**Dynamic Reversals, Dynamic Heterogeneities and Stokes-Einstein Scaling in a Supercooled Molecular Liquid**

Malcolm Ramsay and Peter Harrowell

School of Chemistry, University of Sydney, Sydney NSW 2038 Australia

Abstract

xxxxxxxxxxxxxx

In this paper we present a critical re-examination of the influence of dynamic heterogeneities on the relaxation kinetics in supercooled liquids and uncover the significant role played by molecular reorientation in the curtailing dynamic reversals. As this discussion will rest on a clear statement of the existing assumptions under discussion in the literature, we shall start with a brief recap. The description of the dynamics in dense liquids has proven a persistent challenge. One potential simplification to this problem is the proposition that the dynamics is governed by a single common underlying rate. This is the essence of the Stokes-Einstein approximation where the choice is made of assuming a common microscopic *friction coefficient.* This assumption (coupled with the assumption of uncorrelated collisions), which we shall refer to as *friction scaling*, results in the following relations,

,  and  (1)

where D, η and τd are the self diffusion coefficient, the shear viscosity and the dipole rotational relaxation time, respectively. T is the temperature. All of the relations in Eq. 1 have been found to provide a reasonable description of experimental measurements in equilibrium liquids. An alternative approach is to assume that all processes are governed by a single *time scale*. This assumption, *time scaling*, leads to the following alternate set of predictions,

, , ,  and (2)

In Eq. 2, we have included the structural relaxation time τs which refers to the relaxation of density fluctuations over the length scale of the atomic diameter. Note that the constancy of Dτd is a prediction of both assumptions. If the temperature dependence of G∞ is neglected, then the scaling in Eq. 2 takes the form , a relationship that has been reported as agreeing with data from liquid metals. Relations from Eqs. 1 and 2 have also been found to reasonably describe results from computer simulation studies for equilibrium liquids.

As has been appreciated since, at least, 1991, the dynamics of supercooled liquids is described by a heterogeneous distribution of time scales whose width increases as the temperature decreases. To see how dynamic heterogeneities might effect the scaling relations, we can retain the time scaling assumption but now assign a different scaling time to each particle, i.e.

and  (3)

(Note that in Eq. 3 we have also assumed that we can meaningfully assign an instantaneous diffusion coefficient Di per particle. The validity of this assumption will be returned to below.) Averaging the relations in Eq. 3 over all the particles gives us

 and  (4)

The arithmetic mean and the harmonic mean of a distribution are only the same in the limit of a very narrow distribution and, hence, their difference will increase with the growing width of the distribution in time scales [szamel]. This would mean that, on supercooling, the scaling from Eq. 2, i.e.  would be increasingly violated with D exceeding the scaling estimation as the temperature decreases. This is qualitatively what has been observed in a number of experimental and simulation studies of supercooled liquids and the argument based on the above application time scaling and dynamical heterogeneities is widely regarded as providing the explanation of this observation. Physically, the idea is that, in averaging the mean squared displacement in the calculation of D, we weight the faster contributions more so than when we calculate <τs>. Note that a) this heterogeneous time scaling argument - there does not appear to be the analogous heterogeneous treatment of friction scaling in the literature, and b) it only effects those scaling relations involving the diffusion coefficient D.

Our goal in this paper is to examine this general picture so as to test whether the various aspects of the time scaling argument and the role of dynamic heterogeneities in a supercooled molecular liquid are correct. To this end we have introduced a model 2D molecular liquid. While the choice of 2D will certainly influence the nature of the couplings between degrees of freedom xxxxx 2D models have proved pivotal in the development of ideas about dynamics and dynamic heterogeneities we would like to test this general picture of scaling violations and the role of dynamic heterogeneities in accounting for this violation.

For this study we have chosen a 2D liquid comprised of an anisotropic trimer constructed with a central particle, *c*, to which two end particles, *e*, are affixed with a fixed distance Dce between centre and end particles. The angle between the two c-e bonds is set to 120o (see Fig. 1). Each site interacts with sites on other molecules by a Lennard-Jones interaction  where ε = 1.0 and σcc = 2.0, σee = 1.275112 and σce = (σcc + σee)/2, where the subscripts *c* and *e* stand for the centre site and an end site, respectively. The mass of each site is set to 1.0 (so the molecular mass is 3.0). We set the distance Dce = σcc/2. Molecular dynamics simulations were carried under fixed pressure and temperature using the HOOMD-blue programs [44] with the pressure and temperature maintained using the Martyna-Tobias-Klein equations of motion [45]. We work in the following reduced units: length in units of σ­cc/2 (i.e. we set σ­cc/2 = 1.0), time in units of , temperature in units ε/kB and pressure in units of . For all calculations the reduced pressure P = 13.5 and the system size is N = 1250 (unless otherwise specified).



**Figure 1.** The shape parameters for the trimer particle.

Let’s start by defining structural relaxation as the translation of a particle’s centre of mass a distance 0.4 or greater from its initial position so that the relaxation time for each particle can be defined as the 1st passage time τ0.4. (A more general description of structural relaxation would include the role of rotations as well but the proposed translational definition is best suited for the purposes of this paper.) We can define a relaxation function F(t) as the fraction of particles whose centre of mass remains within 0.4 the initial position after time t. An average structural relaxation time τs can be defined as F(τs)=1/e. In Fig. 2 we plot both τs and <τ0.4> vs 1/T and find that they are very similar over the entire temperature range studied. The self diffusion coefficient is obtained by xxxxxxxx where the displacements refer to those of the centre of mass of the molecule.

**Fig. 2 τs and <τ0.4> vs 1/T Inset: F(t) vs t for a range of T**

**Fig. 3 Plot of D<τ0.4>, D<1/τ0.4>-1 , <D><τL> and <τ0.4><1/τ0.4> vs 1/T**

As shown in Fig. 3, our molecular liquid exhibits a large increase in heterogeneity as indicated by the rise in <τ0.4><1/τ0.4> as T decreases. We also find D<τ0.4> is not constant with respect to T – i.e. simple time scaling fails as we would expect from our linkage between simple scaling and heterogeneity. The problem is that D is *smaller* than that predicted by simple scaling, the opposite expected from Eq. 3. According to heterogeneous time scaling D should vary as <1/τs> but, as shown in Fig. 1, it clearly does not. So the heterogeneous time scaling assumption also fails - but what could be wrong with the intuition that the fast particles will increase D more than they will decrease <τ0.4>?

The relaxation time τ0.4 is associated with a significant displacement, one large enough to contribute to the decorrelation of structure in the liquid. This structural significance, however, does not ensure that such a displacement cannot be subsequently reversed. If the 1st passage is regularly reversed then it means that the associated time scale is of little relevance to transport. To explore this possibility we shall define a ‘last’ passage time τL as the time interval before a particle achieves a escape from its initial volume that persists for at least a threshold time, here chosen to be xxxx. By definition . What is not clear is how this relationship depends on the magnitude of τs. In Fig.4 we plot the probability of reversal within the threshold time as a function of τs . We find that the reversal probability higher for small τs than for large τs resulting in the two times exhibiting quite different distributions and temperature dependencies.

**Figure 4. The probability of reversal within the threshold time as a function of the 1st passage time τs at a low T. Inset: A plot of <τs>, <τL> and <τR> as a function of 1/T.**

As shown in Fig. 3, a new scaling relation is found to roughly hold across the entire studied temperature range. The fact that diffusion is determined by the time scale for translations to have escaped reversals [question – even random walks have a probability of reversal – what is different here?] is perhaps not surprising, at least in hindsight. What is less obvious is why doesn’t the structural relaxation exhibit a similar dependence on the time scale for persistent escapes. To understand this difference we must re-emphasise the point that these reversals are not just simple vibrational motions – the threshold amplitude is well beyond the validity of the harmonic approximation. The particles that have passed beyond the threshold distance can persist out there for a time less than our threshold only to be returned. The growth of the populations of these particles in limbo is large enough to result in relaxation as measured by F(t). Here, then, we reach our first major conclusion. The primary reason for the breakdown of the scaling prediction in Eq. 2 is not the intervention of dynamic heterogeneities, although they are present, but the breakdown of the time scaling assumption itself. There is no single time scale governing both structural relaxation and diffusion, even locally. As we have shown, these processes are governed by two distinct time scale <τ0.4> and <τL>, respectively. The growing difference between these times may well share a common cause with dynamic heterogeneities {xx we should plot this} so that the development of multiple time scales may occur simultaneously with DH.

How is that reversals of translations are still probable after such a significant displacement? We shall argue that the likelihood of reversals in molecular liquids is dependent on the reorientation of the molecule. A fast translation can presumably only occur if it can occur without significant reorientation. That means that even after moving the structural relaxation length, the persistent orientation of the molecule serves as a structural memory and facilitates the reversal of the translation. If this picture is correct, the rotational relaxation time should vary with T in the same manner as <τL>. This is indeed what we find (see Fig.5 Inset). This suggests that the rotational relaxation time represents the essential ‘irreversible’ step … a rare large amplitude rearrangement. As shown in Fig. 1, we recover something resembling our simple scaling result with the relations

D<τL> or D<τR>.

Note that the success of the latter scaling does not imply any kinematic coupling between translations and rotations. It occurs, as we have demonstrated, from the significance of ‘irreversible’ motions to both degrees of freedom. *[can we simply expand out configuration space to include the rotation?]*

**Figure 5. The distribution of angular displacements at τs and τL.Inset: Angle as a function of time for a collection of individual particle trajectories. Large reorientations occur as jumps?**

Having argued against the involvement of the heterogeneous time scaling argument in accounting for the failure of the Dτs scaling, there remains the problem of accounting for the observed D<τL> scaling. The distribution of the last passage times τL is even broader than that of the 1st passage times, so why doesn’t the heterogeneous argument apply here? Why isn’t the scaling D<1/τL>-1 as predicted by the heterogeneous time scaling?

A problem with the heterogeneous time scale argument is that it is based on an instantaneous distribution of time scales while the diffusion constant is measured over some finite time interval. A given heterogeneous ‘assignment’ of a time scale to a particle persists for some characteristic time τmix before the environment changes sufficiently to sample a new time. If our observation time is long relative to τmix it is impossible for the heterogeneities to influence the value of D since the particle has sampled a sufficient number of kinetic environments such that it inly ‘sees’ the average.

We can express the relationship between the time averaging along a trajectory and the averaging of different particles as follows. In general 

if t < τmix then  as has been suggested previously

if t > τmix  and a simple scaling is retained

**Figure 6. A scatter plot of the average value of τL averaged over n consecutive events as a function of n. Also plotted is the average <τL> taken over all particles in the system.**

In Fig. 6 we have established that τL averaged over n transitions has essentially recovered the ensemble average <τL>. These jumps correspond to an average particle displacement of ????. Diffusion constant measured over distances of at least this distance do not ‘see’ the dynamic heterogeneities since they have sampled enough of the distribution of dynamic environments during the observation time to have effectively averaged them out. In general, dynamic heterogeneities do not affect transport coefficients when measured over time scales longer than the lifetime of the heterogeneities.

In conclusion

- the failure of the scaling Dτs is not the result of dynamic heterogeneities. Rather it is a consequence of the failure of the assumption that a single (local) time governs diffusion and structural relaxation. The difference between the two times is a result of the increasing capacity of the supercooled liquid to induce reversal of motions, even after displacements large enough to contribute to structural relaxation.

- in the molecular liquid, this capacity for reversals is linked to rotational relaxation in the sense that, until a molecule has undergone a substantial reorientation, its retention of the initial orientation serves as a repository of structural memory facilitating reversal. It is through this link between reorientation and ‘irreversible’ translation that we find the scaling DτR holds – it is not a result of any direct kinematic coupling between the two types of motion.

- Finally, the heterogeneous time scale argument is only applicable to transport processes measured over time scales shorter than the dynamic mixing time. Failure of time scaling for transport coefficients measured over longer times require an alternate explanation. The advent of multiple times scales through persistent reversals represents just such an alternate explanation.