of the fluid medium, yields the SE relation [1]. Thus the SE relation should be valid at times longer than the structural relaxation time of the solvent.

A generalized form of the SE relation that holds at all frequencies has been proposed [6–8],

$$D(\omega)\eta(\omega) = \frac{k_B T}{c\pi a}, \quad (2)$$

where  $D(\omega)$  and  $\eta(\omega)$  are the frequency-dependent diffusion coefficient and shear viscosity, respectively. In Eq. (2) it is assumed that the Stokes relation for viscous fluids can be extended to describe the viscoelastic drag at all frequencies. This is correct in the limit of purely viscous fluids. In addition, it is assumed that at all frequencies the diffusion of

particles through a medium occurs by motions in random directions, uncorrelated with one another. Experimental studies on a variety of systems show good qualitative agreement with the frequency-dependent SE relation [6,7]. Quantitative agreement is found at high frequencies [9,10].

Validity of the SE relation in supercooled liquids is not generally expected. This is because over a wide range of time scales the dynamics in some regions of these systems are characterized by cooperative motion [11]. This generates dynamical heterogeneities where the motion of the particles is not uniform; particles in some regions exhibit large displacements due to correlated, rapid motion, while other regions are much less mobile [12,13]. At times much longer than the  $\alpha$ -relaxation time, the particles exhibit diffusive behavior, and particle dynamics are homogenous. Despite long time homogeneous behavior, experimental [14–17] and computational [18,19] studies indicate a breakdown of the zero frequency SE relation, which presumably reflects heterogeneous behavior at earlier times.

It should be noted that mode-coupling theory (MCT) calculations predict that hard sphere colloidal suspensions near the glass transition do obey the frequency-dependent SE relation [8]. While MCT is believed to include some level of particle correlation (via a cage-effect), it is currently unclear to what extent MCT captures spatially correlated fluctuations in supercooled systems [20]. The MCT result predicting the validity of the SE relation in supercooled systems together with experimental and simulation results showing SE breakdown in these same systems suggests that correlated motion is not sufficient to necessitate SE breakdown, but that correlated motion (of some type) is necessary for SE breakdown.

In this study, we perform molecular dynamics (MD) simulations to examine the validity of the frequency-dependent SE relation over a wide range of frequencies in supercooled liquids. The generalized SE relation is investigated by explicit calculation of  $D(\omega)$  and  $\eta(\omega)$ . Since the magnitude of dynamical heterogeneities is a function of frequency, this approach elucidates how heterogeneities both affect the values of  $D(\omega)$  and  $\eta(\omega)$  and effect deviations from the generalized SE relation. The model system consists of a Lennard-Jones (LJ) binary mixture of large,  $A$ , and small,  $B$ , particles, with parameters similar to those used by Kob and Andersen [21]. Specifically,  $\sigma_{AA}=1.0$  and  $\epsilon_{AA}=1.0$  for interactions be-

tween the  $A$  particles and  $\sigma_{BB}=0.80\sigma_{AA}$  and  $\varepsilon_{BB}=0.5\varepsilon_{AA}$  for interactions between the  $B$  particles. The LJ parameters between the  $A$  and  $B$  particles,  $\sigma_{AB}=0.88\sigma_{AA}$  and  $\varepsilon_{AB}=1.5\varepsilon_{AA}$ , ensure the system does not crystallize. Particle masses are taken to be  $m_A=m_B=1.0$ . The simulations were carried out, and the results are reported below, in terms of reduced variables  $r^*=r/\sigma_{AA}$ ,  $T^*=k_B T/\varepsilon_{AA}$ , and  $t^*=t(k_B T/m_A \sigma_{AA}^2)^{1/2}$ . The interparticle potentials were shifted to zero and truncated at a cutoff distance of  $3.0\sigma_{AA}$ . The number of mixture particles,  $N_A=800$  and  $N_B=200$ , and the length of the cubic simulation box  $L^*=9.41036$ , yielded a number density of  $\rho^*=1.2$ . Newton's equations of motion were integrated using the "velocity Verlet" algorithm. Four sets of simulations were performed at four different temperatures:  $T^*=0.56, 0.66, 0.76$ , and  $2.00$ . The initial configurations were taken from simulations of similar supercooled liquids [21]. The systems were further equilibrated for at least  $10^7$  MD steps. The required temperature was achieved by multiplying the velocities, only during the equilibration stage, every  $2 \times 10^5$  MD steps, by an appropriate constant. In the data collection stage, the simulations were performed in the microcanonical ( $N, V, E$ ) ensemble. To allow efficient construction of time correlation functions on an exponential time scale, we performed simulations with time steps of  $\delta t^*=0.005$  and  $0.01$ , and used different time intervals to correlate properties at short, intermediate, and long times. For each simulation, the results were obtained by averaging eight independent runs, starting from different particle configurations, to obtain better statistics.

The frequency-dependent shear viscosity and diffusion coefficient were defined by the modulus of the Fourier transform (Filon algorithm) of the corresponding Green-Kubo relations. Namely, the diffusion coefficient was obtained from the velocity autocorrelation function,

$$D(\omega) = \int_0^\infty \langle v_x(0)v_x(t) \rangle e^{i\omega t} dt, \quad (3)$$

and the shear viscosity from the stress autocorrelation function,

$$\eta(\omega) = (k_B T V)^{-1} \int_0^\infty \langle \sigma_{xz}(0)\sigma_{xz}(t) \rangle e^{i\omega t} dt. \quad (4)$$

The stress tensor is defined by

$$\sigma_{xz} = \sum_{i=1}^N \left( m_i v_{i,x} v_{i,z} - \sum_{j>i} \frac{x_{ij} z_{ij}}{r_{ij}} \left. \frac{\partial \phi(r)}{\partial r} \right|_{r_{ij}} \right), \quad (5)$$

where  $\phi(r)$  is the interparticle potential. Both autocorrelations were averaged over the three independent spatial components. Prior to the Fourier transform operation, the stress autocorrelation function was fit to a ten parameter function of two exponentials and two half Lorentzians. In addition, the decay of the negative tail ( $t^* > 3.5$ ) of the velocity autocorrelation function to zero was fit to a  $t^{-3/2}$  function [22–24]. These fits were necessary to avoid numerical instabilities. Nevertheless, the low frequency regime of the Fourier transformed diffusion coefficient,  $D(\omega)$ , for  $T^*=0.56$  did exhibit instability. Therefore it was interpolated (for  $\omega^* < 0.1$ ) to its limiting value at zero frequency [ob-

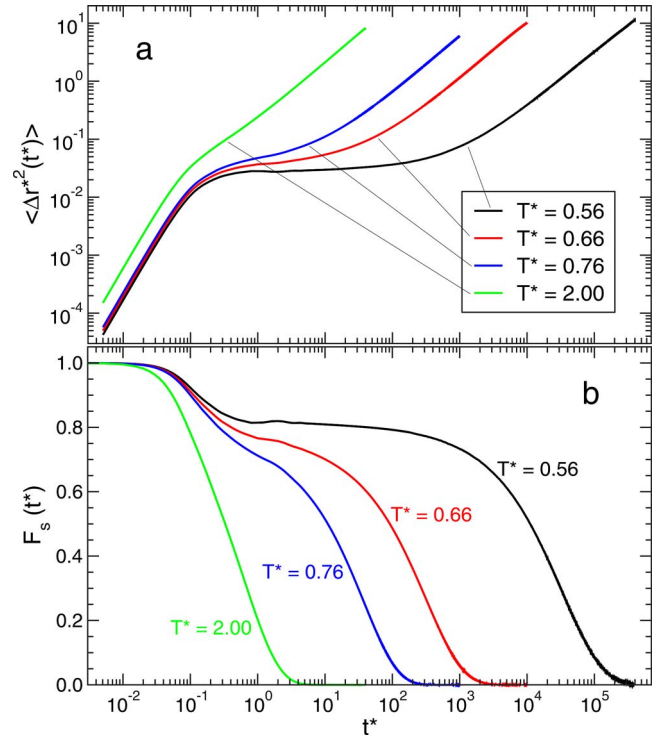


FIG. 1. (Color online) (a) MSD and (b)  $F_s(t^*)$  (for a wave vector near the first peak of the structure factor,  $q^*=6.6769$ ) as a function of time, plotted for different temperatures.

tained from the Einstein relation,  $\langle \Delta r^2(t) \rangle = 6Dt$ , at long times] using the cubic spline method. For  $T^*=0.66, 0.76$ , and  $2.00$ , we found that  $D(\omega=0)$  was approximately equal to the diffusion coefficient calculated from the mean-squared displacement (MSD) at long times.

One of the most obvious characteristics of supercooled liquids is the dramatic retardation of their dynamics as the temperature is decreased by a small amount near the glass transition. This is attributed to the cage-effect, the lack of vacancies in the first-neighbor shell surrounding a particle inhibiting large displacements. The retarded dynamics of the supercooled liquids studied are displayed in Fig. 1. It shows the MSD and the self part of an intermediate scattering function [ $F_s(t^*)$ ] for  $T^*=0.56, 0.66, 0.76$ , and  $2.00$ . The plots of all functions in this study were averaged over all particles ( $A$  and  $B$ ) in the system. At high temperature ( $T^*=2.00$ ), the liquid largely exhibits only ballistic and diffusive motion. However, at lower temperatures ( $T^*=0.56, 0.66$ , and  $0.76$ ) there is an onset of a subdiffusive regime in the MSD and a  $\beta$ -relaxation regime in  $F_s(t^*)$ , at intermediate times. These features are a manifestation of the cage-effect.

Figure 2 displays the non-Gaussian parameter calculated by  $\alpha_2(t) = 3\langle \Delta r^4(t) \rangle / (5\langle \Delta r^2(t) \rangle^2) - 1$ . Deviations of  $\alpha_2(t)$  from zero represent departures from a Gaussian distribution of particle displacements (i.e., from Fickian dynamics). The time at which  $\alpha_2(t)$  exhibits a maximum,  $t_{max}$ , is often interpreted as the time at which the system experiences the strongest degree of dynamical heterogeneity [25,26]. While for  $T^*=2.00$  the deviations of  $\alpha_2$  from zero are very small and occur only due to backscattering of the first collision event,

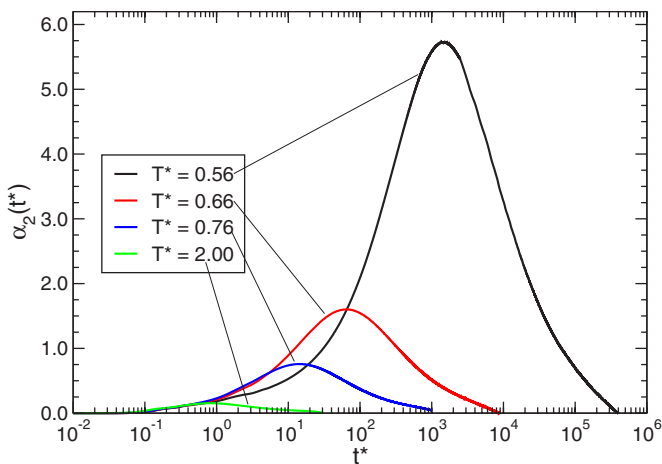


FIG. 2. (Color online) The non-Gaussian parameter as a function of time.

increasingly strong deviations are observed as the temperature is decreased. The values of  $t_{max}^*$  appear to increase approximately exponentially with decreasing temperature and occur at  $t_{max}^* = 0.8, 14, 66,$  and  $1440$  for  $T^* = 2.00, 0.76, 0.66,$  and  $0.56,$  respectively.

Figure 3 shows the diffusion coefficient and the shear viscosity as a function of frequency. For all temperatures, the curves of  $D(\omega)$  are maximum during short time ballistic motion and decay to a constant in the long time diffusive re-

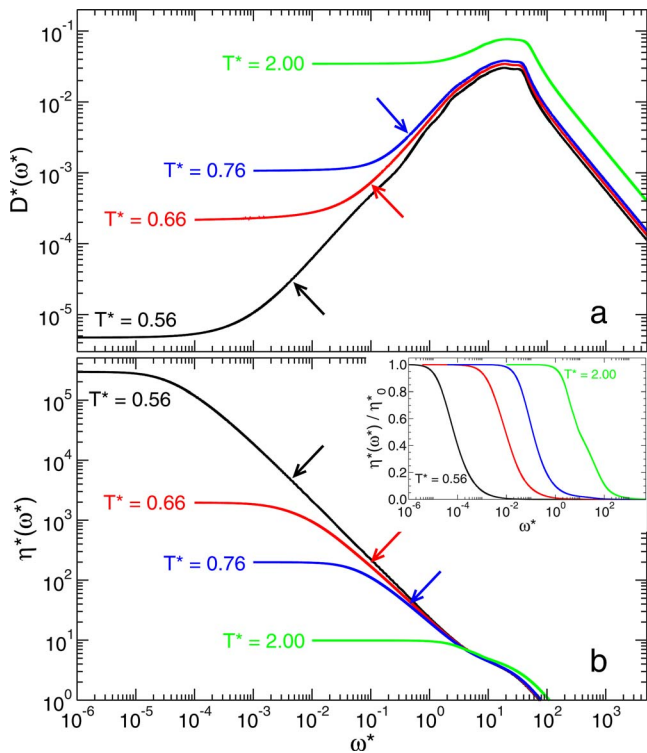


FIG. 3. (Color online) (a) The frequency- $(\omega^* = 2\pi/t^*)$  dependent diffusion coefficient and (b) shear viscosity, on a log-log scale. The arrows indicate the frequencies at which  $\alpha_2$  is maximum. The inset in (b) shows the shear viscosity, scaled by  $\eta^*(\omega^* = 0)$ , on a semilog plot.

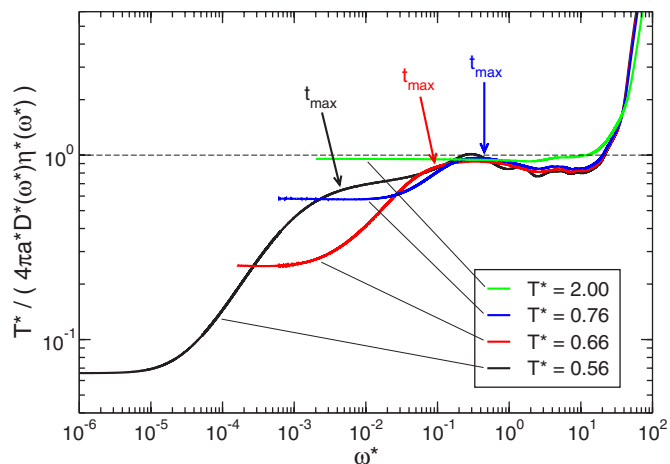


FIG. 4. (Color online) Deviations from the frequency-dependent SE relation. The value of the expression  $T^*/[4\pi a^* D^*(\omega^*) \eta^*(\omega^*)]$  is plotted as a function of frequency.

gime. The plots of  $\eta(\omega)$  exhibit an ascent to a constant as the frequency decreases. In the curves of  $D(\omega)$  and  $\eta(\omega)$ , the values of  $t_{max}$  for different temperatures occur at approximately the same relative position on the decaying-ascending segments. This indicates that the development of both  $D(\omega)$  and  $\eta(\omega)$  are correlated with the changing magnitude of dynamical heterogeneity of the system over time. Except for  $T^* = 2.00$ , the decay of  $D(\omega)$  to a constant occurs at larger frequencies than the ascent of  $\eta(\omega)$  to a constant. The difference in frequencies increases with decreasing temperature and for  $T^* = 0.56$  is about one order of magnitude. This indicates that in supercooled liquids the characteristic relaxation time for momentum transport is larger than that for mass transport, and that the difference in relaxation times is greater in more deeply supercooled systems.

Breakdown of the SE relation in the frequency domain is shown in Fig. 4 by the value of the expression  $T^*/[c\pi a^* D^*(\omega^*) \eta^*(\omega^*)]$ . Deviations from the value of one indicate discrepancies with the SE relation. We use the slip boundary condition [3]  $c=4$  and a weighted average for estimating the effective radius of the particles in the system,  $a^* = 0.488$ . At high temperature,  $T^* = 2.00$ , the SE relation is valid, and the value of  $T^*/[4\pi a^* D^*(\omega^*) \eta^*(\omega^*)]$  at frequencies smaller than those corresponding to ballistic motion is approximately 0.95.

It is remarkable that also for the supercooled systems ( $T^* = 0.76, 0.66,$  and  $0.56$ ), within a wide range of frequencies that cover the entire  $\beta$ -relaxation regime and the onset of the  $\alpha$ -relaxation regime, the SE relation is obeyed to a good approximation. This is possible because the slope of the decay of  $D(\omega)$  is equal to the slope of the ascent of  $\eta(\omega)$  but with opposite sign (Fig. 3). These findings are intriguing because it has been shown [27,28] that dynamical heterogeneities do exist in the  $\beta$ -relaxation regime. Figure 4 thus demonstrates that the existence of dynamical heterogeneity does not necessitate the breakdown of the SE relation. This is because even though the dynamics are heterogeneous in this time regime, all particles are still largely caged: though the fast particles exhibit increased motion relative to slow par-



ticles, they have not yet moved sufficiently to effect a change in the slope of  $D(\omega)$  relative to  $\eta(\omega)$ . Only over time scales on which particles, on average, move at least a particle diameter will the relative slopes change significantly.

Indeed, significant discrepancies from the SE relation start to develop at frequencies around (or just smaller than)  $t_{max}$ . At these frequencies,  $D(\omega)$  starts to level-off, while  $\eta(\omega)$  continues to rise, indicating that at lower frequencies either  $D(\omega)$  or  $\eta(\omega)$  is larger than predicted by the SE relation. Supercooled liquids are not purely viscous but also elastic. Therefore we may expect (positive) deviations of the viscosity from the value predicted by the SE relation to occur at frequencies where the elasticity of the system is still manifest, i.e., during the  $\beta$ -relaxation regime. However, since this is not the case, we argue that it is the value of  $D(\omega)$  that is higher than expected by the SE relation. This is likely a consequence of correlated motion of the “mobile” particles, which is neglected in simple treatments of the SE relation. Note that at zero frequency the diffusion coefficient is still maximally underestimated despite the homogenous stochastic dynamics of the particles in this regime. This is because in the SE relation, the step size of the random walk model (which determines the diffusion coefficient) is correlated to the friction coefficient. However, since the step size in supercooled liquids is an outcome of the correlated motion of the mobile particles, it is larger than expected based on the friction coefficient. The frequencies at which the deviations from the SE relation descend to a constant (Fig. 4) imply that the strongest degree of cooperative motion in the system

occurs at frequencies smaller than the location of the maximum of  $\alpha_2(t_{max})$ . Indeed, the largest amplitude of heterogeneity as depicted by the bimodal distribution of the self-part of the van Hove function is observed at times larger than  $t_{max}$  [29]. Consequently, Flenner and Szamel proposed a new non-Gaussian parameter that represents the maximum in the heterogeneity of the system at times later than  $t_{max}$  [30].

As the temperature decreases, the deviation from the SE relation at zero frequency increases. The value of  $T^*/[4\pi a^* D^*(\omega^*) \eta^*(\omega^*)]$  as  $\omega^* \rightarrow 0$  is 0.58, 0.25, and 0.066 for  $T^* = 0.76, 0.66,$  and  $0.56$ , respectively. Thus the product  $D\eta$  is larger than expected from the SE relation, in agreement with experimental [15,16] and other computational [18,19] studies.

In conclusion, the values of  $D(\omega)$  and  $\eta(\omega)$  for supercooled liquids were calculated independently as a function of frequency to assess the validity of the generalized SE relation. We find that the SE relation is obeyed at frequencies that correspond to the caging of the particles, indicating that dynamical heterogeneities do not necessitate breakdown of the SE relation. Large deviations start to develop as the particle motion evolves toward diffusive behavior. Our results suggest that the breakdown of the SE relation in supercooled liquids is due to correlation in the dynamics of the particles that is not taken into account by stochastic models and is not captured by MCT.

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