

Alternative View of Self-Diffusion and Shear Viscosity[†]

Frank H. Stillinger*[‡] and Pablo G. Debenedetti[§]

Department of Chemistry, Princeton University, Princeton, New Jersey 08544, and
Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

Received: September 24, 2004; In Final Form: November 17, 2004

By performing an elementary transformation, the conventional velocity autocorrelation function expression for the temperature and density dependent self-diffusion constant $D(T, \rho)$ has been reformulated to emphasize how initial particle momentum biases final mean displacement. Using collective flow variables, an analogous expression has been derived for $1/\eta(T, \rho)$, the inverse of shear viscosity. The Stokes–Einstein relation for liquids declares that D and T/η should have a fixed ratio as T and ρ vary, but experiment reveals substantial violations for deeply supercooled liquids. Upon analyzing the self-diffusion and viscous flow processes in terms of configuration space inherent structures and kinetic transitions between their basins, one possible mechanism for this violation emerges. This stems from the fact that interbasin transitions become increasingly Markovian as T declines, and though self-diffusion is possible in a purely Markovian regime, shear viscosity in the present formulation intrinsically relies on successive correlated transitions.

I. Introduction

The interparticle interactions present in condensed phases, and the local structures that they produce, influence dynamic properties of those phases at all length scales. The self-diffusion process and its associated temperature (T) and number density (ρ)-dependent diffusion constant $D(T, \rho)$ provide an obvious example of this influence at the molecular length scale. At the opposite extreme, where macroscopic hydrodynamics becomes relevant, the shear viscosity $\eta(T, \rho)$ supplies a corresponding example. It has long been a source of wonder and insight that these two extremes could be tied together, at least empirically, by the Stokes–Einstein relation for liquids:^{1–4}

$$D(T, \rho) = k_B T / C a \eta(T, \rho) \quad (1.1)$$

Here k_B is Boltzmann's constant, a is the effective hydrodynamic radius of the diffusing particle, and C is a positive constant with a value that depends on the hydrodynamic boundary condition enforced at the particle surface ($C = 6\pi$ for “stick”, $C = 4\pi$ for “slip”).

Application of the Stokes–Einstein relation to liquids in their equilibrium and moderately supercooled regimes succeeds well in correlating the temperature and density variations of $D(T, \rho)$ and of $\eta(T, \rho)$, which experimentally can span many orders of magnitude. However, such correlations can break down severely for deeply supercooled liquids, especially those that are conventionally identified as “fragile glass formers”.^{5–7} This failure has stimulated recent publications offering tentative explanations for its occurrence.^{8,9}

Exact statistical mechanical expressions of the Mori–Kubo–Zwanzig type are available for both $D(T, \rho)$ and $\eta(T, \rho)$.^{10,11} Interpreting those relations for any material of interest so as to produce quantitative theoretical predictions is difficult, however. In such circumstances it can be beneficial to have in hand

alternative representations of those two properties. Offering such alternatives forms the basis of the present paper.

Section II focuses on the self-diffusion process, and trivially transforms a well-known velocity autocorrelation function expression for $D(T, \rho)$ into a new form with a somewhat unconventional interpretation. Section III considers $\eta(T, \rho)$, and derives an autocorrelation function expression for its inverse; this latter relation can be interpreted in a manner roughly analogous to that of the self-diffusion constant. Section IV relates results from the prior sections II and III to the multidimensional “landscape” representation, in particular involving inherent structures (potential energy minima) and their encompassing basins.^{12–16} Discussion of the Stokes–Einstein relation and its low-temperature failure forms the subject in section V. Connections to empirical heat capacity and viscosity measurements, leading to inferred Kauzmann paradoxes, and to so-called “ideal glass transitions” receive attention in section VI. Section VII discusses our approach and summarizes conclusions.

II. Self-Diffusion

In a macroscopic many-particle system at a state of thermal equilibrium, the self-diffusion constant D measures the mean-square displacement of a single particle in the long-time limit:

$$D = \lim_{t \rightarrow \infty} \langle [\Delta \mathbf{r}_i(t)]^2 \rangle / 6t$$

$$\Delta \mathbf{r}_i = \mathbf{r}_i(t) - \mathbf{r}_i(0) \quad (2.1)$$

Here $\mathbf{r}_i(t)$ is the location of particle i at time t , and the brackets $\langle \dots \rangle$ indicate an average over an equilibrium ensemble. By expressing the position vector for particle i as a time integral of its velocity, eq 2.1 can be converted into the familiar velocity autocorrelation form:

$$D = (1/3) \int_0^\infty \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle dt \quad (2.2)$$

Although the integrand in this latter expression can be negative

[†] Part of the special issue “David Chandler Festschrift”.

[‡] Department of Chemistry.

[§] Department of Chemical Engineering.

for some time displacements t , the integral itself obviously must be nonnegative.

For the purposes of this paper it will be useful to express D in a form that amounts to a “hybrid” of eqs 2.1 and 2.2. One has

$$\begin{aligned} D &= (1/3)\lim_{t \rightarrow \infty} \langle \mathbf{v}_i(0) \cdot \int_0^t \mathbf{v}_i(s) ds \rangle \\ &= (1/3m)\lim_{t \rightarrow \infty} \langle \mathbf{p}_i(0) \cdot \Delta \mathbf{r}_i(t) \rangle \end{aligned} \quad (2.3)$$

where m is the particle mass and $\mathbf{p}_i = m\mathbf{v}_i$ is the momentum of particle i . The meaning of this last expression is clear: it relates D to the ultimate mean displacement of the position of a particle chosen for observation, as biased by its initial momentum. In an isotropic medium, specifically a liquid, that mean displacement and the initial momentum producing it will necessarily be collinear.

The initial momentum $\mathbf{p}_i(0)$ possesses an equilibrium Maxwell–Boltzmann distribution P_{eq} appropriate for the prevailing equilibrium temperature $T \equiv 1/k_B\beta$:

$$P_{\text{eq}}(\mathbf{p}) = \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp\left(-\frac{\beta p^2}{2m} \right) \quad (2.4)$$

It will be conceptually helpful to resolve the contributions to D in eq 2.3 according to the values of that initial momentum, so we write

$$D = \left(\frac{1}{3m} \right) \int d\mathbf{p}_i(0) P_{\text{eq}}[\mathbf{p}_i(0)] \langle \Delta \mathbf{r}_i(\infty) | \mathbf{p}_i(0) \rangle \quad (2.5)$$

Here the symbol $\langle f(t) | \mathbf{p}_i(0) \rangle$ indicates an equilibrium average of f at time t , subject to the constraint that the momentum of particle i had the indicated value at $t = 0$. In (2.5) as written, the infinite-time limit has been abbreviated but should cause no confusion. Equation 2.5 is our alternative representation for the self-diffusion constant $D(T, \rho)$, relating it specifically to mean displacement biased (i.e., determined) by initial momentum. From the practical point of view, the influence of the initial momentum should die out rather quickly, so using $\langle \Delta \mathbf{r}_i(t^*) | \mathbf{p}_i(0) \rangle$ for moderately large finite time t^* in the integrand of eq 2.5 in place of $\langle \Delta \mathbf{r}_i(\infty) | \mathbf{p}_i(0) \rangle$ should suffice. With such a t^* choice, the distribution of initial-momentum-biased displacements $\Delta \mathbf{r}_i(t^*)$ will have a manageable width and shape and should be readily accessible in molecular dynamics computer simulations.

In any centrosymmetric medium (in particular an isotropic fluid), the restricted average appearing in the integrand of eq 2.5 must be an odd function of the initial momentum:

$$\langle \Delta \mathbf{r}_i(\infty) | \mathbf{p}_i(0) \rangle = -\langle \Delta \mathbf{r}_i(\infty) | -\mathbf{p}_i(0) \rangle \quad (2.6)$$

The hydrodynamic model underlying the Stokes–Einstein relation involves a frictional retarding force strictly proportional to particle velocity. Consequently, that approximate model implies that (2.6) would be strictly proportional to the initial momentum. The corresponding specific form that emerges from the Stokes–Einstein hydrodynamic model is the following:

$$\langle \Delta \mathbf{r}_i(\infty) | \mathbf{p}_i(0) \rangle \cong (1/Ca\eta)\mathbf{p}_i(0) \quad (2.7)$$

which of course obeys eq 2.6. Nevertheless, in an exact description it is reasonable to suppose that such linearity in initial momentum would be substantially violated at very large magnitudes of that momentum. The sign of the deviation from

linearity may vary, depending on the substance involved, as well as its thermodynamic state.

The expressions exhibited thus far in this section have referred to states of thermodynamic equilibrium. However, extension to metastable supercooled liquids is both important and feasible. This requires that the configurational part of the ensemble averaging denoted above by $\langle \dots \rangle$ be modified so as to be phase-restricted, i.e., to include only those portions of the multidimensional configuration space that would be visited by the system while in the homogeneous metastable state.^{17,18} Subject to this proviso, eq 2.5 describes self-diffusion in supercooled liquids down to their glass transition temperatures.

III. Shear Viscosity

The traditional autocorrelation function expression for shear viscosity was originally derived by Green, utilizing Fokker–Planck theory.¹⁹ Subsequent derivations have relied on calculation of linear response to suitable external forces, within the complete Newtonian dynamical formalism for many-particle systems.^{10,11,20} That expression has the following form:

$$\eta = (1/k_B TV) \int_0^\infty \langle J^{xy}(0) J^{xy}(t) \rangle dt \quad (3.1)$$

where $V = L_x L_y L_z$ is the macroscopic system volume and J^{xy} is the x, y component of a momentum flux tensor:

$$J^{xy} = \sum_{j=1}^N (p_{jx} p_{jy} / m + x_j F_{jy}) \quad (3.2)$$

F_{jy} is the y component of the force experienced by particle j . In a manner similar to that mentioned above for the self-diffusion process, (3.1) can be extended in its application to metastable phases by enforcing a suitable configurational constraint on the ensemble averaging operation $\langle \dots \rangle$. The very large viscosities exhibited by glass-forming liquids as they are cooled toward their empirical glass-transition temperatures are covered by this extension and are associated with long-time persistence of the fluctuating J^{xy} quantities. This persistence stems from the sluggishness of those configurational rearrangement processes that are required to reduce and eventually to eliminate the initial system-spanning stress. It seems fair to state that the formally exact expression (3.2) for shear viscosity has had only limited value in relating the wide range of experimentally observed temperature and pressure variations for that transport property, to molecular details for various substances of interest. No doubt this stems in part from the great diversity and complexity of molecular structures and interactions involved, and of the intermolecular forces that they produce.

Consider next the following quantity, which will play a role roughly conjugate to that of (3.2):

$$J_{xy}(k) = \sum_{j=1}^N \sin(ky_j) (p_{jx} / m) \quad (3.3)$$

where $k = 2\pi n/L_y$, with n a positive integer. This quantity has a vanishing average value at equilibrium:

$$\langle J_{xy}(k) \rangle = 0 \quad (3.4)$$

but at any instant, for the macroscopic system as a whole, it provides a measure of a wavevector- k flow pattern in the x direction, created by momentary fluctuations. The corresponding equilibrium average of the instantaneous second moment (i.e., zero-time autocorrelation) is easily evaluated using independent

Maxwell–Boltzmann distributions P_{eq} for the particle momenta:

$$A(k,0) = \langle J_{xy}^2(k) \rangle = Nk_B T/2m \quad (3.5)$$

It should be noted that the existence of a nonvanishing value of $J_{xy}(k)$ at $t = 0$ has no implication for the value of the conjugate quantity J^y , eq 3.2, at that same instant.

Although the equal-time autocorrelation for $J_{xy}(k)$, eq 3.5, is independent of the y -direction wavevector magnitude k , the same is not the case for the time-displaced quantity ($t \neq 0$):

$$A(k,t) = \langle J_{xy}(k,0) J_{xy}(k,t) \rangle \quad (3.6)$$

However, by time-reversal symmetry in the equilibrium ensemble, this must be an even function of t . If the potential energy function describing interactions in the system is continuous and many-times differentiable away from particle coincidence, one should expect the autocorrelation function $A(k,t)$ to have a series expansion in powers of t^2 . The leading terms of this series describe a rapid transient regime during which the matter flow resulting from the initial momentum distribution generates a stress field. That stress field resists the flow, causing it ultimately to vanish.

Provided that the wavevector magnitude k is sufficiently small, so that the corresponding wavelength $2\pi/k$ is much larger than typical molecular lengths, then it is appropriate to identify the regression of $J_{xy}(k,t)$ with macroscopic hydrodynamic flow. However, this requires time t to be beyond the rapid transient regime (the Maxwell relaxation time), during which very little of the final regression will have occurred.²¹ The relevant hydrodynamic velocity field $\mathbf{u}(\mathbf{r},t)$ for comparison at those later times has the following spatial dependence:

$$\begin{aligned} u_x(\mathbf{r},t) &\propto \sin(ky) \\ u_y = u_z &= 0 \end{aligned} \quad (3.7)$$

This type of flow field involves pure shear and thus entails no macroscopic density change. The compressibility of the moving fluid thus is irrelevant. Consequently, in the required small- k limit (but with $k > 0$) this flow amounts to a macroscopic motion that could equally well be exhibited by an incompressible fluid. Therefore, aside from the rapid initial transient reflecting viscoelastic properties that becomes irrelevant in the $k \rightarrow 0$ limit,²¹ the flow field will be validly described by the standard Navier–Stokes equation for incompressible fluids.^{21,22} This connection allows one to conclude that $\mathbf{u}(\mathbf{r},t)$ for positive times (beyond that initial viscoelastic transient) decays exponentially to zero at a rate determined by the macroscopic shear viscosity:

$$u_x(\mathbf{r},t) = u_0 \sin(ky) \exp(-\eta k^2 t/m\rho) \quad (3.8)$$

As before ρ denotes the number density N/V . Time-reversal symmetry implies that the ensemble-averaged, fluctuation-induced buildup substantially prior to $t = 0$ must be an exponential rise, to be consistent with this positive-time exponential decay.

Although one can consistently neglect short-time transients when the primary objective is the zero-frequency viscosity $\eta(T,\rho)$, an extension of the present analysis could be developed that would yield expressions for the full frequency-dependent viscoelastic response. This would involve examination of the k dependence of autocorrelation functions, and of their entire time of regression $t \geq 0$. However, that extension falls outside the scope of the present investigation.

Upon combining eqs 3.5 and 3.8, one obtains

$$\langle J_{xy}(k,0) J_{xy}(k,t) \rangle = [(Nk_B T/2m) + l(k,t)] \exp(-\eta k^2 t/m\rho) \quad (3.9)$$

where $l(k,t)$ is a correction term for the initial transient with the property $l(k,0) = 0$, and with negligible long-time effect in the small- k limit of interest. In view of this feature, it is possible to extract $1/\eta$ by integrating this last expression over all positive times with neglect of the contribution of $l(k,t)$. The explicit result may be written as follows:²³

$$1/\eta = (2/N\rho k_B T) \lim_{k \rightarrow 0^+} k^2 \int_0^\infty \langle J_{xy}(k,0) J_{xy}(k,t) \rangle dt \quad (3.10)$$

Notice the inverse relationship between the pair of autocorrelation function expressions (3.1) and (3.10). As before, eq 3.10 is amenable to extension into the metastable supercooling regime by phase-restricting the ensemble averaging operation $\langle \dots \rangle$ that appears in its integrand.

It is again trivial to rewrite (3.10) in a format analogous to the “hybrid” representation shown in the earlier eq 2.3 for diffusion constant D . For this purpose, let K_{xy} denote the net matter displacement at time t in the wavevector- k shear pattern contingent upon the specific initial condition $J_{xy}(k,0)$:

$$\begin{aligned} K_{xy}[k,t|J_{xy}(k,0)] &= \int_0^t J_{xy}(k,t') dt' \\ &= \sum_{j=1}^N \int_0^t \sin[ky_j(t')] [p_{jx}(t')/m] dt' \end{aligned} \quad (3.11)$$

Using this definition, eq 3.10 transforms to the following:

$$1/\eta = (2/N\rho k_B T) \lim_{k \rightarrow 0^+} \lim_{t \rightarrow \infty} k^2 \langle J_{xy}(k,0) K_{xy}[k,t|J_{xy}(k,0)] \rangle \quad (3.12)$$

It is important to note at this stage that if the Stokes–Einstein relation (1.1) were indeed valid, then the combination $T/\eta(T,\rho)$ obtained from eq 3.12, and $D(T,\rho)$ from eq 2.5, would remain exactly proportional to one another as both T and ρ vary.

IV. Potential Energy Landscape

The Newtonian dynamics that underlies the self-diffusion and viscous flow processes is controlled by the potential energy function $\Phi(\mathbf{r}_1 \dots \mathbf{r}_N)$ specifying interactions in the N -particle system. This function defines a multidimensional “landscape”, the various topographic features of which are probed differently at different temperatures. For some purposes it is useful to divide the full multidimensional configuration space into “basins of attraction” belonging to each of the local Φ minima (“inherent structures”) by means of a steepest-descent mapping procedure.^{16,24,25} As a result of this partitioning of the configuration space, the time-varying position $\mathbf{r}_j(t)$ of any particle j can be resolved into two distinct components:²⁶

$$\mathbf{r}_j(t) = \mathbf{R}_j(t) + \mathbf{S}_j(t) \quad (4.1)$$

Here $\mathbf{R}_j(t)$ is the spatial position of particle j in the inherent structure for the basin inhabited at time t , and $\mathbf{S}_j(t)$ is the intrabasin displacement away from that inherent structure. Of course these two components exhibit canceling discontinuities each time the Newtonian dynamics for the N -particle system crosses a shared boundary between a pair of contiguous basins.

It has been pointed out theoretically, and verified by simulation, that eq 2.1 continues to yield the correct self-diffusion coefficient $D(T,\rho)$ if the Newtonian positions $\mathbf{r}_i(t)$ in that

expression are replaced by the corresponding inherent structure positions.^{26,27} Therefore, one has the equivalent expression:

$$D = \lim_{t \rightarrow \infty} \langle [\Delta \mathbf{R}_i(t)]^2 \rangle / 6t$$

$$\Delta \mathbf{R}_i(t) = \mathbf{R}_i(t) - \mathbf{R}_i(0) \quad (4.2)$$

This invariance stems from the fact that intrabasin displacements are order-unity quantities, whereas the time-dependent mean-square displacements, both before and after mapping to minima, grow without bound as t increases. Consequently, the $\mathbf{S}_i(t)$ have no effect in the $t \rightarrow \infty$ limit.

The possibility of replacing Newtonian positions with inherent structure positions in eq 2.1 naturally raises the question about whether a similar treatment is justified for the “hybrid” D expression in eq 2.3, or in eq 2.5. However, those alternatives involve averages with only single occurrences of configurational coordinate changes $\Delta \mathbf{r}_i(t)$, not their squares, and these single occurrences have bounded ensemble averages as $t \rightarrow \infty$. Consequently no appeal to divergence of averages with increasing time t is available to justify neglect of intrabasin displacements $\mathbf{S}_i(t)$. Nevertheless, intrinsic interest surrounds the comparison of the two corresponding quantities:

$$\mathbf{b}[t|\mathbf{p}_i(0)] = \langle \Delta \mathbf{r}_i(t) | \mathbf{p}_i(0) \rangle \quad (4.3)$$

and

$$\mathbf{B}[t|\mathbf{p}_i(0)] = \langle \Delta \mathbf{R}_i(t) | \mathbf{p}_i(0) \rangle \quad (4.4)$$

representing the two versions of the time-dependent mean displacements for a representative particle i , with the same initial momentum bias. Assuming that rigid cores are not present in the interparticle interactions, particles execute essentially linear trajectories over very short time intervals. Consequently, it is easy to see that the small-time behavior of \mathbf{b} must be the following:

$$\mathbf{b}[t|\mathbf{p}_i(t)] = [\mathbf{p}_i(0)/m]t + O(t^3) \quad (4.5)$$

i.e., independent of interactions in leading order. The analogous short-time result for \mathbf{B} also exhibits a leading-order linear term,

$$\mathbf{B}[t|\mathbf{p}_i(t)] = \mathbf{B}_1[\mathbf{p}_i(0)]t + O(t^3) \quad (4.6)$$

whose presence depends on interactions via the nonvanishing probability that the system configuration was initially close to a basin boundary, and managed to execute an interbasin transition during the short time span t . But at very low temperature, interbasin transition rates become extremely low, so in that regime one naturally expects $|\mathbf{B}_1| \ll |\mathbf{p}_i(0)/m|$.

It is the opposite time extreme, $t \rightarrow \infty$, that is relevant to $D(T,\rho)$. A straightforward working hypothesis (that could be checked eventually by molecular dynamics computer simulation for several distinct models) is that a contributing interbasin transition is more likely to occur if $\mathbf{r}_i(0)$ is near a boundary-occupying transition state toward which $\mathbf{p}_i(0)$ is pointing, rather than remote from that transition state in the initially occupied basin. Such first transitions can be expected to make major contributions to the final \mathbf{b} , \mathbf{B} values. If this is indeed correct, then more frequently than not one would have $|\Delta \mathbf{R}_i| > |\Delta \mathbf{r}_i|$ for that initial transition. This reasoning would seem to imply in turn that for large times:

$$|\mathbf{b}[t|\mathbf{p}_i(0)]| < |\mathbf{B}[t|\mathbf{p}_i(0)]| \quad (4.7)$$

Consequently, the tentative hypothesis suggests that replacement of Newtonian positions by inherent structure positions in the “hybrid” representations (2.3) and (2.5) would lead to an upper bound for $D(T,\rho)$. Presumably, the same kind of considerations apply to the quantity K_{xy} in (3.12) for $1/\eta(T,\rho)$; i.e., the replacement of Newtonian positions with inherent structure positions would yield a lower bound for $\eta(T,\rho)$. We stress that these suggested relations are very much in the realm of conjecture and deserve to be the subject of future deeper analysis.

V. Stokes–Einstein Relation

The configurationally “coarse-grained” dynamical description of the system’s time evolution, in which the particle positions $\mathbf{r}_1(t) \dots \mathbf{r}_N(t)$ are replaced by the inherent structure positions $\mathbf{R}_1(t) \dots \mathbf{R}_N(t)$ may offer some insight into a mechanism whereby the Stokes–Einstein relation breaks down for strongly supercooled liquids. At very low temperature, interbasin transitions are infrequent and are separated by complicated intrabasin vibrations described by the vector set $\mathbf{S}_1(t) \dots \mathbf{S}_N(t)$. This produces a loss of “memory”, so that the sequence of successive interbasin transitions reduces to a Markov process.²⁸ In this limiting circumstance, the coarse-grained time dependence of the system’s state can be described by a master equation.²⁹ Let $p_\alpha(t)$ be the occupancy probability of basin α at time t . These basin probabilities obey the time-independent normalization condition:

$$\sum_{\alpha} p_{\alpha}(t) = 1 \quad (5.1)$$

The master equation that determines their temporal evolution has the following form:

$$dp_{\alpha}(t)/dt = \sum_{\gamma(\neq\alpha)} [k_{\gamma \rightarrow \alpha}(E) p_{\gamma}(t) - k_{\alpha \rightarrow \gamma}(E) p_{\alpha}(t)] \quad (5.2)$$

As indicated here, the transition rates $k_{\gamma \rightarrow \alpha}$ and $k_{\alpha \rightarrow \gamma}$ depend on the (conserved) system total energy E . The only rates that can differ from zero are those for basin pairs α, γ sharing a nonzero boundary element. Furthermore, the forward and reverse rate pairs for such contiguous basin pairs must satisfy detailed balance.²⁹

An important distinction to be drawn is that the self-diffusion process survives low-temperature reduction to Markov kinetics, whereas hydrodynamic flow does not. Individual particles can eventually move over arbitrary distances within the macroscopic system as a result of a long sequence of uncorrelated interbasin transitions. However, the macroscopic spatially and temporally coherent flow that characterizes hydrodynamics is inextricably connected to basin transition memory effects. The collection of particles comprising the system, when behaving hydrodynamically, continues to move in substantially the same direction, as viewed either in 3 or in $3N$ dimensions, cutting across portions of a huge sequence of basins. Incidentally, this observation suggests that the “hybrid” equation (3.12) for $1/\eta(T,\rho)$ would remain valid if y -components of Newtonian positions, $y_j(t)$ in K_{xy} (eq 3.11), were to be replaced by their inherent structure mappings $Y_j(t)$, thus indicating a qualitative difference with the hybrid $D(T,\rho)$ expression, eq 2.3.

As the temperature of a liquid is reduced, first through the thermodynamically stable range, then across the melting temperature toward the deeply supercooled regime, one must anticipate that the basin-transition chronological sequence trends inevitably toward the Markovian limit. This creates a situation that increasingly works against the cooperative phenomenon of

shear flow, compared to the single-particle property of self-diffusion. Such a distinction constitutes a mechanism for decoupling between the two kinetic processes by disproportionately foreshortening the integrand in eq 3.10 for $1/\eta$. Consequently η is disproportionately increased. This offers at least a partial explanation for low-temperature violation of the Stokes–Einstein relation, eq 1.1, wherein $D(T,\rho)$ substantially exceeds its prediction based on the value of $\eta(T,\rho)$.

It needs to be emphasized at this stage that Markovian transition character, and dynamical heterogeneity, are distinct and independent attributes. The latter refers to the clustering in three dimensions of configurational shifts during small time intervals and could be either Markovian or not. Dynamical heterogeneity might indeed be another contributing phenomenon to break down the Stokes–Einstein relation.⁹ It has also been implicated in the experimental observation that molecular rotational diffusion is considerably less decoupled from shear viscosity, in deep supercooling, than is translational diffusion.⁸

VI. “Ideal” Glass Transitions

To expand the context in which the present alternative representations can be viewed, it will be helpful to revisit the historically prominent concept of “ideal” glass transitions, closely connected to the so-called “Kauzmann paradox”.³⁰ On one hand, experimental glass formers exhibit an empirical glass transition of strictly kinetic origin at a glass transition temperature $T_g > 0$, where completion of structural relaxation processes begins to take longer than experimental cooling rates permit. But on the other hand it has often been suggested that if the cooling rate could be slowed arbitrarily to maintain structural equilibration through and below T_g , then a lower but still positive temperature T_K (the “Kauzmann temperature”) would appear, at which the system configurationally had fallen into, and become trapped within, the deepest amorphous basin.³¹ To be more precise, this deepest amorphous basin is one of $N!$ structurally equivalent basins that differ only by particle permutations, and which are uniformly distributed throughout the multidimensional configuration space. This trapping presumption has been based on both calorimetric and kinetic measurements, each extrapolated in a seemingly innocuous manner to temperatures below T_g .

If indeed the ideal glass presumption were correct for one or more glass formers, then both self-diffusion and viscous flow would be completely shut down. In particular, $\Delta \mathbf{R}_i(t)$ would vanish identically at all t , implying similarly that

$$\mathbf{B}[t|\mathbf{p}_i(0)] = 0 \quad (6.1)$$

Also one would have

$$\mathbf{b}[t \rightarrow \infty | \mathbf{p}_i(0)] = 0 \quad (6.2)$$

as a result of thermal equilibration within the trapping basin.

For all glass forming materials with finite molecular weight, the interaction potential $\Phi(\mathbf{r}_1 \dots \mathbf{r}_N)$ that produces the multidimensional “landscape”, and thus its basins and inherent structures, obeys a set of general conditions. The conditions relevant to the present context are (a) Φ is bounded below by $-KN$, where K is an N -independent positive constant, (b) Φ is continuous and at least twice differentiable away from nuclear coincidences, and (c) the change in Φ resulting from a local rearrangement of $O(1)$ particles, avoiding nuclear coincidences, is itself $O(1)$. From the last of these it is not possible to endorse eq 6.1 above. At any positive temperature in a macroscopic system of particles, the Maxwell–Boltzmann momentum dis-

tribution (2.4) requires that there exists a positive probability for particle i to possess any arbitrarily large (but finite) momentum $\mathbf{p}_i(t)$. This would virtually always create a local structural disruption as the “fast” particle rips its way through its cage of neighbors, thus causing the system to exit its basin to occupy instead an alternative basin, and possibly one that has a higher inherent structure energy.

Nevertheless, it is conceivable that the transitions induced by high particle momentum might cause the system to pass from one lowest-lying amorphous basin to one of the other $N! - 1$ related to it simply by permutational exchange of particle positions. However, any one permutation can in principle be attained from any other by a sequence of particle pair (or other low order) exchanges. Thus, local permutations would eventually have the effect of transporting particles diffusively throughout the entire system. In contrast to the ideal glass transition presumption, $D(T,\rho) > 0$ for all $T > 0$ in systems of macroscopic size.

A sequence of permutational transitions would not involve viscous shear flow if those transitions were a strictly Markovian process. As argued in the preceding section, lowering the temperature causes a closer and closer approach to the Markov ideal. But there is no compelling reason to suppose that absolutely strict Markov kinetics ever obtains at any positive temperature. A small amount of non-Markovian “memory” in basin transition sequences should be found at any positive temperature. This implies that $\eta(T,\rho)$ remains finite at all positive temperatures, though admittedly its actual values might be enormous by conventional standards. Again, the implication of the simply interpreted ideal glass transition concept is unacceptable.

Although it has not been directly invoked in the arguments just presented, another approach also undermines the idea of an ideal glass transition for molecular glass formers.^{17,32} This approach involves general aspects of basin enumeration as a function of depth (i.e., inherent structure potential energy) and establishes the connection of that enumeration to phase-restricted thermal equilibrium properties. It concludes that the existence of an ideal glass transition would contradict the nature of realistic molecular interactions and of the low-energy amorphous inherent structures that they can produce. Although it is no doubt possible to construct mathematical models whose exact properties exhibit some form of a low temperature “ideal glass transition”, they apparently would do so only at the cost of violating realistic potential energy landscape attributes.

VII. Discussion and Conclusions

By virtue of a trivial transformation, the familiar velocity autocorrelation function expression for the self-diffusion constant $D(T,\rho)$ has been recast into a form that emphasizes the mean displacement of a chosen particle, owing to the rearrangement of its neighbors, biased by the initial momentum of that chosen individual. An analogous rearrangement can be applied to an autocorrelation function expression for $T/\eta(T,\rho)$, that emphasizes mean hydrodynamic displacement of the entire collection of particles comprised in the system, biased by an initial matter flow pattern. The Stokes–Einstein approximation, eq 1.1, declares that these two expressions should retain the same numerical ratio under arbitrary changes in T and in ρ .

However, it has become a well-established experimental fact that many liquids that conform closely to the Stokes–Einstein behavior above, and somewhat below, their thermodynamic melting temperatures, deviate more and more significantly from Stokes–Einstein behavior as they are brought into the deeply

supercooled regime. The analysis provided in section V offers a plausibility argument based upon the multidimensional potential energy landscape, its division into discrete basins for the potential energy minima (inherent structures), and the kinetics of transitions between those basins. We plan to investigate this computationally. As temperature becomes strongly reduced, those interbasin transitions become more and more Markovian, a trend that does not in itself intrinsically affect self-diffusion. However, viscous flow necessarily relies upon interbasin kinetic memory (persistence) effects, and so is disproportionately inhibited, compared to self-diffusion. This distinction permits $D(T, \rho)$ to exceed the small magnitude that the viscosity-containing Stokes–Einstein relation would predict.

Molecular dynamics computer simulation can play an illuminating role in this “hybrid” context. In particular, it should be able to evaluate the quantities $\mathbf{b}[t|\mathbf{p}_j(0)]$ and $\mathbf{B}[t|\mathbf{p}_j(0)]$ for various interactions, temperatures, and densities. The extent to which these quantities deviate from linearity in initial particle momentum $\mathbf{p}_j(0)$ as the magnitude of that momentum substantially exceeds normal thermal values should eventually be one of the foci of investigation.

Considering the fact that binary mixtures are a favorite family of models for simulation of low-temperature liquid behavior,^{33–36} we note in passing the obvious fact that the self-diffusion and shear viscosity expressions derived above for a single component system, generalize straightforwardly to mixtures. Hybrid expressions of the type (2.3) and (2.5) are immediately available for the self-diffusion constants $D_\mu(T, \rho_1, \dots, \rho_\nu)$ for each of the ν distinct components in mixed systems. Of course only a single shear viscosity is present for a mixture, with J_{xy} and K_{xy} in (3.12) each involving a sum over all particles of whatever species might be present. One desirable objective would be to see if strong supercooling causes the separate D_μ to deviate from the Stokes–Einstein predictions by a common factor, or whether they manifest deviations in rather distinct, individual fashion for each species μ .

Acknowledgment. The authors thank M. Scott Shell for the benefit of illuminating discussions concerning several aspects of the analysis reported herein, and of its simulational implementation. P.G.D. gratefully acknowledges financial support by the U.S. Department of Energy, Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, Grant No. DE-FG02-87ER13714.

References and Notes

- (1) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: New York, 1976; p 278.
- (2) Rössler, E. *Phys. Rev. Lett.* **1990**, *65*, 1595.
- (3) Jonas, J.; Hasha, D.; Huang, S. G. *J. Phys. Chem.* **1980**, *84*, 109.
- (4) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed. (revised); Butterworth: London, 1965; p 12.
- (5) Fujara, F.; Geil, B.; Sillescu, H.; Fleischer, G. *Z. Phys. B* **1992**, *88*, 195.
- (6) Cicerone, M. T.; Ediger, M. D. *J. Phys. Chem.* **1993**, *97*, 10489.
- (7) Swallen, S. F.; Bonvallet, P. A.; McMahon, R. J.; Ediger, M. D. *Phys. Rev. Lett.* **2003**, *90*, 015901.
- (8) Stillinger, F. H.; Hodgdon, J. A. *Phys. Rev. E* **1994**, *50*, 2064.
- (9) Jung, Y.; Garrahan, J. P.; Chandler, D. *Phys. Rev. E* **2004**, 061205.
- (10) Zwanzig, R. W. *Annu. Revs. Phys. Chem.* **1964**, *16*, 67.
- (11) McQuarrie, D. A. *Statistical Mechanics*; Harper & Row: New York, 1976; Section 22–5.
- (12) Goldstein, M. *J. Chem. Phys.* **1969**, *51*, 3728.
- (13) Stillinger, F. H.; Weber, T. A. *Phys. Rev. A* **1982**, *25*, 978.
- (14) Stillinger, F. H.; Weber, T. A. *Science* **1984**, *225*, 983.
- (15) Debenedetti, P. G.; Truskett, T. M.; Lewis, C. P.; Stillinger, F. H. *Adv. Chem. Engin.* **2001**, *28*, 21.
- (16) Wales, D. J. *Energy Landscapes*; Cambridge U. P.: Cambridge, 2003.
- (17) Stillinger, F. H. *J. Chem. Phys.* **1988**, *88*, 7818.
- (18) Corti, D. S.; Debenedetti, P. G.; Sastry, S.; Stillinger, F. H. *Phys. Rev. E* **1997**, *55*, 5522.
- (19) Green, M. S. *J. Chem. Phys.* **1954**, *22*, 398.
- (20) Kubo, R.; Toda, M.; Hashitsume, N. *Statistical Physics II. Non-equilibrium Statistical Mechanics*; Springer-Verlag: Berlin, 1985; p 196.
- (21) Landau, L. D.; Lifshitz, E. M. *Theory of Elasticity* (translated by J. B. Sykes and W. H. Reid); Pergamon Press: London, 1959; pp 130–131.
- (22) Landau, L. D.; Lifshitz, E. M. *Fluid Mechanics* (translated by J. B. Sykes and W. H. Reid); Pergamon Press: London, 1959; p 49.
- (23) Stillinger, F. H. *J. Chem. Phys.* **1988**, *89*, 6461.
- (24) Stillinger, F. H.; Weber, T. A. *Phys. Rev. A* **1983**, *28*, 2408.
- (25) Stillinger, F. H. *Science* **1995**, *267*, 1935.
- (26) Shell, M. S.; Debenedetti, P. G.; Stillinger, F. H. *J. Phys. Chem. B* **2004**, *108*, 6772.
- (27) Keyes, T.; Chowdhary, J. *Phys. Rev. E* **2002**, *65*, 041106.
- (28) Korn, G. A.; Korn, T. M. *Mathematical Handbook for Scientists and Engineers, 2nd Edition*; McGraw-Hill Book Co.: New York, 1968; Sect. 18.11–4.
- (29) Stillinger, F. H. *J. Phys. Chem.* **1984**, *88*, 6494.
- (30) Kauzmann, W. *Chem. Rev.* **1948**, *43*, 219.
- (31) Debenedetti, P. G. *Metastable Liquids, Concepts and Principles*; Princeton University Press: Princeton, 1996; pp 247–253.
- (32) Debenedetti, P. G.; Stillinger, F. H.; Shell, M. S. *J. Phys. Chem. B* **2003**, *107*, 14434.
- (33) Weber, T. A.; Stillinger, F. H. *Phys. Rev. B* **1985**, *31*, 1954.
- (34) Kob, W.; Andersen, H. C. *Phys. Rev. Lett.* **1994**, *73*, 1376.
- (35) Sastry, S. *J. Phys.: Condens. Matter* **2000**, *12*, 6515.
- (36) Vogel, M.; Doliwa, B.; Heuer, A.; Glotzer, S. C. *J. Chem. Phys.* **2004**, *120*, 4404.