Glass-forming Liquids and Polymers:
With a Little Help from Computational Statistical Physics

S. C. Glotzer[1*], Y. Gebremichael[1], N. Lacevic[1], T.B. Schrøder[2] and F.W. Starr[3]

[1]*Departments of Chemical Engineering and Materials Science and Engineering,
University of Michigan, Ann Arbor, 48109*
[2]*IMFUFA, Roskilde University, DK-4000 Roskilde, Denmark*
[3]*Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*

Submitted August 18, 2001

The past decade has seen a resurgence in the study of the glass transition, particularly using computational approaches. Advances in computer architectures and algorithms have allowed the study of larger system sizes for longer time scales, which has enabled computational scientists to explore both new aspects of supercooled liquids, glasses, and the glass transition, as well as to re-investigate old puzzles.

One aspect of these systems in particular that is currently receiving a great deal of attention, and which has seen progress in part due to the use of computational statistical physics, is the elucidation of the detailed molecular motion and how this motion changes as a liquid approaches the glass transition. In particular, simulation has led to the discovery of dynamical, ordered structures within the disordered, glass-forming liquid [1-10].

It has long been known that despite the similarity in structure of a liquid and its glass, relaxation times, diffusivities and viscosities change by up to 14 orders of magnitude as a liquid is cooled through its glass transition. Why the dynamics can change so dramatically while static structure seemingly changes so little has been a longstanding, open question in the field of glass research. Clearly, molecular motion becomes increasingly difficult as the temperature or specific volume decreases, but how precisely does the motion change, and why does this change lead to such long relaxation times? Mode coupling theory (MCT) provides a partial answer to this question for the initial approach to the glass transition; that is, for temperatures where diffusivities are still orders of magnitude higher than at T_g [11] The theory makes specific predictions for the slowing down of fluids from their equilibrium structure, which hold asymptotically near a crossover temperature T_{mct}, which is typically 1.1 to 1.5 times higher than T_g. In hard-sphere, colloidal suspensions, where $T_c \approx T_g$, MCT is able to describe the dynamics closer to T_g. However, the theory in its current form does not provide spatial information revealing how the dynamics change *locally* in a fluid as it is cooled, nor does it specify how molecular motion occurs.

Many clues abound that point to a dramatic change in the mechanism of molecular motion in cold, dense liquids. One example is provided by the intermediate scattering function $F(q,t)$, which measures the decay of density fluctuations and can be obtained directly by neutron spin echo experiments or through a Fourier transform of the dynamic structure factor $S(q,\omega)$. At high temperature T, this function decays exponentially in time. At lower T and or larger density ρ, it

---

* Email: sglotzer@umich.edu

develops a plateau at intermediate times, and at longer times decays as a stretched exponential with a characteristic time τ_α that grows rapidly with decreasing T [12]. The plateau indicates the temporary localization or "caging" of molecules, and can also be observed in a plot of the mean squared displacement vs. time [13]. Both the appearance of the plateau and the non-exponential decay indicate an increasing complexity in the fluid dynamics   MCT, which is a theory based on the caging of molecules and on the collective motions associated with caging, describes well much of the behavior of F(q,t) above T_{mct} [12, 14-17].

Another dramatic indication of a change in molecular mechanism in equilibrium liquids on cooling is provided by the relationship between translational and rotational diffusivity and viscosity. At high T, these transport coefficients are related by the Stokes-Einstein (SE) and Stokes-Einstein-Debye (SED) relations. At sufficiently low T, the SE relation breaks down, and the diffusion coefficient of a probe in the fluid is higher (in some instances, by several orders of magnitude) than would be predicted by the viscosity from the SE relation [18-21]. This so-called "decoupling" of transport coefficients demonstrates a breakdown of continuum hydrodynamics, and an increasing complexity in the fluid dynamics [22, 23].

Through a combination of 4D-NMR experiments, optical photobleaching, flourescence and solvation spectroscopy experiments, dielectric hole burning experiments, and computer simulations, there is an abundance of evidence that both stretched exponential relaxation and the decoupling of transport coefficients can be rationalized if glass-forming liquids are *spatially heterogeneous in their dynamics* (SHD) [19, 23-25]. Indeed, we now believe that as the glass transition approaches, particle (or molecule) motion becomes strongly correlated over increasingly larger distances. This leads to an emergence of increasing dynamical order in the fluid, and to the appearance of large-scale fluctuations in the local molecular mobilities.

Computational statistical physics is helping us to describe these spatiotemporal fluctuations in the local mobilities, as well as to elucidate the precipitating events that we believe initiate high mobility regions. In particular, computational statistical physics has allowed us to make specific predictions regarding the nature of these regions [1-7], including their size, shape, and dynamical character ---- predictions that have now been confirmed in experiments [26-29].

Two of the most often used models for studying the dynamics of glass-forming liquids and polymers are the binary mixture and bead-spring model, respectively. We have investigated correlated particle motion in molecular dynamics simulations of two different binary mixtures – the 80:20 mixture of Kob-Anderson (KA), and a 50:50 mixture, both containing 8000 particles. In both models, the interaction parameters are chosen to prevent phase separation and crystallization. We have also studied the dynamics of a polymer melt described by a bead-spring model, where again the interaction parameters are chosen to prevent crystallization. In this system, we simulate roughly 120 chains of 10 monomers each, short enough that the melt is unentangled. The details of our simulations are discussed elsewhere [1-7]. In all systems, we perform simulations in the NVE or NVT ensembles at many different state points, in equilibrium above or at the mode-coupling temperature T_c. Typically, $T_c \approx 1.1\text{-}1.5\ T_g$ in these models. Our longest simulations span more than 10^8 MD steps, or tens to hundreds of nanoseconds per run in Argon units.

By visualizing the raw data from the simulation and watching the motion of individual particles (monomers in the case of the melt), it is immediately apparent that at temperatures below that corresponding to the onset of caging, particle motion becomes "intermittent" [13]; in any given time interval, most of the particles are localized in cages formed by their neighbors, and only a handful (between 5 and 12%) escape from their cages at a time [1, 30]. It is also obvious from watching the simulation that below the "onset" temperature, particles escape from their cages in "groups" or "clusters", and thus molecular motion becomes spatially correlated (heterogeneous) on cooling. Thus over long times, many particles remain fixed relative to their initial position, and within this "immobile" matrix emerge "fluidized patches" within which particles move [23]. It is also immediately evident from the simulation that the number of particles involved in a typical cluster grows with decreasing T, indicating the growing range of spatially heterogeneous dynamics on cooling.

This heterogeneity can be quantified using methods from percolation theory and by constructing suitable correlation functions, such as displacement-displacement correlation functions and four-point, time-dependent density correlation functions liquid [1-10]. Different statistical quantities highlight different aspects of dynamical heterogeneity; some focus on the mobile regions, and some on the immobile regions, of the fluid.

For example, spatially heterogeneous dynamics can be easily observed by comparing snapshots of a glass-forming liquid at two different times, provided the time interval between them is not so short that particle motion is ballistic (in the case of atomic, molecular or polymeric fluids), and not so long that particle motion is diffusive. Confocal microscope images of suspensions of effectively hard-sphere colloids can be used for this purpose, and the "difference" between two snapshots separated by a timescale in the plateau region indicates regions of "activity" and "inactivity"; that is, regions where particles appear not to have moved from their initial positions, and regions where rearrangement has taken place. From these snapshots, it is possible to construct a correlation function $g_4(r,t)$ and corresponding generalized susceptibility $\chi_4(t)$ related to the fluctuations in the number $Q(t)$ of "overlapping" particles; that is, particles which appear not to have moved during the time interval of the comparison [9, 31-34]. These quantities have been calculated in simulations, and show that the fluctuations in $Q(t)$ depend on the time interval of observation, peak near the α-relaxation time τ_α, and increase rapidly with decreasing T [9, 33, 34]. Correspondingly, the correlation function $g_4(r,t)$ of overlapping particles develops increasing structure, and increasing range, with decreasing T [34]. Thus a correlation length associated with overlapping particles can be measured directly in simulations and in microscopy studies of colloidal suspensions. Our simulations predict that this length begins to increase below the temperature corresponding to the onset of caging, and continues to increase rapidly on cooling or densification. Theoretical calculations support the simulation predictions, and due to the mean-field nature of the calculations predict a diverging length scale at $T_{mct.}$ [32, 33].

The overlapping particles described above are dominated by localized particles, but a simple replacement of Q by 1-Q in the theory essentially transforms localized regions into delocalized regions and vice versa [9]. To gain further insight into the dynamically heterogeneous nature of these liquids, and to specifically explore the high-mobility fluctuations, correlations functions of particles that incorporate the scalar or vector displacement can be used. We constructed such a correlation function whose corresponding generalized susceptibility is proportional to the

fluctuations in the total system displacement U in a given time interval [4, 35]. By construction, the correlation function is most heavily weighted by particles with large displacements. The susceptibility $\chi_U(t)$ and corresponding correlation function $g_U(r,t)$ display qualitatively the same time-dependent and temperature-dependent behavior as $\chi_4(t)$ and $g_4(r,t)$, but peak and have the longest range, respectively, at a time in the late beta/early-alpha relaxation regime; i.e. at a time that precedes, and scales with T differently than, τ_α. This suggests that many high mobility fluctuations – that is, spatially correlated particle rearrangements – are necessary for structural relaxation. In both the 80:20 LJ mixture and the polymer melt, $\chi_U(t)$ is well fitted by a power law with singular temperature $T_c = T_{mct}$. Although we do not necessarily expect a true divergence of the susceptibility or correlation length at T_{mct}, the behavior of the data demonstrates the rapidity with which these regions grow. Whether these quantities cross over to slower growth below T_{mct}, become constant, or even shrink will require further investigation of substantially lower T simulations, which currently poses a substantial computational challenge because of the prohibitively long relaxation times required to properly equilibrate the liquid.
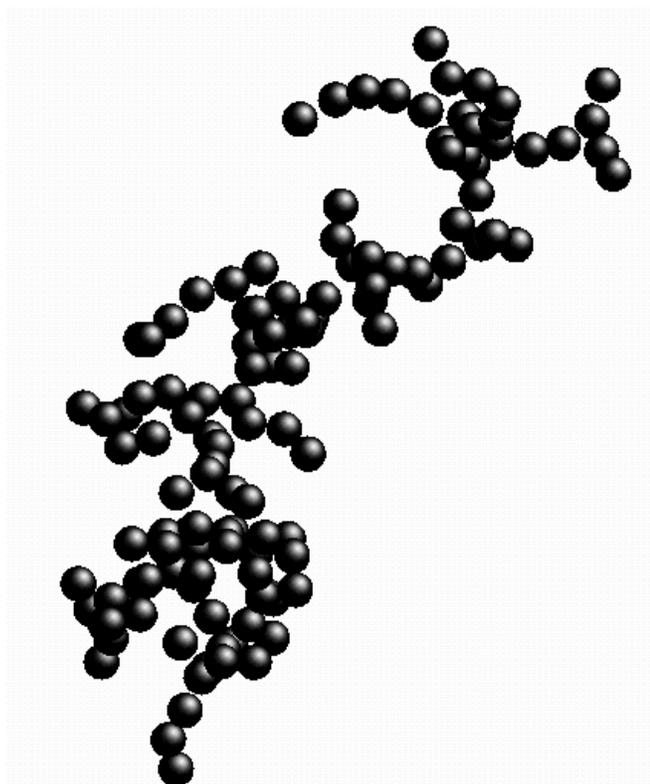
Figure 1. Example of a large cluster of particles in the 80:20 LJ liquid imaged from the subset of particles that exhibit the largest displacement in a time interval near the end of the plateau (caging) regime. The cluster is composed of many individual sub-groups of particles that move coherently in one-dimensional "strings", where each particle moves nearly one particle diameter in the direction of its highly mobile neighbor The actual motion within a string is relatively fast, and thus different strings within a single cluster may be "active" at different times. From [3].

To further characterize the nature of the mobile regions of glass-forming liquids, we have performed detailed studies of the clustering of highly mobile particles (i.e., particles that, in a

given time interval, exhibit the largest scalar displacement) [3, 5, 6, 30]. We find that these particles form non-compact, highly ramified clusters whose size depends on the time interval of observation (Figs. 1 and 2). This behavior is consistent with the time-dependent behavior of the susceptibilities $\chi_4(t)$ and $\chi_U(t)$. Notably, the largest clusters are observed at a characteristic time which scales with T like the MCT β-relaxation timescale τ_ε [30]. The cluster size distribution approaches a power law as $T \to T_{mct}^+$ with an exponent near two, and the mean cluster size grows rapidly; in the polymer system, the maximum weight-average cluster size grows from roughly two to nearly 20 monomers over the range of T studied. Depending on the system, we have found both power laws and Vogel-Fulcher expressions fit the data well. It is important to note that in all systems studied, and at any given {T,ρ}, *a highly mobile subset of particles can be found that maximizes the mean cluster size*. Depending on T, this subset constitutes between roughly 5 and 12% of the total particles in the system [30].
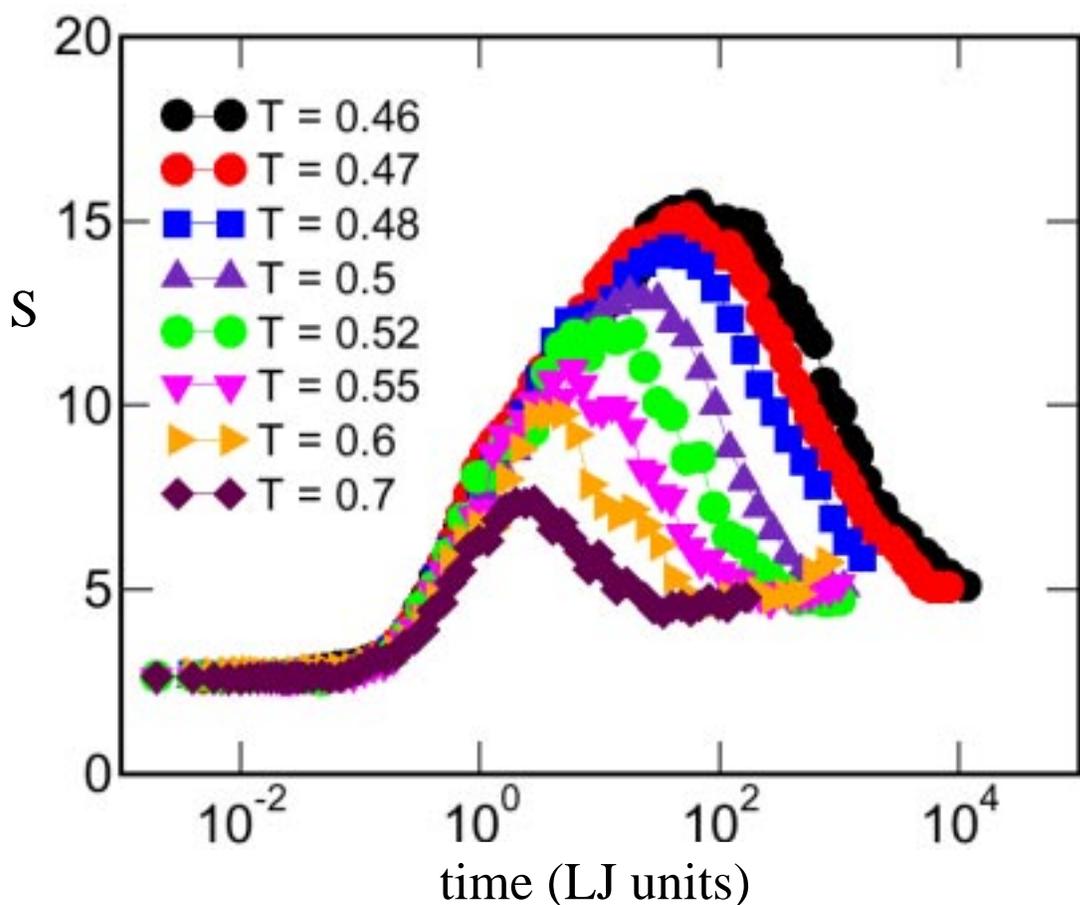

Figure 2. Weight-averaged cluster size S plotted vs. time for different state points as indicated. Data obtained from a simulation of a bead-spring polymer melt. At short times, the mean cluster size is given by the value corresponding to grouping nearest neighbor particles from a randomly chosen subset of monomers (subset contains 6.5% of the total number of monomers). At later times, the monomers within the subset become increasingly spatially correlated, as indicated by the increasing value of S. Beyond the peak time, monomer motion becomes less spatially correlated, as indicated by the decreasing value of S at late times. In the diffusive regime (not shown), S again equals the random value. [30]

.

Upon closer inspection, we find that within any group of mobile particles, smaller subsets move together coherently, following each other to form a quasi-one-dimensional "string" [2]. In the case of the 80:20 LJ mixture, these strings have an exponential length distribution, with an average size that grows slowly with decreasing T. If fitted by a power law over the relatively narrow range of temperatures simulated, the average string length would appear to diverge at a temperature near the Kauzmann temperature, significantly outside the range of our simulations [7].

These strings likely represent the fundamental particle motions underlying the back-flow process on which mode-coupling theory is based. Additionally, they may represent the cooperative groups envisioned by Adam and Gibbs. It appears that these strings are not perfectly coherent in the T range of our simulations, in that they do not perfectly replace other particles. If they did, these string-like motions would not contribute directly to the decay of density fluctuations, since the system before and after a perfectly coherent, string-like rearrangement would be identical. Instead, the strings appear to facilitate the motion of their neighbors by perturbing the neighborhood around them. This idea is supported by studies of transitions between basins of the potential energy landscape, which at and below T_{mct} appear to be facilitated by the string-like motion of large groups of particles, which accompany many small displacements of surrounding particles [10]. Thus clusters of highly mobile particles as discussed above consist of both strings and particles whose motion is facilitated by strings. As T decreases, more and more mobile particles appear to move in strings [2].

Simulations clearly indicate the presence of a rapidly growing dynamical correlation length, despite the absence of a significantly growing static correlation length. However, the local dynamics of a molecule should be related in some way to the structure of its neighborhood. Preliminary results [36] indicate a positive correlation between the Voronoi volume of a particle and its mobility, so that the larger the volume, the larger the mobility, in agreement with previous studies. This result is consistent with previous findings that highly mobile particles tend to have a larger potential energy before becoming mobile [3], implying that the immediate neighborhood around a particle may become slightly expanded just prior to motion. Detailed investigations of this are ongoing [36].

With some help from simulation, the spatially heterogeneous nature of the dynamics of glass-forming liquids is now clearly established, but many open questions remain, and many connections remain to be made between the different phenomena that accompany the glass transition. Presumably, the increasing dynamical correlation length – which corresponds to the distance over which particle motion is correlated – is responsible for the increasing relaxation times that plague liquids as they are cooled. Indeed, the correlation length associated with "overlapping" regions of the fluid appears to be largest at a time that scales with T like the structural α-relaxation time. Can a revised mode coupling theory, which includes higher order density correlations and goes beyond the usual Gaussian approximation, predict our results? How universality is spatially heterogeneous dynamics; for example, does the presence or details of SHD depend on the fragility of the glass-former? How do the length scales observed in the

simulation of simple model liquids map onto real systems, or more realistic (i.e. atomistic) simulations? How are the mobility fluctuations observed in simulations above T_{mct} related to those observed in experiments near T_g? The growing mobility fluctuations in glass-forming liquids are reminiscent in some respects of growing density fluctuations in liquids near critical points; how useful is such an analogy? Are string-like rearrangements related to the Boson peak? What happens to spatially heterogeneous regions in liquids quenched to the glass state? Do high mobility regions become trapped in the glass, and govern aging, creep, shear banding, etc? What about supercooled liquids prior to nucleation and growth of the crystal phase? Are their dynamics spatially heterogeneous, and, if so, what are the ramifications for theories of nucleation? Are force chains present in glass-forming liquids with attractive interactions, and how are these structures related, if at all, to SHD? Can we use information on cooperative or correlated dynamics to construct acceleration algorithms for glassy systems, especially at low T where dynamics may be dominated by rare events? Computational statistical physics will help to answer some of these questions, and will continue to make important contributions to the general understanding of liquids and the glass transition.

1.   Kob, W., C. Donati, S.J. Plimpton, P.H. Poole, and S.C. Glotzer, *Dynamical heterogeneities in a supercooled Lennard-Jones liquid.* Physical Review Letters, 1997. **79**(15): p. 2827-2830.

2.   Donati, C., J.F. Douglas, W. Kob, S.J. Plimpton, P.H. Poole, and S.C. Glotzer, *Stringlike cooperative motion in a supercooled liquid.* Physical Review Letters, 1998. **80**(11): p. 2338-2341.

3.   Donati, C., S.C. Glotzer, P.H. Poole, W. Kob, and S.J. Plimpton, *Spatial correlations of mobility and immobility in a glass- forming Lennard-Jones liquid.* Physical Review E, 1999. **60**(3): p. 3107-3119.

4.   Donati, C., S.C. Glotzer, and P.H. Poole, *Growing spatial correlations of particle displacements in a simulated liquid on cooling toward the glass transition.* Physical Review Letters, 1999. **82**(25): p. 5064-5067.

5.   Gebremichael, Y., T.B. Schroeder, and S.C. Glotzer, *Clustering of cooperatively moving monomers in a glass-forming polymer liquid.* Abstracts of Papers of the American Chemical Society, 2000. **220**: p. 412-PHYS.

6.   Glotzer, S.C. and C. Donati, *Quantifying spatially heterogeneous dynamics in computer simulations of glass-forming liquids.* Journal of Physics-Condensed Matter, 1999. **11**(10A): p. A285-A295.

7.   Glotzer, S.C., *Spatially heterogeneous dynamics in liquids: insights from simulation.* Journal of Non-Crystalline Solids, 2000. **274**(1-3): p. 342-355.

8.   Bennemann, C., C. Donati, J. Baschnagel, and S.C. Glotzer, *Growing range of correlated motion in a polymer melt on cooling towards the glass transition.* Nature, 1999. **399**(6733): p. 246-249.

9. Glotzer, S.C., V.N. Novikov, and T.B. Schroder, *Time-dependent, four-point density correlation function description of dynamical heterogeneity and decoupling in supercooled liquids.* Journal of Chemical Physics, 2000. **112**(2): p. 509-512.

10. Schroder, T.B., S. Sastry, J.C. Dyre, and S.C. Glotzer, *Crossover to potential energy landscape dominated dynamics in a model glass-forming liquid.* Journal of Chemical Physics, 2000. **112**(22): p. 9834-9840.

11. Bengtzelius, U., W. Gotze, and A. Sjolander, *Dynamics of Supercooled Liquids and the Glass-Transition.* Journal of Physics C-Solid State Physics, 1984. **17**(33): p. 5915-5934.

12. Kob, W. and H.C. Andersen, *Testing Mode-Coupling Theory for a Supercooled Binary Lennard- Jones Mixture - the Van Hove Correlation-Function.* Physical Review E, 1995. **51**(5): p. 4626-4641.

13. Allegrini, P., J.F. Douglas, and S.C. Glotzer, *Dynamic entropy as a measure of caging and persistent particle motion in supercooled liquids.* Physical Review E, 1999. **60**(5): p. 5714-5724.

14. Bennemann, C., W. Paul, J. Baschnagel, and K. Binder, *Investigating the influence of different thermodynamic paths on the structural relaxation in a glass-forming polymer melt.* Journal of Physics-Condensed Matter, 1999. **11**(10): p. 2179-2192.

15. Bennemann, C., J. Baschnagel, and W. Paul, *Molecular-dynamics simulation of a glassy polymer melt: Incoherent scattering function.* European Physical Journal B, 1999. **10**(2): p. 323-334.

16. Bennemann, C., J. Baschnagel, W. Paul, and K. Binder, *Molecular-dynamics simulation of a glassy polymer melt: Rouse model and cage effect.* Computational and Theoretical Polymer Science, 1999. **9**(3-4): p. 217-226.

17. Bennemann, C., W. Paul, K. Binder, and B. Dunweg, *Molecular-dynamics simulations of the thermal glass transition in polymer melts: alpha-relaxation behavior.* Physical Review E, 1998. **57**(1): p. 843-851.

18. Deppe, D.D., R.D. Miller, and J.M. Torkelson, *Small molecule diffusion in a rubbery polymer near T-g: Effects of probe size, shape, and flexibility.* Journal of Polymer Science Part B-Polymer Physics, 1996. **34**(17): p. 2987-2997.

19. Ediger, M.D., *Spatially heterogeneous dynamics in supercooled liquids.* Annual Review of Physical Chemistry, 2000. **51**: p. 99-128.

20. Sillescu, H., *Translation-rotation paradox for diffusion in fragile glass- forming liquids - Comments.* Physical Review E, 1996. **53**(3): p. 2992-2994.

21. Hall, D.B., A. Dhinojwala, and J.M. Torkelson, *Translation-rotation paradox for diffusion in glass-forming polymers: The role of the temperature dependence of the relaxation time distribution.* Physical Review Letters, 1997. **79**(1): p. 103-106.

22. Stillinger, F.H. and J.A. Hodgdon, *Translation-Rotation Paradox for Diffusion in Fragile Glass- Forming Liquids.* Physical Review E, 1994. **50**(3): p. 2064-2068.

23. Stillinger, F.H., *Shear viscosity and diffusion in supercooled liquids*, in *Supercooled Liquids*. 1997. p. 131-139.

24. Sillescu, H., *Heterogeneity at the glass transition: a review.* Journal of Non-Crystalline Solids, 1999. **243**(2-3): p. 81-108.

25. Bohmer, R., R.V. Chamberlin, G. Diezemann, B. Geil, A. Heuer, G. Hinze, S.C. Kuebler, R. Richert, B. Schiener, H. Sillescu, H.W. Spiess, U. Tracht, and M. Wilhelm, *Nature of the non-exponential primary relaxation in structural glass-formers probed by dynamically selective experiments.* Journal of Non-Crystalline Solids, 1998. **235**: p. 1-9.

26. Weeks, E.R., J.C. Crocker, A.C. Levitt, A. Schofield, and D.A. Weitz, *Three-dimensional direct imaging of structural relaxation near the colloidal glass transition.* Science, 2000. **287**(5453): p. 627-631.
27. Kegel, W.K. and A. van Blaaderen, *Direct observation of dynamical heterogeneities in colloidal hard-sphere suspensions.* Science, 2000. **287**(5451): p. 290-293.
28. Russina, M., E. Mezei, R. Lechner, S. Longeville, and B. Urban, *Experimental evidence for fast heterogeneous collective structural relaxation in a supercooled liquid near the glass transition.* Physical Review Letters, 2000. **84**(16): p. 3630-3633.
29. Glotzer, S., *Colloids Reinforce Glass Theory.* Physics World, 2000(April): p. 22-23.
30. Gebremichael, Y., F. Starr, T. Schroeder, and S. Glotzer, Physical Review E, In press.
31. Dasgupta, C., A.V. Indrani, S. Ramaswamy, and M.K. Phani, *Is There a Growing Correlation Length near the Glass-Transition.* Europhysics Letters, 1991. **15**(3): p. 307-312.
32. Franz, S., C. Donati, G. Parisi, and S.C. Glotzer, *On dynamical correlations in supercooled liquids.* Philosophical Magazine B-Physics of Condensed Matter Statistical Mechanics Electronic Optical and Magnetic Properties, 1999. **79**(11-12): p. 1827-1831.
33. Donati, C., S. Franz, S. Glotzer, and G. Parisi, preprint.
34. Lacevic, N., T. Schroeder, F. Starr, V. Novikov, and S. Glotzer, preprint.
35. Poole, P.H., C. Donati, and S.C. Glotzer, *Spatial correlations of particle displacements in a glass- forming liquid.* Physica A, 1998. **261**(1-2): p. 51-59.
36. Starr, F., S. Sastry, J. Douglas, and S. Glotzer, in preparation.