

Fractional Stokes-Einstein and Debye-Stokes-Einstein Relations in a Network-Forming Liquid

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We study the breakdown of the Stokes-Einstein (SE) and Debye-Stokes-Einstein (DSE) relations for translational and rotational motion in a prototypical model of a network-forming liquid, the ST2 model of water. We find that the emergence of fractional SE and DSE relations at low temperature is ubiquitous in this system, with exponents that vary little over a range of distinct physical regimes. We also show that the same fractional SE relation is obeyed by both mobile and immobile dynamical heterogeneities of the liquid.

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The translational (D) and rotational (D_r) diffusion constants of a macroscopic object in a simple liquid are well characterized by the Stokes-Einstein (SE) relation, $D\tau/T = c$, and the Debye-Stokes-Einstein (DSE) relation, $D_r\tau/T = c_r$. In these relations, τ is a relaxation time proportional to the viscosity of the liquid, T is the temperature, and the constants c and c_r depend on the geometry of the object and the boundary conditions. While these relations were originally formulated for the diffusion of macroscopic objects, they are known to hold when the diffusing object is itself a molecule of the liquid [1,2]. Hence the SE and DSE relations provide a simple connection between mass and momentum transport in a liquid.

As T decreases and the liquid becomes increasingly viscous (assuming crystallization is avoided), numerous experiments have shown a failure of the SE relation for $T \lesssim 1.3T_g$, where T_g is the glass transition temperature [3–8]. Specifically the ratio $D\tau/T$ is found to increase by as much as 2 or 3 orders of magnitude on cooling [8]. Translational diffusion is thus said to be enhanced relative to viscosity. When the SE relation fails, it has been empirically found that a “fractional” Stokes-Einstein (F-SE) relation, $D \sim (\tau/T)^{-\xi}$ holds for a wide range of liquids [3,7,9–11], where $0.5 \leq \xi \leq 0.95$, with values between 0.7 and 0.8 being most commonly reported. While a definitive theoretical prediction of the value of ξ has been elusive, various theoretical models predict ξ in the same range [12–15]. The situation is more complex for the DSE equation. In the same T range where the SE equation fails, the DSE equation has been experimentally found to be valid for most liquids [4,5]. However, in other experiments [8,16,17] a fractional Debye-Stokes-Einstein (F-DSE) relation, $D_r \sim (\tau/T)^{-\xi_r}$, has been observed. Further complicating the situation is the fact that D_r is experimentally inaccessible, and experiments must test the DSE relation using a reorientational correlation time, which may not be simply related to D_r . Molecular dynamics simulations can directly evaluate D_r , and simulations of dumbbell molecules show a failure of the DSE relation using D_r [18].

A commonly proposed explanation for the breakdown of the SE relation is the presence of dynamical heterogeneity

(DH) [19,20], i.e., spatially correlated regions of relatively high or low mobility that persist for a finite lifetime in the liquid, and that grow in size as T decreases. The existence of DH has been confirmed and quantified in both experiments [4,5] and simulations [21]. However, only a few liquid simulation studies directly probe the relationship between DH and the breakdown of the SE relation [22,23].

In this Letter, we study the breakdown of the SE and DSE relations in simulations of the ST2 model of water [24]. The ST2 model is a tetrahedral arrangement of charges, centered within a Lennard-Jones envelope, that qualitatively reproduces a number of water’s anomalies. However, our goal is not to elucidate the properties of water specifically; indeed there are many water models more accurate than ST2. Rather, we choose this model because it is known to display a diversity of extreme liquid behavior within a single system (Fig. 1). At high density ρ , ST2 behaves as a typical fragile glass-forming molecular liquid. However, near $\rho = 0.93 \text{ g/cm}^3$ and $T = 240 \text{ K}$, a liquid-liquid critical point occurs in the equation of state, demarcating the onset of phase separation between a low density liquid (LDL) and a high density liquid (HDL) phase [25]. At still lower ρ , near 0.83 g/cm^3 , the behavior of ST2 is dominated by the emergence of an increasingly well-structured random tetrahedral network (RTN) as T decreases. The emergence of the RTN is associated with the onset of a fragile-to-strong crossover in the liquid transport properties [26]. We study each of these three distinct regimes to test how the character of SE and DSE breakdown changes as the behavior of the liquid state itself changes. We also test if the origins of the F-SE relation can be found in the DH of the system.

Unless otherwise indicated, our data are generated by molecular dynamics simulations using $N = 1728$ molecules with a time step of 1 fs. Simulations consist of equilibration, followed by a production phase, each of which is run for the longer of 100 ps or the time needed for the mean-squared displacement per molecule $\langle r^2 \rangle$ to reach 1 nm^2 —roughly three molecular diameters. Simulations are carried out in the range $250 \text{ K} \leq T \leq 400 \text{ K}$ at

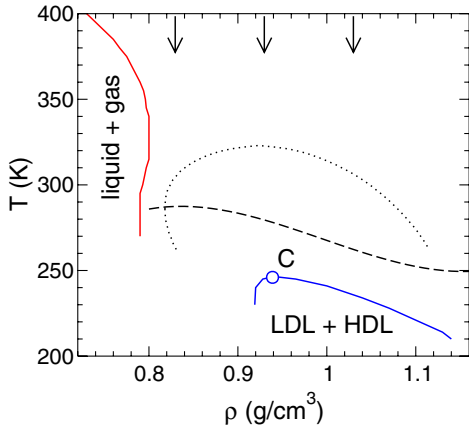


FIG. 1 (color online). ST2 phase behavior in the ρ - T plane. Solid curves show spinodals bounding regions of liquid-gas and HDL-LDL liquid phase separation. C is the critical point of the HDL-LDL transition. The three arrows indicate the densities focused on in subsequent plots. The dotted line is the locus of density extrema. The dashed curve is the locus of points at which $D\tau/T$ is 1.5 times its value at 400 K, along isochores.

intervals of 5 K and for $0.80 \text{ g/cm}^3 \leq \rho \leq 1.20 \text{ g/cm}^3$ at intervals of 0.01 g/cm^3 . For simplicity of the figures, we only present data along three representative isochores: (i) $\rho = 0.83 \text{ g/cm}^3$, where the RTN structure dominates; (ii) $\rho = 0.93 \text{ g/cm}^3$, approximately the critical density for the liquid-liquid transition; and (iii) $\rho = 1.03 \text{ g/cm}^3$ at which the system behaves more as a simple fragile liquid. The simulations are carried out at fixed ρ and T , employing the Berendsen heat bath with a time constant of 2 ps. Electrostatic interactions are truncated at 0.78 nm, and the energy and pressure are corrected using the reaction field method [27].

We evaluate D from the asymptotic behavior of $\langle r^2 \rangle = 6Dt$ and D_r by tracking the mean-squared angular displacement $\langle \phi^2 \rangle$ of the molecular dipole moment vector and use the asymptotic relation $\langle \phi^2 \rangle = 4D_r t$ [28]. The alpha-relaxation time τ is defined as the time where the normalized coherent intermediate-scattering function decays to a value of $1/e$, evaluated at the closest discrete wave number to $q = 18 \text{ nm}^{-1}$, the approximate location of the first peak in the static structure factor. The dipole relaxation time τ_2 is defined as the time at which the correlation function $\langle P_2[\cos\theta(t)] \rangle$ decays to a value of $1/e$, where P_2 is the second Legendre polynomial and $\theta(t)$ is the angle defined by the orientations of the dipole moment vector of a molecule at times t and zero.

To determine in which regions of the phase diagram the SE and DSE relations are valid, we show the behavior of $D\tau/T$ and $D_r\tau/T$ in Fig. 2. For $T \geq 300 \text{ K}$, Figs. 2(a) and 2(b) show that both the SE and DSE ratios are nearly constant, as expected. The growth of the SE relation reflects the expected enhanced translational diffusion. In the same sense, we also find enhanced rotational diffusion; noting that Fig. 2(b) employs a log scale, the enhancement of rotational motion exceeds that of translational motion.

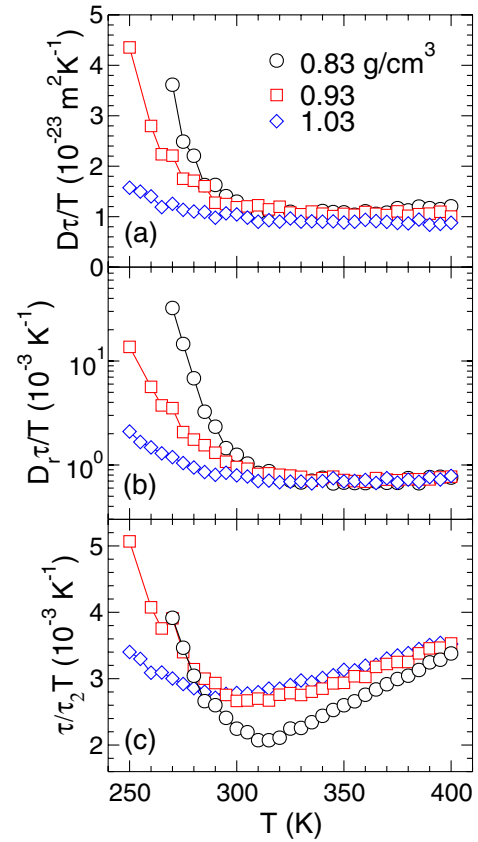


FIG. 2 (color online). (a) Breakdown of the SE relation at low T . (b) Test of the DSE relation using D_r . (c) Test of the DSE relation using $1/\tau_2$ as a proxy for D_r .

This is consistent with spin-lattice relaxation experiments on water [29]. The T at which the SE relation breaks down is weakly ρ dependent, as shown in Fig. 1.

The deviation from the DSE relation can be seen as somewhat surprising since many (but not all) experiments have found that the DSE relation appears to be valid even when the SE relationship fails [4,5]. In experimental studies, D_r cannot be directly measured. As a result, the inverse dipole relaxation time τ_2^{-1} is frequently used as a substitute, since it can be readily measured. Since we found a deviation from the DSE relation using D_r , we consider whether the using τ_2 yields different results, as shown in Fig. 2(c). Curiously, using τ_2 we find no T range where the DSE relation appears valid. For the system we study, the difference found using τ_2 vs D_r may result from large reorientational motions associated with hydrogen bond switching. Whatever the cause, Fig. 2(c) illustrates that substitution of D_r with τ_2 may not, in general, be appropriate [16].

To test if the SE relation is replaced by the F-SE form at low T , we parametrically plot the relation between D and τ/T in Fig. 3(a). We find that there are two distinct regions: (i) $T \geq 275$ where we find an exponent $\xi = 1$, consistent with the SE relation, and (ii) lower T where we find a F-SE relation with an exponent in the commonly observed range $0.7 \leq \xi \leq 0.8$. Moreover, the value of ξ is nearly indepen-

dent of ρ . Since the DSE relation is also clearly violated in this system, we check for a F-DSE relation in Fig. 3(b). Indeed, analogous to Fig. 3(a), we find that a high- T DSE regime is replaced at low T by a F-DSE relation with $\xi_r \approx 0.25$, significantly smaller than ξ for the F-SE relation. The smaller value of ξ_r compared to ξ is also observed in experiments on orthoterphenyl (OTP) [16] and is consistent with our finding that the rotational motion is more dramatically enhanced than the translational diffusion. Like ξ , we find that ξ_r varies weakly with ρ , if at all. Hence, despite the wide variation of liquid state properties over the density range studied here, the quantitative form of the F-SE and F-DSE behaviors is strikingly uniform.

We next analyze the behavior of the ST2 model to test for a connection between DH and F-SE behavior. We focus on the $\rho = 0.83 \text{ g/cm}^3$ isochore, and conduct 40 independent simulations with $N = 216$ molecules at each T for $255 \leq T \leq 275 \text{ K}$, at 5 K intervals, again using the criterion that each run continues until $\langle r^2 \rangle = 1 \text{ nm}^2$. The smaller system (compared to $N = 1728$) allows us to probe much longer time scales and to generate an ensemble of many runs in a computationally accessible time. As DH

emerges at low T , each member of the ensemble at the same T becomes more strongly influenced by transient mobile and immobile regions. As a consequence, some members of the ensemble take a longer time to reach the run-time criterion, and some shorter. Thus, we can study the differences between systems dominated by mobile and immobile DH subdomains without the need to classify individual molecules by their mobility [30].

It has been hypothesized that the SE violation is due primarily to the presence of transient mobile regions [4,19,20]. In this picture, a “background” of largely immobile regions obeys the normal SE behavior, while mobile regions violate the SE relation. If true, we should find that the ensemble members that are dominated by mobile regions should exhibit a prominent F-SE behavior, while the members dominated by immobile regions should tend to follow a normal SE behavior. In this case, a parametric scatter plot of D against τ/T (Fig. 4) for all ensembles should show a local curvature of the data for each ensemble at a given T , such that the low- D envelope of the data reflects SE behavior, and the high- D envelope gives F-SE behavior. This is not what Fig. 4 shows. Rather, we find that all systems, both those that are relatively fast and those that are slow, all obey the same F-SE relation with $\xi \approx 0.77$. Therefore, for the ST2 model of water at $\rho = 0.83 \text{ g/cm}^3$, both the mobile and immobile regions of the liquid deviate in the same way from the SE relation. In this sense, the violation of the SE relation is spatially homogeneous, despite the existence of DH in the system.

We note that $\xi = 0.77$ matches the prediction of the entropic barrier hopping theory of Ref. [14], although Ref. [14] assumes the SE relation is valid over small domains, and that F-SE behavior arises from averaging over spatial variation of the domains. However, more

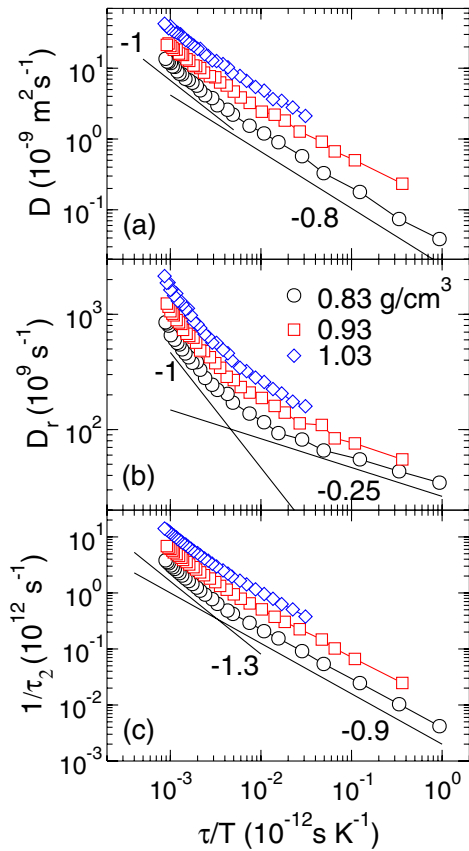


FIG. 3 (color online). Testing for (a) F-SE behavior; (b) F-DSE behavior using D_r ; and (c) F-DSE behavior using $1/\tau_2$. Curves for $\rho = 0.93$ and 1.03 g/cm^3 have been multiplied by arbitrary factors to facilitate comparison. Solid lines have the slopes indicated.

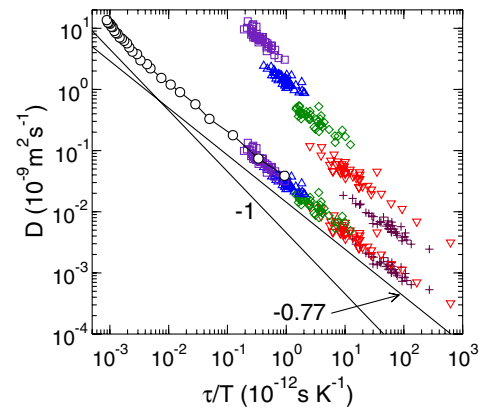


FIG. 4 (color online). Testing for F-SE behavior at $\rho = 0.83 \text{ g/cm}^3$. Circles are data from $N = 1728$ simulations. The “clouds” of other symbols are obtained from ensemble simulations of a $N = 216$ system at 255 K (+), 260 K (v), 265 K (diamond), 270 K (triangle), and 275 K (square). The “cloud” for each T has been repeated and shifted by an arbitrary factor to reveal its shape in isolation from the other clouds. Solid lines have the slopes indicated.

recent work by the same authors [31] observes a spatially ubiquitous F-SE, as found in this work. Very recently, Ref. [22] studied the impact of heterogeneous dynamics on the SE relation in the hard sphere system by identifying a subset of “hopping” mobile molecules; their results indicated that only the hopping molecules violate the SE relation, though they did not investigate F-SE behavior. Such an analysis in our system is complicated by the difficulty of defining hopping molecules at the temperatures we study [32]. Therefore, in parallel a similar analysis is being completed by partitioning molecules into “fast” and “slow” subsets [28,33]. Preliminary results of this work are consistent with the results of this Letter; i.e., both the fast and slow subsets deviate from the standard SE relation. In addition, we are also investigating the temporal nature of the violation, since the time scale on which D can be evaluated exceeds the typical lifetime of heterogeneous regions. It would also be useful to explicitly evaluate the size and lifetime distributions of DH subdomains in simulations where the system size is comparable to the characteristic length scale of DH, to elucidate observations based the ensemble approach described above.

Overall, our results demonstrate the remarkable robustness of the F-SE and F-DSE behaviors to variations in both the mean and local molecular environment. The fractional behavior is observed across three distinct physical regimes (fragile, critical, and network forming), with little variation of the exponents ξ and ξ_r , indicating an almost complete insensitivity to changes in the average liquid structure. Even the large static fluctuations associated with the approach to a second order critical point do not observably effect the manifestation of the F-SE and F-DSE relations. We also find no sensitivity of the F-SE behavior on the relative proportion of mobile and immobile dynamical heterogeneities within a given system. Both locally fast and slow regions of the system obey the same F-SE relation, so the phenomenon cannot be attributed to any one extreme subset. We emphasize that our results do not imply that F-SE behavior and DH are disconnected, since the two phenomenon emerge in the same range of T [34], only that the relationship is not the anticipated one. Our analysis also does not indicate a specific alternative origin for F-SE and F-DSE behaviors. However, it does suggest that in a successful theory of the phenomena, F-SE and F-DSE behaviors should emerge as an intrinsic behavior of the liquid state as $T \rightarrow T_g$, insensitive to the details of the structural and dynamical fluctuations occurring in the system. This is certainly consistent with the nearly ubiquitous observation of SE breakdown in glass-forming liquids.

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