

Copyright (2013) American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

The following article appeared in (**J. Chem. Phys.**, **138**, 12A526, **2013**) and may be found at (<http://link.aip.org/link/?JCP/138/12A526>).

Relaxation processes in liquids: Variations on a theme by Stokes and Einstein

Zane Shi, Pablo G. Debenedetti, and Frank H. Stillinger

Citation: *J. Chem. Phys.* **138**, 12A526 (2013); doi: 10.1063/1.4775741

View online: <http://dx.doi.org/10.1063/1.4775741>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v138/i12>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities fast

www.goodfellowusa.com

Relaxation processes in liquids: Variations on a theme by Stokes and Einstein

Zane Shi,¹ Pablo G. Debenedetti,² and Frank H. Stillinger³

¹*Department of Physics, Princeton University, Princeton, New Jersey 08544, USA*

²*Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, USA*

³*Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*

(Received 5 November 2012; accepted 27 December 2012; published online 18 January 2013)

We investigate numerically the temperature and density dependence of the Stokes-Einstein ratio, $D\eta/T$, and of two commonly-used variants thereof, $D\tau$ and $D\tau/T$, where D is a diffusivity, η the shear viscosity, and τ a structural relaxation time. We consider a family of atomic binary mixtures with systematically-softened repulsive interactions, and the Lewis-Wahnström model of ortho-terphenyl (OTP). The three quantities grow significantly as the temperature decreases in the supercooled regime, a well-known phenomenon. At higher temperatures, $D\tau$ exhibits negative violations of Stokes-Einstein behavior, i.e., decrease upon cooling, for the atomic systems, though not for OTP. We consider two choices for the relaxation time, one based on the decay of the self-intermediate scattering function, and the other on the integral of the stress autocorrelation function. The instantaneous shear modulus exhibits appreciable temperature dependence for the two classes of systems investigated here. Our results suggest that commonly-invoked assumptions, such as $\tau \sim \eta$ and $\tau \sim \eta/T$, should be critically evaluated across a wide spectrum of systems and thermodynamic conditions. We find the Stokes-Einstein ratio, $D\eta/T$, to be constant across a broad range of temperatures and densities for the two classes of systems investigated here. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4775741>]

I. INTRODUCTION

The well-known Stokes-Einstein equation, which combines Einstein's analysis of the diffusion of small suspended particles,¹ and Stokes' formula for the drag on a rigid spherical particle moving through a viscous fluid,² is given by

$$D = \frac{k_B T}{C\eta a}. \quad (1)$$

Here, D is the diffusion coefficient of the macroscopic spheres of radius a , η is the shear viscosity of the surrounding fluid at temperature T , and k_B is Boltzmann's constant. C is a constant that depends on the boundary conditions at the particle-fluid interface, and ranges from 6π for no-slip to 4π for slip boundary conditions.³

Equation (1) has been successfully applied to a wide variety of situations, including enhancement in the thermal conductivity of nano-particle suspensions,⁴ diffusion of proteins or other macromolecules in solution,^{5–8} transport in cells,⁹ and magma flow beneath the earth's crust.^{10,11} In these cases, a is taken to be an effective hydrodynamic radius.¹² Furthermore, although Eq. (1) was derived for a sphere of supermolecular dimensions suspended in a continuum, a molecular-level version of the Stokes-Einstein equation, where D now represents the self-diffusion coefficient of a uniform fluid, has been found experimentally to be valid over a wide range of temperatures for many liquids.^{13–20} Thus, for a given liquid, we can define a quantity, $D\eta/T$, whose constancy, or lack thereof, over a range of thermodynamic con-

ditions, serves as a measure of the validity of the Stokes-Einstein equation at the molecular level. One then says that the Stokes-Einstein equation is valid when

$$\frac{D\eta}{T} = \text{constant} \quad (2)$$

and any deviations away from Eq. (2) would indicate a Stokes-Einstein violation.

A well-known condition where Stokes-Einstein violation occurs is when a liquid undergoes deep supercooling.^{18–23} As the temperature is decreased into the supercooled regime, the rate at which the viscosity increases can become orders of magnitude larger than that at which the self-diffusion coefficient decreases, and $D\eta/T$ then deviates strongly from Eq. (2). Interestingly, the rotational analog of Eq. (1) (known as the Stokes-Einstein-Debye equation²⁴), $D_r = k_B T / C' \eta a^3$, where D_r is the rotational diffusion coefficient and C' is a numerical constant, can remain valid even when Eq. (2) begins to break down.^{25–27} This decoupling of translational and rotational diffusion has been explained by invoking dynamic heterogeneity, which refers to the presence of transient spatially separated regions with vastly different relaxation times.²⁴ The microscopic origin of this supercooled Stokes-Einstein violation, and of the decoupling between translational and rotational motion, is a topic of considerable research interest.^{28–37}

Molecular dynamics simulation, which has the advantage of being able to track each atom individually, offers a useful and insightful perspective for the microscopic

investigation of the mechanisms underlying the Stokes-Einstein violation. Simulations calculating the Stokes-Einstein parameter $D\eta/T$ for soft-sphere systems have shown good qualitative agreement with experiments;^{38,39} Eq. (2) is obeyed at moderately high temperatures, but deviations occur as the temperature is progressively decreased. However, because the shear viscosity, η , is a computationally intensive quantity to calculate in simulations,³⁸ it has become increasingly common in computational studies to reinterpret the physical meaning of the Stokes-Einstein relation simply as the product of a diffusion coefficient and a relaxation time. Indeed, many studies of the Stokes-Einstein violation use a structural relaxation time, τ , as a substitute for the viscosity, η .^{25,40-46} The functional form of the relation between τ and η varies among different studies; the two most often used are $\tau \propto \eta$ ⁴⁴⁻⁴⁶ and $\tau \propto \eta/T$.^{25,40-43}

The proportionality between η and τ is based on the expression $\eta = G_\infty \tau$, where G_∞ is the instantaneous shear modulus, and τ is now a *stress* relaxation time. It is commonly assumed in the simulation literature that the structural and stress relaxation times are interchangeable; the validity of this assumption has not been systematically tested. Although G_∞ does have a slight temperature dependence,⁴⁷ in the supercooled regime both η and τ can increase by many orders of magnitude as a result of modest decreases in temperature. Thus G_∞ is treated as a constant, leading to the approximate relation $\tau \propto \eta$, which in turn gives $D \propto T/\tau$. The second relation, $\tau \propto \eta/T$ results from the Gaussian solution to the diffusion equation,⁴⁸ given by $F_s(k, t) = \exp(-k^2 Dt) \equiv \exp(-t/\tau)$, where $F_s(k, t)$ is the self-intermediate scattering function and k is the associated wave vector. It follows then that $D \propto 1/\tau$, which implies $\tau \propto \eta/T$. Yamamoto and Onuki have shown empirical evidence in support of this second relationship.⁴³ It is important to point out that although the relations $\tau \propto \eta$ and $\tau \propto \eta/T$ differ by a factor of $1/T$, both appear to be reasonable approximations when studying the Stokes-Einstein violation in the deeply supercooled regime, when small temperature changes result in order of magnitude changes in both τ and η .

Although it has become standard in numerical studies to calculate $D\tau/T$ or $D\tau$ as substitutes for $D\eta/T$ when investigating the Stokes-Einstein violation, a systematic study of the various forms of the Stokes-Einstein ratio has not been carried out over broad ranges of thermodynamic conditions. The goal of this work is to investigate numerically the temperature and density dependence of the three Stokes-Einstein ratios, $D\eta/T$, $D\tau/T$, and $D\tau$, for selected atomic and molecular model systems. We seek to highlight some non-trivial distinctions between the true Stokes-Einstein equation, where viscosity is used, and the “proxy” Stokes-Einstein equations, where a relaxation time is used instead. We also investigate the validity of the assumption of interchangeability between structural and stress relaxation times. In Sec. II we define the models and provide details of the computational methods utilized in our investigation. The qualitative differences that arise between the three variants of the Stokes-Einstein relation are presented and analyzed in Sec. III. The principal conclusions and suggestions for further study are presented in Sec. IV.

II. METHODS

A. Model atomic system

We seek to investigate the Stokes-Einstein relation in both model atomic and molecular systems. For the model atomic system, we choose a family of systematically softened $(n, 6)$ pair potentials⁴⁹ with the following functional form:

$$\phi(r) = 4\epsilon \left[\lambda \left(\frac{\sigma}{r} \right)^n - \alpha \left(\frac{\sigma}{r} \right)^6 \right], \quad (3)$$

where

$$\lambda = \frac{3}{2} \left(\frac{2^{n/6}}{n-6} \right) \quad \alpha = \frac{n}{2(n-6)}. \quad (4)$$

The parameters λ and α are chosen such that the well depth and radial location of the minimum of the generalized $(n, 6)$ potentials coincide with the minimum of the standard (12, 6) Lennard-Jones potential. A detailed discussion of the thermodynamic and dynamic properties of binary mixture systems interacting via this family of potentials is given in Ref. 49. In this study, we will use a representative sample of potentials defined by Eq. (3), with $n = 7, 9$, and 12. For each interaction potential, we apply the well-known Kob and Andersen binary glass-forming mixture parameterization,⁵⁰ namely, a mixture of 80%A particles and 20%B particles, with parameters $\epsilon_{AA} = 1.0$, $\epsilon_{BB} = 0.5$, $\epsilon_{AB} = 1.5$, $\sigma_{AA} = 1.0$, $\sigma_{BB} = 0.88$, and $\sigma_{AB} = 0.8$. Both types of particles have the same mass, m . For these atomic systems, all quantities are expressed in reduced units: length in units of σ_{AA} , temperature in units of ϵ_{AA}/k_B , and time in units of $\sigma_{AA}(m/\epsilon_{AA})^{1/2}$. In order to ensure continuity of the potential and its first derivative at a cutoff distance r_c , we apply a shifted force (sf) correction to the potentials:

$$\phi^{sf}(r) = \begin{cases} \phi(r) - \phi(r_c) - (r - r_c)\phi'(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}. \quad (5)$$

To minimize the effects of the shift on the shape of the various potentials, a rather large cutoff of $r_c = 3.5$ is chosen.

B. Model molecular system

For our molecular system, we choose the Lewis and Wahnström model for ortho-terphenyl⁵¹ (1,2-diphenylbenzene, OTP). In this model each phenyl ring is represented by a Lennard-Jones site ($\epsilon = 5.276$ kJ/mol, $\sigma = 4.83$ Å), and the three sites constitute a rigid isosceles triangle, with a vertex angle of 75° and a bond length of 4.83 Å for the two equal sides. For simplicity, each site is assigned the same mass of $m = 78$ g/mol. Although this is a somewhat simplistic model for OTP, it allows us to observe how the results from the atomic systems change when rotational degrees of freedom are added. The rigid bond constraints are maintained by the SHAKE algorithm, and for the OTP simulations, all quantities are expressed in real units.

C. Viscosity and structural relaxation time

In molecular dynamics simulations, the shear viscosity can be calculated by a Green-Kubo time-correlation

relation:⁴⁸

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle P_{xy}(0) P_{xy}(t) \rangle, \quad (6)$$

where P_{xy} is an off-diagonal element of the stress tensor, given by

$$P_{xy} = \frac{1}{V} \left[\sum_i m_i v_{ix} v_{iy} + \sum_i \sum_{j>i} (r_{ix} - r_{jx}) F_{ijy} \right], \quad (7)$$

where v_{ix} and v_{iy} are, respectively, the x and y components of the velocity vector for atom i , and F_{ijy} is the y component of the force on atom i due to atom j . We use the “atomic” form of the virial to calculate the pressure tensor,^{52,53} i.e., the sums are over each individual “atom” (force center) in the system, and the double summation virial term includes contributions from intra-molecular constraint forces, should any exist.

By exploiting the tensorial properties of the viscosity constant, Daivis and Evans⁵⁴ have shown that it is possible to incorporate all elements of the pressure tensor into the calculation of viscosity to improve statistics. The Green-Kubo relation then becomes⁵⁵

$$\eta = \frac{V}{10k_B T} \int_0^\infty dt \sum_{\alpha\beta} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \rangle, \quad (8)$$

where $\alpha\beta = xx, yy, zz, xy, xz, yx, yz, zx, zy$,

$$P_{\alpha\beta} = (\pi_{\alpha\beta} + \pi_{\beta\alpha})/2 - \delta_{\alpha\beta} \left(\sum_\gamma \pi_{\gamma\gamma} \right) / 3 \quad (9)$$

and

$$\pi_{\alpha\beta} = \frac{1}{V} \left[\sum_i m_i v_{i\alpha} v_{i\beta} + \sum_i \sum_{j>i} (r_{i\alpha} - r_{j\alpha}) F_{ij\beta} \right]. \quad (10)$$

The $1/10$ prefix in Eq. (8) follows from the fact that the stress tensor is symmetric and consists of five independent components:⁵⁶ $P_{xy}, P_{yz}, P_{xz}, P_{xx} - P_{yy}, P_{yy} - P_{zz}$.

We define a characteristic structural relaxation time by using the self-intermediate scattering function $F_s(k, t) = \langle \exp[i\mathbf{k} \cdot \Delta\mathbf{r}(t)] \rangle$, where \mathbf{k} is a chosen wave vector and $\Delta\mathbf{r}(t)$ is the center of mass displacement experienced by an

atom or molecule in time t . In each of the systems, the magnitude of the wave vector \mathbf{k} is chosen to correspond to the first peak of the molecular center-of-mass static structure factor. The relaxation time τ is then defined by $F_s(k, \tau) = 1/e$.

III. RESULTS AND DISCUSSION

A. The Stokes-Einstein relations for a softened atomic system

We compute the three forms of the Stokes-Einstein ratio: $D\eta/T, D\tau/T, D\tau$, for our family of softened potentials for densities of $\rho = 1.2, 1.25$, and 1.3 . Here, D corresponds to the diffusion coefficient of the A particles for the various potentials, and the wave number k used to calculate the self-intermediate scattering function corresponds to the first peak of the structure factor for the A - A interactions, $S_{AA}(k)$. While there has been experimental evidence that the Stokes-Einstein relation can break down for one component while holding for others in glass-forming alloys,⁵⁷ we note that for our system the calculations based on either the A or B components are qualitatively similar, and the results we report here are calculated using the dynamic properties of the A particles.

In each case, we use a high temperature reference point at $T = 1.2$, which is well above the landscape onset temperature, below which mechanically stable packings sampled upon energy minimization begin to depend sensitively on the system’s temperature prior to minimization.⁵⁸ The condition $T = 1.2$ thus corresponds to a state in which the system can freely sample all portions of energy landscape. Along each isochore we compute the ratio $\chi(T)/\chi(T = 1.2)$, where $\chi = D\eta/T, D\tau$, or $D\tau/T$. Any deviation away from the horizontal line of height 1 indicates a violation of the particular Stokes-Einstein relation under investigation.

In Figure 1, we plot the temperature dependence of the three ratios at a fixed density of $\rho = 1.25$ for $n = 7, 9$, and 12 . Although all three ratios show a Stokes-Einstein violation at low enough temperatures, their behavior at higher temperatures exhibits pronounced differences. In particular, the “true” Stokes-Einstein relation, $D \propto T/\eta$, is in fact valid for a wide range of temperatures, regardless of n . The ratio $D\tau/T$ shows large deviations from unity across the entire

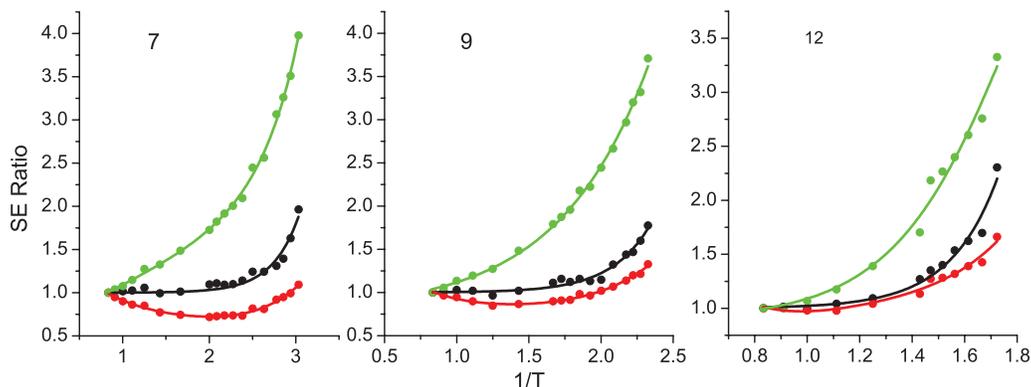


FIG. 1. The Stokes-Einstein relations as a function of inverse temperature for a system interacting via softened potentials of $n = 7$ (left), 9 (center), and 12 (right). The Stokes-Einstein (SE) ratio is defined and color-coded as follows: $D\eta/T$ (black), $D\tau$ (red), and $D\tau/T$ (green), all normalized to their respective values at $T = 1.2$. Note the wide range in temperature where the Stokes-Einstein relation holds when viscosity is used to calculate the SE ratio.

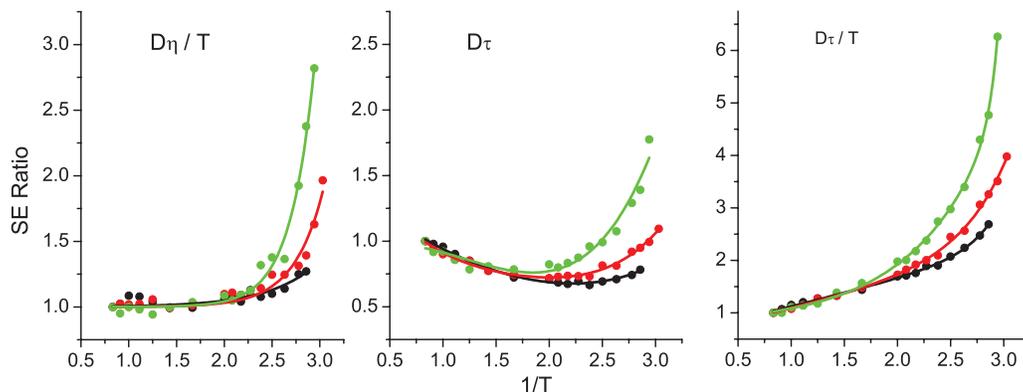


FIG. 2. The three Stokes-Einstein relations plotted as a function of inverse temperature for a system interacting via a softened potentials of $n = 7$ for a density of $\rho = 1.2$ (black), 1.25 (red), and 1.3 (green). The Stokes-Einstein (SE) ratio is defined as $D\eta/T$ (left), $D\tau$ (center), and $D\tau/T$ (right), and all normalized to their respective values at $T = 1.2$. A horizontal line at 1 would indicate that the Stokes-Einstein relation is observed.

temperature range investigated, and hence exhibits qualitatively different behavior. The product $D\tau$ approaches the Stokes-Einstein behavior as repulsions become steeper ($n = 12$). Note, however, that $D\tau$ actually exhibits a negative violation at high temperatures, an effect especially pronounced when the softness of the interaction potential is increased. Here, we use the terminology “negative violation” to denote the *decrease* of a Stokes-Einstein ratio below the high temperature limit, corresponding to an *increase* of the effective hydrodynamic radius upon cooling.

For the case of $n = 7$, we also investigate how the three Stokes-Einstein relations change as the density of the system is varied (Figure 2). In all three cases, the large (positive) violation due to supercooling occurs at a higher temperature when the density is increased. This is a direct consequence of the increase in the landscape onset temperature⁴⁹ as the density is increased, effectively raising the temperature of the supercooled regime. However, the striking feature here is that the original Stokes-Einstein ratio that uses viscosity is indeed constant over a broad range of temperatures. Note again the negative Stokes-Einstein violation for the quantity $D\tau$, an effect that disappears gradually upon compression. Although $D\tau$ and $D\tau/T$ show the expected violation of Stokes-Einstein behavior at low temperatures, neither shows a range of temperatures where the quantity of interest remains constant, in marked contrast to $D\eta/T$.

B. The Stokes-Einstein relations for OTP

In Figure 3, we plot the three Stokes-Einstein variants for the Lewis and Wahnström model of OTP. At liquid temperatures, the Stokes-Einstein relation is again valid when $D\eta/T$ is used for the calculation. However, in contrast to the atomic systems, none of the three ratios show a “negative violation” at higher temperatures. In fact, the results of Figure 3 suggest that for this particular system, the product $D\tau$ is actually a quite good substitute for the original Stokes-Einstein ratio of $D\eta/T$. This suggests that the validity of using a relaxation time instead of viscosity when studying Stokes-Einstein behavior depends on the specifics of the system being inves-

tigated; a substitution that works well for one system might not work well for another. As was the case for the family of systematically-softened atomic systems, the ratio $D\tau/T$, based on the approximation $\tau \sim \eta$, deviates very substantially from

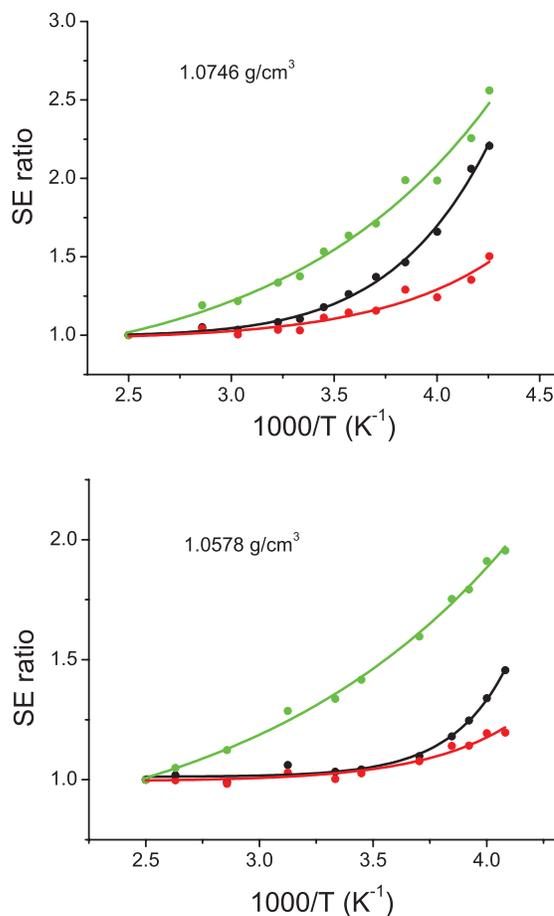


FIG. 3. The three Stokes-Einstein relations plotted as a function of inverse temperature for a system of Lewis and Wahnström OTP molecules at a density of $\rho = 1.0746 \text{ g/cm}^3$ (top) and 1.0578 g/cm^3 (bottom). The SE ratio is defined and color-coded as $D\eta/T$ (black), $D\tau$ (red), and $D\tau/T$ (green), all normalized to their respective values at $T = 400 \text{ K}$. Note again the wide range in temperatures where the Stokes-Einstein relation holds when viscosity is used for the calculation.

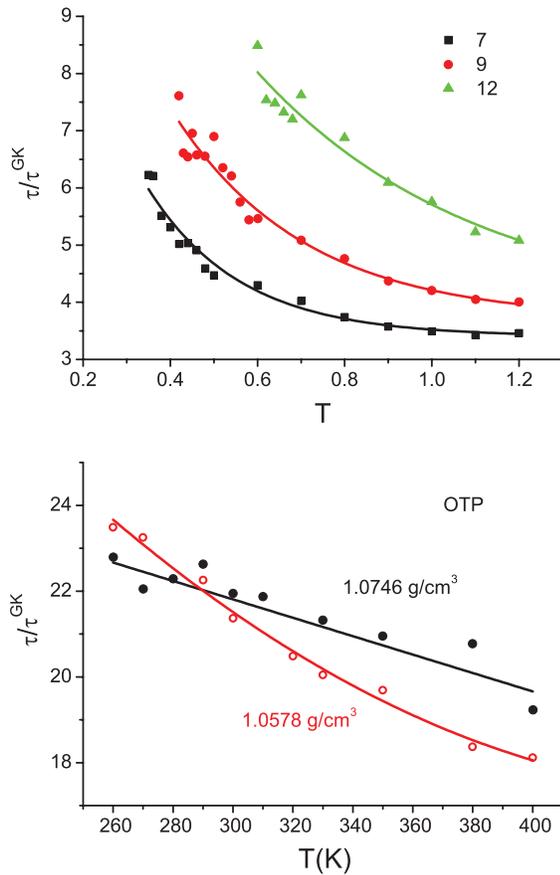


FIG. 4. The ratio of the structural and stress relaxation times, τ/τ^{GK} , as a function of temperature for the softened potential systems (top, $\rho = 1.25$) and OTP (bottom, $\rho = 1.0746 \text{ g/cm}^3$ and 1.0578 g/cm^3).

“Stokes-Einstein”-like behavior, $D\tau/T = \text{constant}$, across the range of conditions investigated in this work for OTP.

C. The instantaneous shear modulus and stress relaxation time

For our atomic systems, neither of the substitutions $\tau \sim \eta$ or $\tau \sim \eta/T$ work very well, and in this section we seek to further clarify the relation between the shear viscosity and relax-

ation times. We begin by rewriting the Green-Kubo relation for viscosity (Eq. (8)) as follows:⁵⁹

$$\eta = \frac{V \sum_{\alpha\beta} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(0) \rangle}{10k_B T} \int_0^\infty dt \frac{\sum_{\alpha\beta} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \rangle}{\sum_{\alpha\beta} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(0) \rangle}. \quad (11)$$

The shear viscosity is commonly written as a product of an instantaneous shear modulus, G_∞ , and a characteristic stress relaxation time, τ :

$$\eta = G_\infty \tau. \quad (12)$$

G_∞ is often approximated to be constant in temperature at constant density, in particular when studying Stokes-Einstein violation, because when a liquid undergoes supercooling, changes on the right-hand side of Eq. (12) are dominated by the order of magnitude increases in τ . However, G_∞ does in fact have a slight temperature dependence,⁴⁷ and we seek to investigate how this temperature dependence affects the qualitative differences observed at liquid temperatures between the Stokes-Einstein relations using η and those using τ .

Comparing Eq. (11) and Eq. (12), we can define $G_\infty(T)$ and a corresponding Green-Kubo stress relaxation time τ^{GK} :⁵⁹

$$G_\infty(T) = \frac{V \sum_{\alpha\beta} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(0) \rangle}{10k_B T}, \quad (13)$$

$$\tau^{GK} = \int_0^\infty dt \frac{\sum_{\alpha\beta} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t) \rangle}{\sum_{\alpha\beta} \langle P_{\alpha\beta}(0) P_{\alpha\beta}(0) \rangle}. \quad (14)$$

Here, we have defined a new relaxation time, τ^{GK} , which we can now use to calculate Stokes-Einstein ratios $D\tau^{GK}$ and $D\tau^{GK}/T$. Note that τ^{GK} is a *stress* relaxation time. Figure 4 compares τ^{GK} with τ , the *structural* relaxation time derived from the self-intermediate scattering function. It can be seen that the temperature dependence of the ratio of relaxation times is non-trivial, with τ/τ^{GK} increasing markedly upon cooling. For the binary atomic mixtures, the ratio τ/τ^{GK} approaches a horizontal asymptote at high temperatures. This suggests a coupling of the structural and stress relaxation times at high temperatures, especially for the softer mixtures, and a progressive breakdown of this coupling as the

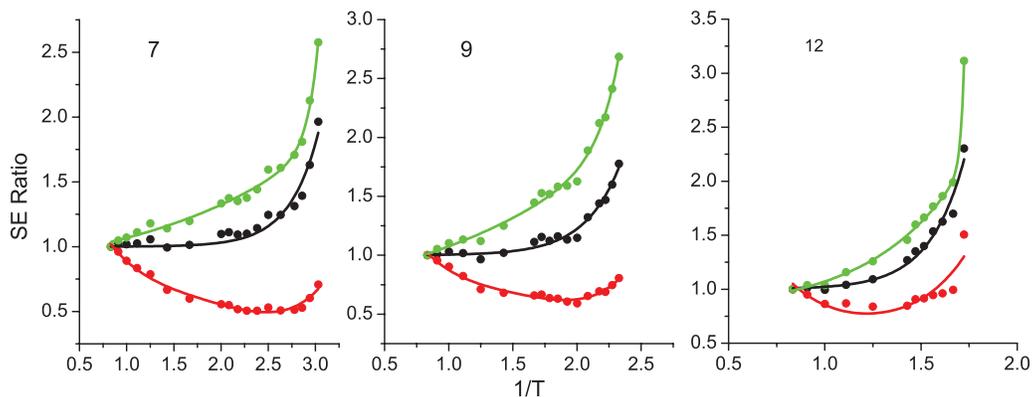


FIG. 5. The Stokes-Einstein relations as a function of inverse temperature for a system interacting via softened potentials of $n = 7$ (left), 9 (center), and 12 (right). The SE ratio is defined and color-coded as follows: $D\eta/T$ (black), $D\tau^{GK}$ (red), and $D\tau^{GK}/T$ (green), all normalized to their respective values at $T = 1.2$. Here, the characteristic relaxation time τ^{GK} is derived from the Green-Kubo expression for viscosity and defined by Eq. (14). These curves behave qualitatively similarly to those of Figure 1, where a characteristic relaxation time derived from the self-intermediate scattering function was used in the calculation.

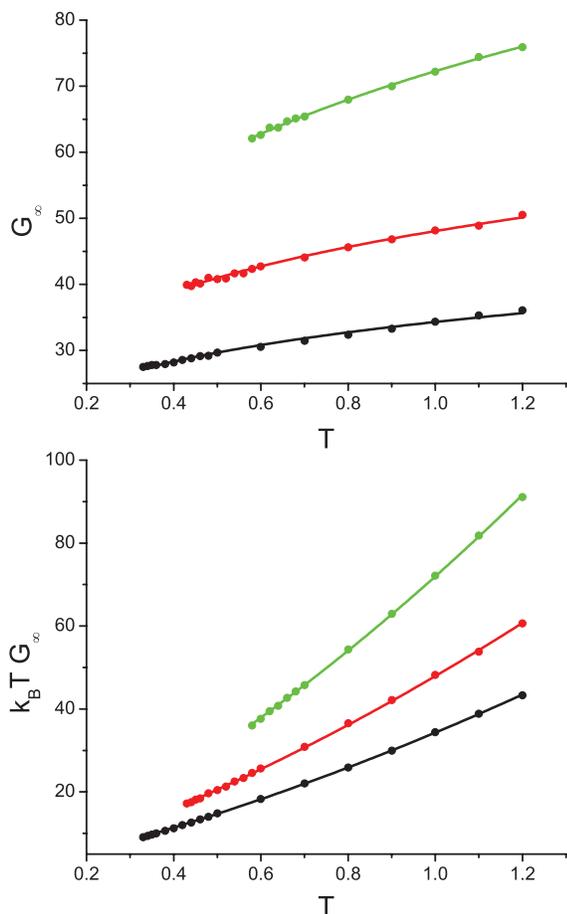


FIG. 6. The temperature dependence of the instantaneous shear modulus, $G_\infty(T)$, as defined by Eq. (13), for a system density of $\rho = 1.25$. The three data sets in each graph correspond to softened potential interactions of $n = 7$ (black), 9 (red), and 12 (green). For the top graph, the fit lines are of the functional form aT^b , resulting in a fitting parameter of $a = 34.311, 48.070, 72.271$ and $b = 0.210, 0.231, 0.275$, respectively, for $n = 7, 9, 12$. For the bottom graph, the fit lines are of the functional form $cT(T+d)$. The regressed values of c and d are 9.744, 13.611, 21.952 and 2.518, 2.520, 2.278 for $n = 7, 9, 12$, respectively.

temperature is decreased.⁶⁰ Figure 5 shows the resulting Stokes-Einstein ratios based on τ^{GK} for the binary atomic systems. We can see that the behavior of these curves, particularly for the softer mixtures, is qualitatively similar to those in Figure 1.

Figure 6 shows the temperature dependence of both G_∞ (in units of $\epsilon_{AA}/\sigma_{AA}^3$) and $G_\infty \cdot k_B T$, also for the binary atomic systems. If we substitute the functional forms for the best fit lines into Eq. (12), the relation between η and τ^{GK} can then be modeled as either $\tau^{GK} \propto \eta/(T + \text{const.})$ or $\tau^{GK} \propto \eta/T^b$, where $0.2 < b < 0.3$. We note that these models are intermediate between the commonly used proxy relations, $\tau \propto \eta$ and $\tau \propto \eta/T$. Indeed, as has already been discussed in connection with Figure 5, $\tau \propto \eta$ overestimates the viscosity contribution to the Stokes-Einstein relation, while $\tau \propto \eta/T$ underestimates it.

Figures 7 and 8 show the results of the same analysis when applied to the Lewis and Wahnström OTP systems. Similar to the softened potential systems, G_∞ increases with increasing temperature. However, $D\tau^{GK}$ now exhibits a negative violation of Stokes-Einstein behavior at higher temperatures.

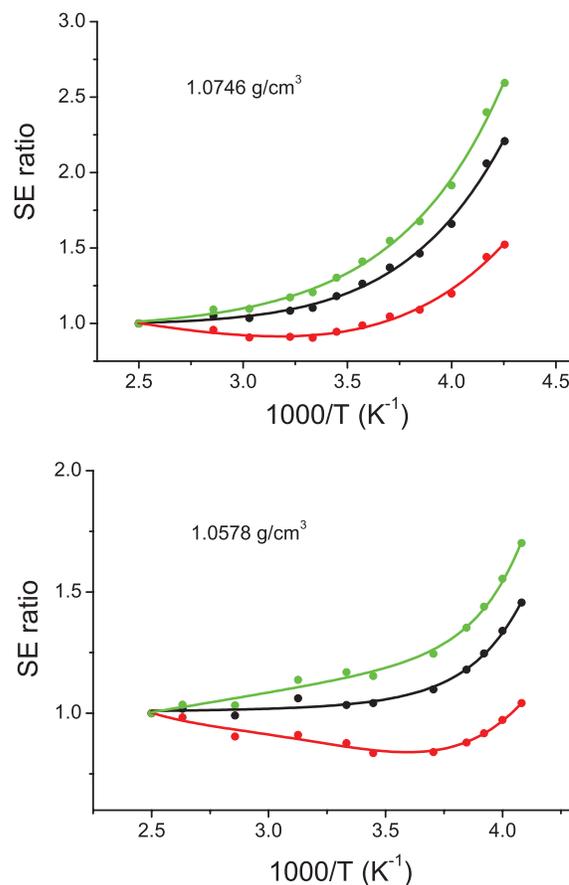


FIG. 7. The Stokes-Einstein relations as a function of inverse temperature for a system of Lewis and Wahnström OTP molecules at a density of $\rho = 1.0746 \text{ g/cm}^3$ (top) and 1.0578 g/cm^3 (bottom). The SE ratio is defined and color-coded as follows: $D\eta/T$ (black), $D\tau^{GK}$ (red), and $D\tau^{GK}/T$ (green), all normalized to their respective values at $T = 400$ K. The characteristic relaxation time used here is τ^{GK} , derived from the Green-Kubo expression for viscosity and defined by Eq. (14).

Collectively, these results show that the temperature dependence of G_∞ is non-trivial. Furthermore, when using relaxation time to investigate Stokes-Einstein validity over a broad range of temperatures, using a different relaxation time (e.g.,

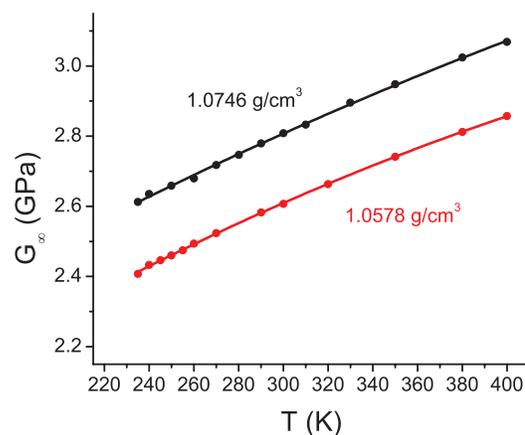


FIG. 8. The temperature dependence of the instantaneous shear modulus, $G_\infty(T)$, for a system of Lewis and Wahnström OTP molecules at a density of $\rho = 1.0746 \text{ g/cm}^3$ and 1.0578 g/cm^3 . The lines are guides to the eye.

structural or stress relaxation times) can result in a qualitatively different behavior. The validity of using a relaxation time as a substitute for viscosity is dependent on both the particular definition of the relaxation time used, and the specifics of the system under study.

IV. CONCLUSIONS

In this work, we have examined three variants of the Stokes-Einstein ratio, namely $D\eta/T$, $D\tau$, and $D\tau/T$, for model atomic and molecular systems, over a broad range of temperatures and densities.

For the family of atomic binary systems investigated here, with τ a structural relaxation time, the ratio $D\tau/T$, based on the approximation $\tau \sim \eta$, increases upon cooling much faster than the true Stokes-Einstein ratio $D\eta/T$. The product $D\tau$, based on the approximation $\tau \sim \eta/T$, exhibits negative Stokes-Einstein violation at moderate temperatures, approaching the true Stokes-Einstein ratio as the repulsive component of the potential becomes progressively steeper. The increase upon cooling exhibited by the three Stokes-Einstein variants occurs at progressively higher temperatures as the fluids are compressed. As can be seen from Figures 1 and 2, the Stokes-Einstein ratio $D\eta/T$ is constant, to a very good approximation, over a broad range of thermodynamic conditions.

The molecular system we studied, the Lewis-Wahnström model of OTP, exhibits similar behavior, with one important difference: the product $D\tau$ is a reasonably accurate proxy for the Stokes-Einstein ratio across the conditions investigated here, and does not show negative violation of Stokes-Einstein behavior. This is consistent with the trend observed in the atomic systems, where the approximation $\tau \sim \eta/T$ gets better as the close range repulsion becomes steeper, since this OTP model consists of three Lennard-Jones sites connected by rigid bonds. For this system, too, $D\eta/T = \text{constant}$ is satisfied over an appreciable range of thermodynamic conditions: $300 \leq T \leq 400$ K at 1.0746 g/cm^3 and $280 \leq T \leq 400$ K at 1.0578 g/cm^3 .

Different choices of relaxation times can affect the behavior of the Stokes-Einstein variants in non-trivial ways. In this work we considered two relaxation times. One, denoted simply by τ in this paper, is a structural relaxation time obtained from the decay of the self-intermediate scattering function; the other, τ^{GK} , is a stress relaxation time obtained from the Green-Kubo stress autocorrelation integral. While both relaxation times lead to similar behavior for the atomic binary mixtures, especially for the softer potentials, for the OTP system τ^{GK} leads to negative Stokes-Einstein violations in $D\tau^{GK}$, in contrast to $D\tau$ which does not show negative violations. Furthermore, the relationship between these two relaxation times displays a non-trivial temperature dependence, especially at low temperatures.

The often-invoked simple proportionality between viscosity and relaxation time is predicated on the assumed constancy of the instantaneous shear modulus, G_∞ . Our numerical study of this quantity based on the Green-Kubo formalism reveals an appreciable temperature dependence for the two

classes of systems investigated here, and G_∞ increases with temperature for both the atomic binary mixtures and OTP.

In this study, we have explored the effects of temperature changes under constant density conditions. Most experiments, on the other hand, are performed under isobaric conditions. It would be interesting to investigate numerically the extent to which the main observations reported here remain valid under the more experimentally-relevant isobaric conditions. Recent experiments suggest that in some glass-forming alloys the product $D\eta$ is constant while Stokes-Einstein violation occurs;⁶¹ it would be interesting to explore computationally the extent to which this scaling applies more broadly to other systems.

The present calculations suggest that commonly-invoked assumptions, such as $\tau \sim \eta$ and $\tau \sim \eta/T$, deserve critical scrutiny when used to construct Stokes-Einstein variants. The behavior of $D\eta/T$, $D\tau$, and $D\tau/T$ needs to be investigated for a wider range of systems than the two considered here, and across as broad a range of temperatures and densities as possible. It is also of interest to explore numerically the behavior of different relaxation times, only two of which have been considered here. It is hoped that such systematic numerical investigation will lead to a deeper understanding of relaxation processes in liquids at both supercooled and ambient conditions. Our approach in this work has been phenomenological. Numerical studies of the microscopic mechanisms underlying the rich behavior presented here constitute a natural direction for future studies.

We wish to stress in closing the remarkably broad range of conditions across which the Stokes-Einstein equation, meant to apply to supermolecular objects suspended in a fluid continuum, is also valid at the molecular level.

ACKNOWLEDGMENTS

We thank Srikanth Sastry for suggesting to us the importance of exploring possible non-trivial relationships between viscosity and relaxation time. The financial support of the National Science Foundation is gratefully acknowledged (Grant No. CHE-1213343 to P.G.D.). Calculations were performed at the Terascale Infrastructure for Groundbreaking Research in Engineering and Science (TIGRESS) at Princeton University.

¹A. Einstein, *Ann. Phys.* **322**, 549 (1905).

²G. G. Stokes, *Trans. Cambridge Philos. Soc.* **9**, 8 (1851).

³L. M. Milne-Thomson, *Theoretical Hydrodynamics*, 4th ed. (Macmillan, 1960), p. 584.

⁴D. H. Kumar, H. E. Patel, V. R. R. Kumar, T. Sundararajan, T. Pradeep, and S. K. Das, *Phys. Rev. Lett.* **93**, 144301 (2004).

⁵M. T. Tyn and T. W. Gusek, *Biotechnol. Bioeng.* **35**, 327 (1990).

⁶M. E. Young, P. A. Carroad, and R. L. Bell, *Biotechnol. Bioeng.* **22**, 947 (1980).

⁷S. Rathgeber, M. Monkenbusch, M. Kreitschmann, V. Urban, and A. Brulet, *J. Chem. Phys.* **117**, 4047 (2002).

⁸M. Terazima, K. Okamoto, and N. Hirota, *J. Phys. Chem.* **97**, 5188 (1993).

⁹M. R. McCarthy, K. D. Vandegriff, and R. M. Winslow, *Biophys. Chem.* **92**, 103 (2001).

¹⁰J. P. Poirier, *Geophys. J.* **92**, 99 (1988).

¹¹B. T. Poe, P. F. McMillan, D. C. Rubie, S. Chakraborty, J. Yarger, and J. Diefenbacher, *Science* **276**, 1245 (1997).

¹²S. G. Schultz and A. K. Solomon, *J. Gen. Physiol.* **44**, 1189 (1961).

¹³A. Noda, K. Hayamizu, and M. Watanabe, *J. Phys. Chem. B* **105**, 4603 (2001).

- ¹⁴J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, and D. Foster, *J. Electrochem. Soc.* **150**, A1351 (2003).
- ¹⁵C. Comminges, R. Barhdadi, M. Laurent, and M. Troupel, *J. Chem. Eng. Data* **51**, 680 (2006).
- ¹⁶D. P. Dobson, J. P. Brodholt, L. Vočadlo, and W. A. Crichton, *Mol. Phys.* **99**, 773 (2001).
- ¹⁷E. D. Snijder, M. J. M. te Riele, G. F. Versteeg, and W. P. M. van Swaaij, *J. Chem. Eng. Data* **38**, 475 (1993).
- ¹⁸S. F. Swallen, P. A. Bonvallet, R. J. McMahon, and M. D. Ediger, *Phys. Rev. Lett.* **90**, 015901 (2003).
- ¹⁹M. K. Mapes, S. F. Swallen, and M. D. Ediger, *J. Phys. Chem. B* **110**, 507 (2006).
- ²⁰F. Mallamace, M. Broccio, C. Corsaro, A. Faraone, U. Wanderlingh, L. Liu, C.-Y. Mou, and S. H. Chen, *J. Chem. Phys.* **124**, 161102 (2006).
- ²¹R. Kind, O. Liechti, N. Korner, J. Hulliger, J. Dolinsek, and R. Blinc, *Phys. Rev. B* **45**, 7697 (1992).
- ²²K. L. Ngai, J. H. Magill, and D. J. Plazek, *J. Chem. Phys.* **112**, 1887 (2000).
- ²³I. Chang, F. Fujara, B. Geil, G. Heuberger, T. Mangel, and H. Sillescu, *J. Non-Cryst. Solids* **172–174**, 248 (1994).
- ²⁴T. G. Lombardo, P. G. Debenedetti, and F. H. Stillinger, *J. Chem. Phys.* **125**, 174507 (2006).
- ²⁵G. Tarjus and D. Kivelson, *J. Chem. Phys.* **103**, 3071 (1995).
- ²⁶F. Blackburn, M. T. Cicerone, G. Hietpas, P. A. Wagner, and M. Ediger, *J. Non-Cryst. Solids* **174**, 256 (1994).
- ²⁷C. Rønne, L. Thrane, Per-Olof Åstrand, A. Wallqvist, K. V. Mikkelsen, and S. R. Keiding, *J. Chem. Phys.* **107**, 5319 (1997).
- ²⁸S. K. Kumar, G. Szamel, and J. F. Douglas, *J. Chem. Phys.* **124**, 214501 (2006).
- ²⁹J. A. Hodgdon and F. H. Stillinger, *Phys. Rev. E* **48**, 207 (1993).
- ³⁰M. D. Ediger, *Annu. Rev. Phys. Chem.* **51**, 99 (2000).
- ³¹V. Lubchenko and P. G. Wolynes, *Annu. Rev. Phys. Chem.* **58**, 235 (2007).
- ³²F. H. Stillinger, *Science* **267**, 1935 (1995).
- ³³R. Zwanzig and A. K. Harrison, *J. Chem. Phys.* **83**, 5861 (1985).
- ³⁴L. Berthier, D. Chandler, and J. P. Garrahan, *Europhys. Lett.* **69**, 320 (2005).
- ³⁵K. L. Ngai, *J. Phys. Chem. B* **103**, 10684 (1999).
- ³⁶G. Diezemann, H. Sillescu, G. Hinze, and R. Böhmer, *Phys. Rev. E* **57**, 4398 (1998).
- ³⁷F. H. Stillinger and J. A. Hodgdon, *Phys. Rev. E* **50**, 2064 (1994).
- ³⁸J.-L. Barrat, J.-N. Roux, and J.-P. Hansen, *Chem. Phys.* **149**, 197 (1990).
- ³⁹D. Thirumalai and R. D. Mountain, *Phys. Rev. E* **47**, 479 (1993).
- ⁴⁰D. Jeong, M. Y. Choi, H. J. Kim, and Y. Jung, *Phys. Chem. Chem. Phys.* **12**, 2001 (2010).
- ⁴¹A. Ikeda and K. Miyazaki, *Phys. Rev. Lett.* **106**, 015701 (2011).
- ⁴²Y. Jung, J. P. Garrahan, and D. Chandler, *Phys. Rev. E* **69**, 061205 (2004).
- ⁴³R. Yamamoto and A. Onuki, *Phys. Rev. Lett.* **81**, 4915 (1998).
- ⁴⁴S.-H. Chen, F. Mallamace, C.-Y. Mou, M. Broccio, C. Corsaro, A. Faraone, and L. Liu, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 12974 (2006).
- ⁴⁵P. Kumar, S. V. Buldyrev, S. R. Becker, P. H. Poole, F. W. Starr, and H. E. Stanley, *Proc. Natl. Acad. Sci. U.S.A.* **104**, 9575 (2007).
- ⁴⁶L. Xu, F. Mallamace, Z. Yan, F. W. Starr, S. V. Buldyrev, and H. E. Stanley, *Nat. Phys.* **5**, 565 (2009).
- ⁴⁷N. B. Olsen, J. C. Dyre, and T. Christensen, *Phys. Rev. Lett.* **81**, 1031 (1998).
- ⁴⁸J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, 1986), Chap. 8.
- ⁴⁹Z. Shi, P. G. Debenedetti, F. H. Stillinger, and P. Ginart, *J. Chem. Phys.* **135**, 084513 (2011).
- ⁵⁰W. Kob and H. C. Andersen, *Phys. Rev. E* **51**, 4626 (1995).
- ⁵¹L. J. Lewis and G. Wahnström, *Phys. Rev. E* **50**, 3865 (1994).
- ⁵²D. N. Theodorou, T. D. Boone, L. R. Dodd, and K. F. Mansfield, *Macromol. Theory Simul.* **2**, 191 (1993).
- ⁵³A. P. Thompson, S. J. Plimpton, and W. Mattson, *J. Chem. Phys.* **131**, 154107 (2009).
- ⁵⁴P. J. Daivis and D. J. Evans, *J. Chem. Phys.* **100**, 541 (1994).
- ⁵⁵S. H. Lee and T. Y. Chang, *Bull. Korean Chem. Soc.* **24**, 1590 (2003).
- ⁵⁶D. Nevins and F. J. Spera, *Mol. Simul.* **33**, 1261 (2007).
- ⁵⁷A. Bartsch, K. Rätzke, A. Meyer, and F. Faupel, *Phys. Rev. Lett.* **104**, 195901 (2010).
- ⁵⁸S. Sastry, P. G. Debenedetti, and F. H. Stillinger, *Nature (London)* **393**, 554 (1998).
- ⁵⁹J. C. Dyre and W. H. Wang, *J. Chem. Phys.* **136**, 224108 (2012).
- ⁶⁰We note that as the temperature is further decreased below the data points shown in Figure 4, τ/τ^{GK} appears to reach a maximum, and decreases upon further cooling. However, further numerical precision is required to obtain accurate low temperature values of τ/τ^{GK} , and we are presently investigating in detail the low temperature relation between τ and τ^{GK} .
- ⁶¹J. Brillo, A. I. Pommrich, and A. Meyer, *Phys. Rev. Lett.* **107**, 165902 (2011).