

# On the Breakdown of the Stokes–Einstein Law in Supercooled Liquids<sup>†</sup>

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The wavevector-dependent shear viscosity,  $\eta(k)$ , is evaluated for a range of temperatures in a supercooled binary Lennard–Jones liquid. The mode coupling theory of Keyes and Oppenheim (*Phys. Rev. A* **1973**, *8*, 937) expresses the self-diffusion constant,  $D$ , in terms of  $\eta(k)$ . Replacing  $\eta(k)$  with the usual viscosity,  $\eta \equiv \eta(k=0)$ , yields the Stokes–Einstein law. It is found that the breakdown of the SE law in this system is well described by keeping the simulated  $k$ -dependence. Simply put, bath processes on all length scales (wavevectors) contribute to  $D$ , the system is much less viscous at finite  $k$ , and thus  $D$  exceeds the SE estimate based upon  $\eta$ . The functional form of  $\eta(k)$  allows for the estimation of a correlation length that grows with decreasing  $T$ .

## I. Introduction

The Stokes–Einstein law for the self-diffusion constant,  $D$ , of a macroscopic particle of radius  $R$  having collision diameter  $\sigma \approx R$  with a bath particle in a continuum fluid with shear viscosity  $\eta$  is

$$D^{\text{SE}} = \frac{k_{\text{B}}T}{c\pi\eta\sigma} \quad (1)$$

where  $c = 6$  and  $c = 4$  for stick and slip boundary conditions at the particle surface, respectively, and  $c = 5$  for a “fluid sphere”.<sup>1</sup> Of course one ordinarily just writes “ $R$ ” for the Brownian case with a structureless continuum solvent, but we are concerned with atomic particles in the following and so introduce  $\sigma$  immediately.

Microscopic derivations of the Stokes–Einstein law have been sought<sup>2–7</sup> for some time. Proper treatment of a large test particle is an essential test of any theory. Furthermore, following the pioneering simulations of Alder, Gass, and Wainright,<sup>8</sup> it is now clear that the SE law is useful on the atomic level; one would like to understand why.

In the mode-coupling theory of Keyes and Oppenheim,<sup>5</sup> tagged particle dynamics is coupled to the shear modes of the bath. The result is

$$D = D^0 + (k_{\text{B}}T/3\pi^2) \int_0^\infty dk \chi^2(k\sigma)/\eta(k) \quad (2)$$

where  $\eta(k)$  is the wavevector-dependent shear viscosity and

$$\chi(x) = 3 \frac{\sin(x) - x \cos(x)}{x^3} \quad (3)$$

the  $\chi$  function cuts off the integral for  $k \gtrsim \pi/\sigma$ . Contributions to  $D$  that are not described by mode-coupling products of conserved variables are swept into  $D^0$ , which vanishes in the Brownian limit. The utility of the SE law on the atomic level suggests that  $D^0$  is small in general.

Ignoring  $D^0$  and the  $k$  dependence of the viscosity, that is, replacing  $\eta(k)$  with “the” usual  $\eta(k=0) \equiv \eta$  in eq 2, the SE law is obtained with (eq 1)  $c = 5$  and  $\sigma$  instead of  $R$ . It was

explained<sup>9</sup> subsequently that the “5” was an artifact arising from ignoring the nonbulk behavior of the boundary layer around the tagged particle. For smooth-sphere potentials  $c = 4$ , as expected. Of course, for a Brownian particle there is no difference between  $R$  and  $\sigma$ , and  $D^0 = 0$ .

Equation 2 was derived when T.K. was a postdoc with Professor Irwin Oppenheim at MIT. Irwin’s idea was that all multilinear products of hydrodynamic variables must be included in a theory of slow dynamics in liquids, and T.K. was among his first students to work on what has become the “multilinear hydrodynamic” formalism. It soon became apparent that the coupling of tagged particle variables to products of bath variables with all intermediate wavevectors provides the microscopic version of Stokes’ friction calculation, in which a moving particle excites vortices of all sizes.

Microscopic derivations of the SE law were very much in the air at the time, and Irwin had<sup>2</sup> co-authored a paper on an alternative approach with Daniel (T.K.’s thesis advisor) and Margy Kivelson. As we were worrying about the “5”, Dorfman and co-workers<sup>3</sup> obtained the same annoying coefficient using kinetic theory. When they found the correct answer for a smooth sphere by treating the fluid velocity eigenvector to higher order, Irwin received a telegram containing one character, “4”.

## II. Breakdown of the Stokes–Einstein Law

Although the SE law gives a semiquantitative (there is some variation in the value of “ $c$ ” among different systems) representation of  $D$  for atoms and molecules in normal liquids, it breaks down<sup>10</sup> upon supercooling, with the ratio  $I \equiv (D/D^{\text{SE}})$ , denoted the “enhancement” in the following, growing with decreasing  $T$ . Near the glass transition, enhancements of as much as  $10^4$  have been observed.

Here we show that the wavevector dependence of the viscosity can explain the breakdown of the SE law. Recognizing that the SE law is obtained from eq 1 when  $\eta(k) \rightarrow \eta$  and that  $D^0$  can only have a minor numerical influence on the enhancement

$$I = (D/D^{\text{SE}}) \approx \frac{\int dk \chi^2(k\lambda\sigma)/(\eta(k)/\eta)}{\int dk \chi^2(k\lambda\sigma)}; \quad (4)$$

$\int dk \chi^2(k\lambda\sigma) = 3\pi/(5\lambda\sigma)$ . The adjustable parameter,  $\lambda$ , is

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**TABLE 1: Relative Potential Parameters**

interaction	AA	AB	BB
$\epsilon$	1.0	0.5	0.8
$\sigma$	1.0	0.88	0.8

introduced because we do not know the exact value for the numerical coefficient “ $c$ ” for the SE law of atoms (we do not even know the proper  $\sigma$ ). Then the mode-coupling result when  $\eta(k) = \eta$  is

$$D^{\text{SE}}(\text{atomic}) = \frac{k_B T}{5\lambda\pi\eta\sigma} \quad (5)$$

where we also represent any possible  $D^0$  term by adjusting (decreasing) the value of  $\lambda$ . The obvious possible range of  $\lambda$  is then from 4/5 (slip with  $\sigma$  playing the role of  $R$ ) to 2/5 (slip with  $\sigma/2$  as  $R$ ), or somewhat smaller. One does not anticipate stick or fluid sphere conditions for smooth atoms. In fact, we will apply eq 5 with  $\sigma = \sigma_{\text{AA}}$  even for B atoms, and  $\lambda$  further takes on the role of correcting the atomic size.

Equation 2 is on solid ground, arising<sup>5</sup> from the fact the tagged particle velocity, which determines  $D$ , is one contributor to the momentum density, which determines  $\eta$ . In a comprehensive mode-coupling theory, it would be combined with a theory of the viscosity, a challenging enterprise<sup>11</sup> requiring various approximations and uncertainties. However, in the following we take the viscosity, containing all of the relevant physical effects, from simulation, and thus do not have to concern ourselves with this important problem.

It will be seen in the next section that the strong rise in  $\eta$  with decreasing  $T$  is mitigated substantially at finite  $k$ , that is,  $(\eta(k)/\eta) < 1$ . If  $(\eta(k)/\eta)$  is small enough over the wavevectors that make a substantial contribution to eq 4 before the integral is cut off, then enhancement will be obtained. For enhancement to grow with decreasing  $T$ ,  $(\eta(k)/\eta)$  must decay with increasing strength, implying a growing correlation length.

Various theories of enhancement have already been given,<sup>10,12–14</sup> based primarily on the concept of<sup>15,16</sup> dynamical heterogeneity. The two approaches need not be incompatible because heterogeneity could cause the viscosity to vary with length scale or wavevector.

### III. Simulations on the Binary Lennard–Jones Liquid

To test the ideas just discussed, we have chosen the much-studied 80:20 binary Lennard–Jones liquid, originally proposed<sup>17</sup> by Kob and Andersen. Atom “A” was taken as argon,  $\epsilon_{\text{AA}} = 120$  K,  $\sigma_{\text{AA}} = 3.4$  Å, and the relative values of the other potential parameters are given in Table 1. Standard reduced units are defined with the A parameters. The simulation box contained 500 atoms at reduced density  $\rho = 1.2$ .

The complex behavior that differentiates a supercooled liquid from a normal liquid becomes fully developed below the mode-coupling<sup>18</sup> temperature,  $T_c$ , where  $D$  extrapolates to zero from above. One expects to best see the breakdown of Stokes–Einstein below  $T_c$ . However, molecular dynamics simulation then becomes problematic. In our case  $T_c = 52$  K, and we have taken data down to 60 K.

Calculation of the self-diffusion constant for both A and B particles is straightforward. The shear viscosity is the transport coefficient governing the decay of the conserved transverse momentum density. Here we are focused on the  $k$ -dependence of  $\eta$ , but it is also frequency-dependent, and we want the zero-frequency value everywhere. If the frequency-dependence is negligible, then

$$\langle g_k^\perp(t) g_{-k}^\perp(0) \rangle / \langle g_k^\perp(0) g_{-k}^\perp(0) \rangle = e^{-k^2 \eta(k)t / (\rho m)} \quad (6)$$

where

$$g_k^\perp = \sum_i g_i^\perp e^{ikr_i} \quad (7)$$

and  $g_i^\perp$  and  $r_i$  denote components of the momentum and position of atom  $i$  perpendicular to the wavevector. With no assumptions about frequency dependence, integration of the time correlation rigorously gives the  $k$ -dependent, zero-frequency viscosity

$$\int_0^\infty dt \langle g_k^\perp(t) g_{-k}^\perp(0) \rangle / \langle g_k^\perp(0) g_{-k}^\perp(0) \rangle = \frac{\rho m}{k^2 \eta(k)} \quad (8)$$

We obtain our  $\eta(k)$  from eq 8. Because A and B particles have the same mass, in this case it is equivalent to integration of the transverse (collective) velocity correlation divided by its  $t = 0$  value (“normalized”). The transverse velocity correlation is averaged until a smooth function is obtained. Good averaging requires a few tens of picoseconds at 300 K and 80 nanoseconds at 60 K.

It is not useful to work directly with a conserved variable time correlation as  $k \rightarrow 0$  because the decay time diverges and would require a diverging simulation run time. Thus, one generally evaluates  $\eta(k = 0)$  via integration of the stress tensor correlation, or with a nonequilibrium simulation. These calculations become computationally challenging as  $T_c$  is approached.

The behavior of  $\eta$  versus  $T$ , and the breakdown of the SE law, has been characterized carefully in this system by Bordat et al.<sup>19</sup> using a nonequilibrium method for  $\eta$ . The available wavevectors in a finite simulation box are discrete; there is minimum nonzero  $k_{\text{min}}$ . At temperatures above 200 K, we find  $\eta(k_{\text{min}}) \approx \eta(\text{Bordat})$ . As  $T$  is decreased,  $\eta(k_{\text{min}})$  increasingly falls below  $\eta(\text{Bordat})$ , with  $\eta(k_{\text{min}}, 60 \text{ K}) \ll \eta(\text{Bordat}, 60 \text{ K})$ , but we have not attempted an independent evaluation of  $\eta(k = 0)$ ; we simply take the value from ref 19, specifically, from eq 2 and the parameters in Table 2.

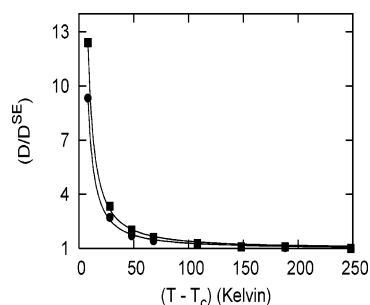
**1. Enhancement of Diffusion.** To evaluate the enhancement from simulation, we calculate an effective “ $c^e$ ” from eq 1, for both  $D_A$  and  $D_B$ , using  $\sigma = \sigma_{\text{AA}} = 3.4$  Å. The results are expected to be on the small side because  $\sigma_{\text{AA}}$  is the largest  $\sigma$ , whereas one’s best guess would be an appropriately weighted average of  $\sigma_{\text{AA}}$  and  $\sigma_{\text{AB}}$  for  $D_A$ , and of  $\sigma_{\text{BB}}$  and  $\sigma_{\text{AB}}$  for  $D_B$ ; also, if  $D^0$  is present, then it will reduce the effective  $c^e$ . SE behavior is signaled by the temperature-independence of  $c$ . Assuming that  $c^e$  attains a constant value in the normal liquid range, we have  $I = c^e(\text{plateau})/c^e(T)$ . A high- $T$  plateau in  $c^e$  is indeed found. For reference, we take the 300 K values,  $c_A^e(\text{plateau}) = 2.0$ ,  $c_B^e(\text{plateau}) = 1.4$ .

The enhancements are shown in Figure 1. Maximum enhancement at 60 K is  $I_A \approx 9$  for  $D_A$  and  $I_B \approx 13$  for  $D_B$ . The difficulty of reproducing full-blown supercooled dynamics via simulation is illustrated clearly. At 60 K we are already averaging for nearly 100 ns, to see a modest enhancement of one decade. The CPU time will rise sharply with decreasing  $T$ , and we are still above  $T_c$ !

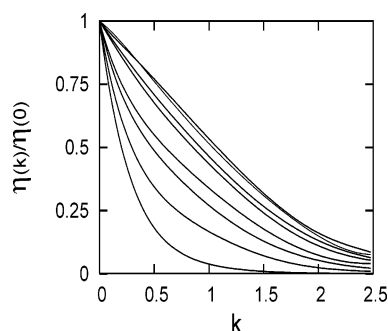
Along with the data points, fits to a mode-coupling power law are shown

$$I = a(T - T_c)^{-b} + 1 \quad (9)$$

An excellent representation is achieved with least-squares values of the parameters. For both A and B atoms, the exponent  $b =$



**Figure 1.** Enhancement  $I = (D/D^{\text{SE}})$  of diffusion with decreasing temperature and mode-coupling fits; squares and upper curve are for smaller “B” atoms, circles and lower curve for “A”.



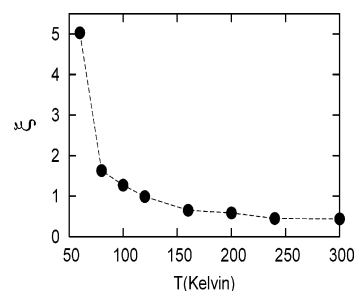
**Figure 2.** Wavevector-dependent viscosity divided by the  $k = 0$  value, vs wavevector in  $\text{\AA}^{-1}$ ; top to bottom, 300 K, 240 K, 200 K, 160 K, 120 K, 100 K, 80 K, 60 K.

1.33 and  $T_c = 52$  K. It is gratifying that the extrapolated divergence of the enhancement occurs precisely at the value of  $T_c$  determined by Kob and Andersen.<sup>17</sup> Just as diffusion does not vanish at  $T_c$  but changes mechanism,  $I$  does not diverge but presumably crosses over to some large finite value consistent with the low- $T$  mechanism.

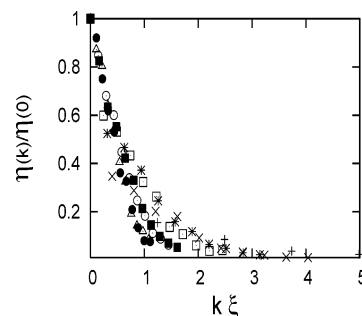
The observation of greater enhancement for smaller (B) atoms was originally made by<sup>10</sup> Cicerone and Ediger and is explained by our theory. Using eq 4 with the single  $\sigma_{AA}$ , smaller atoms will have a smaller  $\lambda$  and a higher wavevector cutoff, and will thus be sensitive to  $\eta(k)$  at higher  $k$ . Because the viscosity is the smallest at the highest  $k$ , the smaller atom senses a less viscous solvent overall and has a greater enhancement. The explanation is qualitative at this point but will be firmed up below.

**2. Wavevector Dependence of Viscosity.** Plots of  $(\eta(k)/\eta)$  for several different temperatures are shown in Figure 2; again, the  $k = 0$  values are taken from ref 19. It is apparent that the finite- $k$  viscosity is drastically less than the conventional  $k = 0$  quantity at our lowest  $T$ ; any aspect of supercooled dynamics that invokes  $\eta(k = 0)$  must be examined carefully to determine if  $k = 0$  is a rigorous condition or an approximation. The curves for  $T \geq 160$  K are quite similar, within the noise. At the higher temperatures, some curvature in the vicinity of  $k = 0$  and a finite high- $k$  value can be seen. We believe that such behavior is always present, but it is masked at low- $T$  by the growing value of  $\eta(0)$ .

If  $(\eta(k)/\eta)$  deviated from unity in a  $T$ -independent fashion, then we would obtain an unsatisfactory  $T$ -independent enhancement. Figure 2 shows that the higher- $T$  functions do more or less collapse on a single curve, but below 160 K the decay becomes sharper with decreasing  $T$ , consistent with a  $(k\xi)$  dependence and a growing correlation length,  $\xi(T)$ . The  $T$ -dependent enhancement of  $D$  stems from the  $T$ -dependent correlation length in  $\eta(k)$ . A good fit is attained with  $\eta(k)/\eta =$



**Figure 3.** Correlation length in  $\text{\AA}$  vs temperature.



**Figure 4.** Master plot of all of the data for  $T \leq 200$  K.

$1 + a \tanh(k\xi)$ , allowing a rough estimate of  $\xi(T)$ . Cooling from 300 to 60 K,  $\xi$  increases from 0.44 to 5.0  $\text{\AA}$ .

Because slow critical point dynamics is clearly associated with a diverging equilibrium pair correlation length, it is natural to search for a growing correlation length to explain the enormous dynamical slowing down in supercooled liquids. The seminal Adam–Gibbs paper<sup>20</sup> argued that a liquid is composed of “cooperative rearranging regions” whose size increases as the inverse of the configurational entropy. However, no length with such strong growth has ever been found. Note that a “rearranging region” is an inherently dynamical quantity that does not easily lead to an equilibrium expression for a correlation length. More recent work has focused on cooperative regions or lengths of small to moderate extent, with the possibility of a dynamical, as opposed to equilibrium, definition. Static domains are explicit in the<sup>21</sup> “fluctuation limited domain” theory of Kivelson and co-workers. Xia and Wolynes consider<sup>14</sup> “entropic droplets” and Liu and Oppenheim<sup>13</sup> have introduced a variable characterizing a cluster into mode coupling. The size of a dynamically heterogeneous domain is<sup>15,16</sup> a possible dynamical definition of a correlation length.

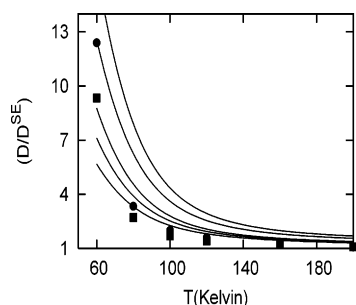
We now find that the wavevector dependence of the viscosity provides another dynamical route to a correlation length. It is not surprising that the increase of  $\xi$  over the states considered in this study still leaves it in the “atomic” range at 60 K. Fully developed supercooled phenomena do not develop until  $T$  falls below  $T_c$ . Above  $T_c$ , the significant observation is the onset of strong growth in the quantity of interest.

The analysis suggests a master plot. In Figure 4, all of the data are plotted versus  $k\xi$ . Reasonable data collapse is obtained, arguing for the role of a correlation length. An even better result is found if the  $T \geq 200$  K data (the low-lying points at  $k\xi \approx 1$ ), presumably influenced strongly by by normal-liquid “background” effects, are removed.

#### IV. Calculation of the Enhancement

Calculation of the enhancement is now straightforward, except for the ambiguity in the value of  $\lambda$  to be used in eq 4; recall that  $c^e \leq 5\lambda$  when  $k$ -dependence is negligible. The enhancement is a very sensitive function of  $\lambda$ , which sets the upper wavenumber





**Figure 5.** Calculated and simulated enhancement: theoretical curves, top to bottom,  $\lambda = 0.6, 0.7, 0.8, 0.9, 1.0$ ; simulation, solid squares and circles, A and B particles.

cutoff on contributions to  $D$  from  $\eta(k)$ . Smaller atoms (smaller  $\lambda$ ) probe more of the low viscosity, high- $k$  regime and experience a larger enhancement.

Rather than attempt a best fit, in Figure 5 we present the simulated enhancements, and calculations for  $1.0 \geq \lambda \geq 0.60$ . Roughly,  $\lambda \approx 0.80$  is reasonable for A particles, and  $\lambda \approx 0.70$  is reasonable for the smaller B particles. These results, deduced from the  $T$ -dependence of  $D$  for states in which wavevector dependence is important, are in excellent agreement with the expectation that, at high  $T$  where wavevector dependence is negligible, the coefficient in the denominator of eq 5 should not be too different from “4” for A particles, and somewhat smaller for B (with  $\sigma = \sigma_{AA}$ ).

However, applying eq 5 in the 300 K normal liquid yields  $\lambda(A) \approx 0.4$  and  $\lambda(B) \approx 0.3$ . To reconcile the different values, we recall that the additive “ $D^0$ ” in eq 2 will tend to make  $c^e$ , and  $\lambda$ , smaller when representing the entire  $D$  with the SE form, eq 5. Also, a calculated enhancement of  $\sim 1.4$  persists even at the 300 K “plateau” (in  $c^e$ ), and representing the “enhanced”  $D$  with eq 5 will similarly give a reduction in  $\lambda$ , by a factor of 1.4.

In short, the value of  $\lambda$  obtained by equating the simulated  $D$  to eq 5 at a normal liquid reference temperature is influenced by several approximations. The enhancement, relative to a reference value, should depend less on such details and be dominated by the wavevector dependence of viscosity, which we are proposing as the physical basis of the breakdown of the SE law. Thus, our best estimates are those from the enhancement,  $\lambda(A) \approx 0.80$ ,  $\lambda(B) \approx 0.70$ , corresponding to the “slip” SE law,  $D = k_B T / (4\pi\eta\sigma)$ .

## V. Discussion

The most important difference between deeply supercooled and normal liquids is the extremely high viscosity of the former. We have seen, however, that the viscosity falls off sharply from its zero wavevector value, “the” viscosity, with increasing  $k$ . At finite  $k$ , the liquid is more fluid. Thus, in assessing the dependence of any quantity on viscosity in supercooled liquids, one must carefully consider which wavevectors contribute. In the case of diffusion by a particle with characteristic dimension  $\sigma$ , roughly, all wavevectors up to a cutoff of  $\sim \pi/\sigma$  are important. If the particle is small enough so that wavevectors where  $\eta(k) \ll \eta(k=0) \equiv \eta$  dominate the friction, no relation between  $D$

and  $\eta$  is possible, that is, the Stokes–Einstein law breaks down. An alternate statement of our proposal is that the SE law does not break down; the effective viscosity for an atom is simply not  $\eta$ .

To go beyond these general considerations, we have obtained  $\eta(k)$  and shown that the Keyes–Oppenheim<sup>5</sup> equation, with a coefficient  $\lambda$  that will approximately give the expected slip SE law when wavevector dependence is negligible, can reproduce the simulated enhancement for both A and B particles in the Kob–Anderson mixture.<sup>17</sup> As is typical with computer simulation, we can probe only the onset of strong enhancement, about one decade. A definitive test awaits results for more deeply supercooled states.

It is obvious within our approach that a smaller particle should have a larger enhancement.<sup>10</sup> The  $T$ -dependence of  $\eta(k)/\eta(k=0)$  yields a dynamically defined correlation length, growing with decreasing  $T$ .

The rise of the enhancement as  $T_c$  is approached is reminiscent of the behavior of an indicator of dynamic reorientational heterogeneity, which we introduced<sup>22</sup> elsewhere. Most theories of the phenomenon do invoke heterogeneity.<sup>10,12–16</sup> It seems reasonable that dynamical heterogeneity will introduce a  $k$ -dependence of viscosity characterized by a domain length, unifying the two approaches and putting the focus on the role of heterogeneity in  $\eta(k)$ .

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## References and Notes

- (1) Landau, L.; Lifshitz, D. *Fluid Mechanics*; Addison-Wesley: Reading, MA, 1968.
- (2) Kivelson, D.; Kivelson, M. G.; Oppenheim, I. *J. Chem. Phys.* **1970**, *52*, 1810.
- (3) Dorfman, J. R.; van Beijeren, H.; Mc Clure, C. *Arch. Mech. Stosow.* **1976**, *28*, 333.
- (4) Cukier, R.; Kapral, R.; Lebenhaft, J.; Mehaffey, J. *J. Chem. Phys.* **1980**, *73*, 5244.
- (5) Keyes, T.; Oppenheim, I. *Phys. Rev. A* **1973**, *8*, 937.
- (6) Mercer, J.; Keyes, T. *J. Stat. Phys.* **1983**, *32*, 35.
- (7) Sung, W.; Dahler, J. *J. Chem. Phys.* **1983**, *378*, 6264.
- (8) Alder, B. J.; Gass, D.; Wainwright, T. *J. Chem. Phys.* **1970**, *53*, 3813.
- (9) Keyes, T.; Masters, A. J. *Adv. Chem. Phys.* **1983**, *58*, 1.
- (10) (a) Cicerone, M.; Ediger, M. D. *J. Chem. Phys.* **1996**, *104*, 7210. (b) Cicerone, M.; Wagner, P.; Ediger, M. *J. Phys. Chem B* **1997**, *101*, 8727.
- (11) Kirkpatrick, T. R. *Phys. Rev. Lett.* **1984**, *53*, 1735.
- (12) Stillinger, F. H.; Hodgdon, J. *Phys. Rev. E* **1994**, *50*, 2061.
- (13) Liu, C.; Oppenheim, I. *Phys. Rev. E* **1996**, *53*, 799.
- (14) Xia, X.; Wolynes, P. G. *Phys. Rev. Lett.* **2001**, *86*, 5526.
- (15) Ediger, M. *Annu. Rev. Phys. Chem.* **2000**, *51*.
- (16) (a) Allegrini, P.; Douglas, J. F.; Glotzer, S. C. *Phys. Rev. E* **1999**, *60*, 5714. (b) Donati, C.; Glotzer, S. C.; Poole, P. H. *Phys. Rev. E* **1999**, *60*, 3107. (c) Gebremichael, Y.; Schroder, T. B.; Starr, F. W.; Glotzer, S. C. *Phys. Rev. E* **2001**, *64*, 051503.
- (17) Kob, W.; Andersen, H. C. *Phys. Rev. E* **1995**, *51*, 4626.
- (18) Goetze, W.; Sjogren, L. *Rep. Prog. Phys.* **1992**, *55*, 241.
- (19) Bordat, P.; Aouard, F.; Descamps, M.; Muller-Plathe, F. *J. Phys.: Condens. Matter* **2003**, *15*, 5397.
- (20) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
- (21) Kivelson, D.; Tarjus, G. *J. Chem. Phys.* **1998**, *109*, 5481.
- (22) Kim, J.; Keyes, T.; Li, W. *Phys. Rev. E* **2003**, *67*, 021506.