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Journal of Non-Crystalline Solids 274 (2000) 342–355

JOURNAL OF
NON-CRYSTALLINE SOLIDS

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Spatially heterogeneous dynamics in liquids: insights from simulation

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Abstract

In this paper, review of recent theoretical and simulation work on dynamical heterogeneity and correlated particle motion in glass-forming liquids and polymers is presented. Evidence for increasing mobility fluctuations in these systems with decreasing temperature, and the relationship between dynamical heterogeneity and decoupling of diffusion and structural relaxation is described. The relationship between dynamical heterogeneity, string-like collective motion, the clustering of strings, and mode-coupling theory is briefly discussed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The existence of spatially heterogeneous local dynamics ('dynamical heterogeneity') in otherwise structurally homogeneous liquids approaching their glass transition is now well established in experiments and simulations. Multi-dimensional nuclear magnetic resonance spectroscopy (NMR) [1–12], optical photobleaching [13–16], non-resonant spectral hole burning [17,18], and other experiments [19] carried out over the past decade on atomic, molecular, and polymeric liquids close to the glass transition temperature, T_g , show that it is possible to select subsets of molecules that rotate or translate farther or shorter distances than the average distance traveled by a molecule, on time scales on the order of the structural relaxation time of the liquid [20–22]. Although the mere fact that it

is possible to distinguish a subset of molecules in this fashion suggests the possibility that these molecules are spatially correlated into domains, no direct spatial information is provided by these experimental approaches [21,22].

Computer simulations of equilibrium model glass-forming liquids and polymers provide direct access to the spatial correlation of the motion of particles, but unlike experiments they have thus far been restricted to temperatures greater than the mode-coupling temperature, T_c [23–27], simply because of the long equilibration times (order of nanoseconds) near T_c and below. Molecular dynamics (MD) simulations of soft-spheres [28–33], hard-spheres [34], Lennard–Jones mixtures [35–42] and polymer melts [43,44] in both two and three dimensions carried out over the past several years by various groups have considered dynamical heterogeneity at temperatures and densities ranging from where caging of the particles first appears, to where time scales have increased by several orders of magnitude. These simulations

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have thus considered the initial approach to the glass transition, i.e., on the range of temperature and density reasonably well described by the ideal mode-coupling theory. Thus, an important open question remains as to how the spatially heterogeneous dynamics observed in simulations is related to that observed experimentally, where the relaxation times are many orders of magnitude larger. In principle, the dynamical heterogeneity observed above T_c may be a ‘weaker’ but similar version of low- T dynamical heterogeneity, or it may be very different; in either case, the high- T dynamical heterogeneity revealed in simulations is certainly a precursor to whatever happens closer to the glass transition.

An exciting opportunity for investigating dynamical heterogeneity, testing the predictions of simulations, and providing a potential bridge between the computationally and experimentally observed dynamical heterogeneity in atomic, molecular and polymeric liquids, lies in new confocal microscopy experiments on dense colloidal suspensions [45–47]. Colloids are ideal experimentally realizable models for atomic liquids because they undergo Brownian motion and obey the laws of statistical mechanics. Hard-sphere colloids in particular obey many key predictions of the ideal mode-coupling theory [48–54]. With confocal microscopy, it is possible to track the motion of individual nanometer- to micron-sized colloidal particles at densities approaching the glass transition density (which for hard-sphere colloids coincides with the ideal mode-coupling density, ϕ_c [48–54]), and thereby investigate correlated particle motion directly in real space. As these experiments produce precisely the same type of raw data produced by MD simulations, the same real-space probes of dynamical heterogeneity can be calculated in experiment and simulation and compared directly.

In this paper, we briefly review some of our main findings from our investigation of dynamical heterogeneity in MD simulations of equilibrium model glass-forming liquids and polymer melts [37–42,44]. We have studied three glass-forming liquids: an 80:20 Lennard–Jones (LJ) binary mixture [39], a 50:50 Lennard–Jones binary mixture [42], and a LJ–FENE bead-spring model of a low

molecular weight polymer liquid [44], all in three spatial dimensions. Details of the simulations of each system may be found in the indicated references. For each system, particle (or monomer) trajectories were calculated in the NVE or NVT ensemble following equilibration at temperatures above and approaching the mode-coupling temperature, T_c . Gigabytes of trajectory data were then stored for subsequent analysis, as described below. All values quoted here are in LJ units.

2. Establishing dynamical heterogeneity: clustering of mobile particles

Identifying subsets of mobile particles; spatial correlations of mobile and immobile particles; cluster analysis; power-law cluster size distributions; a possible percolation transition near T_c .

Dynamical heterogeneity in glass-forming liquids can be easily observed by simply monitoring the displacements of particles (or monomers) in the liquid within some time interval, Δt , and coloring particles according to how far they have moved. As shown in Fig. 1, for a supercooled polymer liquid, monomers moving the farthest (light) or shortest (dark) distance tend to cluster together provided the time window of observation has exceeded the ballistic regime, but is short compared to the time required for structural relaxations to decay to zero (i.e., within or immediately after the plateau regime in the mean-square displacement). That the local dynamics become spatially correlated appears to be a natural result of ‘caging’ or temporary localization of particles, and the subsequent breaking up of cages in these dense fluids. At higher temperatures or lower densities, where no caging and hence no plateau in the mean-square displacement or intermediate scattering function is observed, particle mobility is observed to be randomly distributed through the sample. At all temperatures, of course, all particles eventually move in a statistically identical fashion.

As has been shown in many supercooled liquids, the self van Hove correlation function, $G_s(r, t)$, becomes non-Gaussian for times in the caging (or plateau) regime, and has a long tail extending to large particle displacements

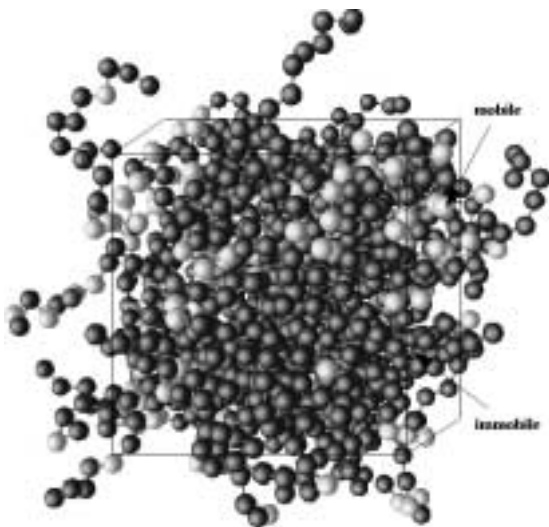


Fig. 1. Snapshot of a simulated equilibrium glass-forming polymer melt at $T = 0.47$, just above the ideal mode-coupling temperature $T_c = 0.451$ [44]. Periodic boundary conditions were used in the MD simulation, and polymers at the edges of the box were 'unfolded' so as to retain chain connectivity in the picture. Monomers have been colored according to the scalar displacement traveled in a time t^* on the order of the α -relaxation time. The top 5% of all monomers moving the farthest in this time interval are colored light grey; the remaining caged monomers are colored dark grey. (The assistance of T. Griffin of the NIST Information Technology Laboratory in making this figure is gratefully acknowledged.)

[37,39,55–58]. This tail is largest at a time, t^* , in the late- β /early- α relaxation regime, when the particles begin breaking out of their cages and the mean-square displacement (or intermediate scattering function) begins increasing (decreasing) out of the plateau. In the systems we have studied, when $G_s(r, t^*)$ is compared with a Gaussian characterized by the same mean-square displacement, the 'super-Gaussian' tail contains approximately 5% of the particles, irrespective of temperatures in the temperature regime studied [37,39]. By examining the positions of the particles in this tail at any time between zero and t^* , it is evident that these particles are spatially correlated, and not randomly distributed throughout the sample (see Fig. 2) [37,39,40]. (Using a slightly different definition of mobility given not by a particle's displacement in the interval $[0, t^*]$, but by the maximum displacement attained by the particle

during this time interval, gives practically identical results [39].) Thus the long tail in the distribution function of particle displacements in supercooled liquids approaching their glass transition, and the resulting non-Gaussianity of this function, arises because of caging and the resulting correlated motion necessary for particles to escape the cages formed by their neighbors. In this sense, the degree of non-Gaussianity, which depends on temperature, indicates the degree of dynamical heterogeneity present in the liquid. On reflection, the spatial correlation of mobile particles might have been anticipated from the appearance of the tail.

The spatial correlation between pairs of particles that are mobile (breaking out of their cages) or immobile (still trapped in their cages) on some time scale can be easily quantified by calculating pair correlation functions that are restricted to particles within largest mobility or smallest mobility subsets, as was done in Refs. [37,39]. Such calculations show the increased tendency for correlation between mobile particles and immobile particles, as well as an increased tendency for anticorrelation between mobile and immobile particles [39], and the transient, dynamical aspect of this correlation.

From Fig. 2, it is clear that the most mobile particles on the time scale, t^* , in our 80:20 LJ liquid form clusters. Using the definition that two mobile particles belonging to the first neighbor shell of the other (given by the static pair correlation function $g(r)$) belong to the same cluster, we calculated for each temperature the probability, $P(n)$, of finding a cluster of size n . We reported in Refs. [39,40] that as $T \rightarrow T_c^+$, $P(n)$ fits well to a power law, $P(n) \sim n^{-1.9}$ (see Fig. 3(a)). As mentioned above, these clusters are dynamical, and they 'grow' and 'shrink' in time as the time window of observation increases. By comparing them at different temperatures at the same T -dependent characteristic time (such as t^* , but other characteristic times may be used), the temperature dependence of the average cluster size can be ascertained. We find that the mean cluster size, $S = \sum n^2 P(n) / \sum n P(n)$, increases as $T \rightarrow T_c = 0.435$ [39]. $S(T - T_p)$ with $T_p = T_c$ fits reasonably well to a power law, implying the intriguing pos-

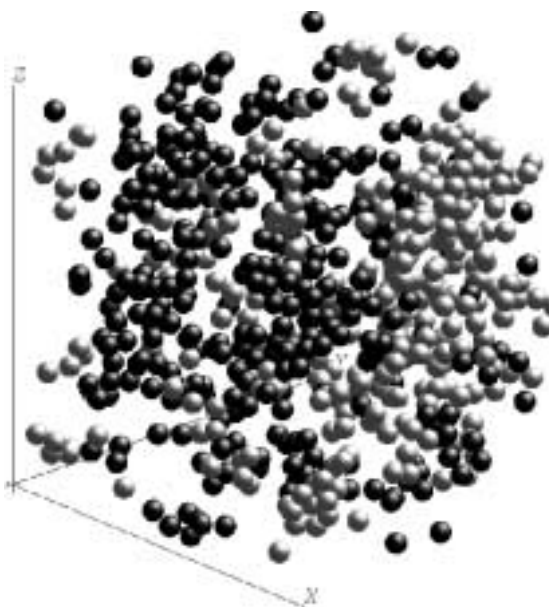


Fig. 2. Snapshot of a simulated, equilibrium, glass-forming 80:20 binary LJ mixture containing 8000 particles, just above the ideal mode-coupling temperature. Only the 5% most mobile (light grey) and 5% least mobile (dark grey) majority particles in a time interval $[0, t^*]$ are shown. Reprinted with permission from [40].

sibility of a percolation transition of clusters of mobile particles in the vicinity of the mode-coupling temperature (see Fig. 3(a)) [39,40]. We note that to test the sensitivity of our cluster analysis to our subset choice, we varied the fraction of mobile particles contained in the subset from 3% to 7%, re-did the cluster analysis in each case, and found that T_p increased with *decreasing* fraction of particles. In all cases, T_p was near T_c ; for higher fractions (close to 10%), a percolating cluster was observed at all T [39] since that fraction was close to the percolation threshold for randomly chosen particles with LJ interactions.

As these clusters are dynamical, they cannot be identified by looking at a single snapshot of the liquid; instead, two snapshots must be compared to ascertain the positions of the particles that moved the farthest from one snapshot to the next. However, there should be some correlation between the mobility of a particle and some aspect of the local structure. Interestingly, we find no obvi-

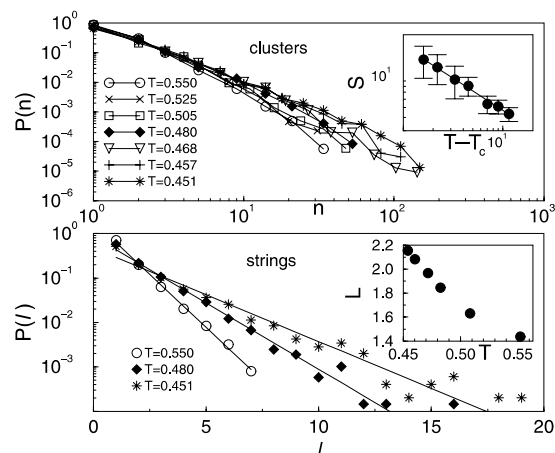


Fig. 3. Cluster size distributions and string size distributions in the 80:20 LJ mixture. (a) Probability distribution $P(n)$ of clusters of size n for several temperatures, plotted log–log to reveal power law dependence. Inset: Mean cluster size S plotted log–log vs. $T - T_c$ to reveal consistency with power law behavior. Data from [39]. (b) Probability distribution $P(l)$ of strings of length l for three of the temperatures in (a), plotted semi-log to reveal exponential dependence. The lines are best fits through the data with no fixed parameters. Inset: Mean string length L vs. T . Data from [38].

ous correlation between the local density of a particle and its mobility [59]. However, we do find a correlation between a particle's potential energy at the beginning of a time interval and its mobility during that time interval [39]; larger potential energy was associated with larger mobility. Thus, there indeed exists a connection between local dynamics and structure, but the precise connection is subtle and requires further investigation which is currently underway.

The clustering of (the 5% most) mobile particles has now been confirmed in recent three-dimensional confocal microscopy experiments on a sterically stabilized, poly(methyl-methacrylate) hard-sphere colloidal suspension at liquid-like densities approaching the glass transition, performed by Weeks et al. [47]. Weeks et al. used a suspension with a mean particle diameter of $2.36 \mu\text{m}$, and slightly less than 5% polydispersity in the sphere sizes to inhibit crystallization. Recall that in hard-sphere colloids, volume fraction ϕ , and not temperature, is the control parameter. Images of the clusters at different ϕ s look

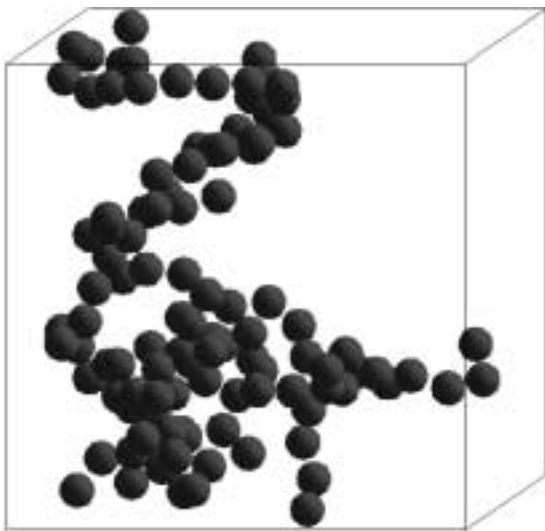


Fig. 4. One of the largest clusters of mobile particles of the majority species observed in the 80:20 LJ mixture at $T = 0.451$, just above T_c . This cluster contains 110 particles. The remaining 7890 particles in the liquid are not shown.

qualitatively identical to those found in our LJ simulations (Fig. 4), and Weeks et al. reported a power law distribution of cluster sizes, as in Fig. 3(a). The cluster size distribution exponent, $\tau = 2.2 \pm 0.2$, was found in their experiments; remarkably, this number is consistent with the value near 2 found in our simulations. Although a functional form for $S(\phi)$ could not yet be determined in the experiments, the dynamical nature of the cluster size was observed, and the mean cluster size was seen to increase with increasing volume fraction up to ϕ_g (which, as previously mentioned, in hard sphere systems is identical to ϕ_c).

3. String-like collective motion within clusters: the elementary unit of cooperativity?

Escaping the cage; string-like collective motion; clusters of strings; exponential string-length distribution; slow growth of mean string length; Kauzmann temperature.

How are these (roughly 5% at any time) mobile particles moving that allows them to move so far, while all other particles remain temporarily local-

ized in cages? By examining the vector displacement of the 5% most mobile particles in our 80:20 LJ mixture in the time interval $[0, t^*]$, we showed in Ref. [38] that these particles ‘follow’ one another in quasi-one-dimensional paths. As depicted in Fig. 5, each cluster of mobile particles analyzed in the previous section is composed of several (up to perhaps 20 for large clusters) smaller ‘strings’ in which the particles move in a collective, or cooperative, manner [40]. This collective string-like motion has now been confirmed by Weeks et al. in experiments on colloids [47].

Preliminary observation of this collective motion in two different LJ mixtures indicates that at short time the particles rattle in their cages relatively independently of each other, then begin moving almost ‘in phase’, and finally coherently and collectively move together almost one entire interparticle distance. Thus, they follow each other only in a spatial sense; in practice, the particle motion appears to be almost simultaneous within a single string close to T_c . (At higher T , the motion is considerably less coherent.) At still lower T , where the long tail in the self van Hove distribution function develops into a secondary peak, this collective motion may be even more coherent.

As depicted in Fig. 5, the string-like motion of particles occurs within the larger clusters discussed in the previous section, and it is important to note several differences between strings and ‘mobile particle clusters’ (see also Fig. 3). In Ref. [38], two particles were defined as belonging to the same string if (1) they belonged to the same mobile-particle cluster as defined in the previous section, and (2) one particle ‘replaced’ the other during the interval $[0, t^*]$. With this definition, the probability distribution of the lengths of the strings is exponential, and the mean string length, L , increases much more slowly than the mean cluster size, S , with decreasing T (see Fig. 3) [38]. Thus, there is a *second* length scale in the system, a ‘cooperativity’ length, L , which shows no tendency to diverge as T_c is approached despite the fact that the mean cluster size S appears to be diverging. Instead, the best power law fit to $L(T)$ over our very limited range of data gives a singular temperature $T \sim 0.3$, substantially less than T_c . Recent calculations [60–62] of the Kauzmann temperature for this

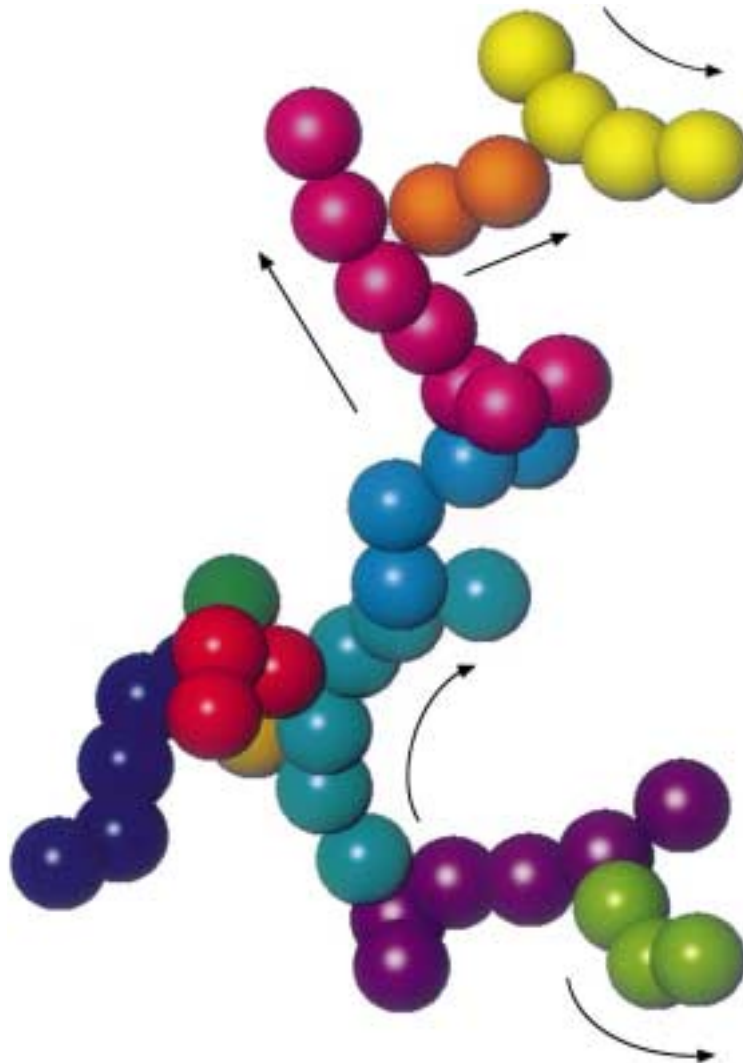


Fig. 5. Schematic picture demonstrating how a typical cluster of mobile particles is composed of smaller, quasi-one-dimensional strings of particles which move collectively as a single unit. Individual strings are indicated by color; arrows indicate direction of motion of particles within selected strings.

system gives $T_K = 0.297 \pm 0.001$ [60]. Of course, a precise determination of the functional form for the temperature dependence of this length scale, and the prediction of a divergence at *any* temperature, is impossible with the present data, and a calculation of $P(l)$ over a much wider T range is needed. Nevertheless, it is intriguing to consider the possibility that the strings may be the elementary cooperatively rearranging regions predicted by Adam and Gibbs [63].

4. Quantifying dynamical heterogeneity via bulk correlation functions: a glimpse of critical phenomena?

4.1. Displacement–displacement correlation function

Constructing a correlation function of particle displacements; the transient nature of dynamical heterogeneity; rapid growth of mobility fluctuations;

apparent power law divergence of size of fluctuations and characteristic time scale near T_c ; analogy with ordinary critical phenomena.

We have observed in our simulations that clusters of mobile particles grow and shrink with time, fluctuating in and out of existence as particles become trapped, escape their cages, and become trapped again, and that the typical size of these clusters increases with decreasing T . Certain aspects of this clustering phenomenon are somewhat reminiscent of critical phenomena, except that these clusters are dynamically defined. Recall that in a fluid approaching a liquid–gas critical point, the isothermal compressibility, κ , increases and diverges as a power law at the critical point [64]. This increase of the compressibility represents the increase of density fluctuations whose characteristic length scale increases to infinity at the critical point. However, it is known that no such growing density fluctuations exist in liquids approaching the glass transition [65,66].

In Refs. [41,67] we showed that it is possible to construct a bulk correlation function, $G_u(\mathbf{r}, \Delta t)$, of particle displacements [68]

$$G_u(\mathbf{r}, \Delta t) = \int d\mathbf{r}' \langle [u(\mathbf{r}' + \mathbf{r}, \Delta t) - \langle u \rangle][u(\mathbf{r}', \Delta t) - \langle u \rangle] \rangle, \quad (1)$$

where $u(\mathbf{r}, \Delta t) = \sum_{i=1}^N \mu_i(\Delta t) \delta(\mathbf{r} - \mathbf{r}_i(t))$ is the local displacement field, and $\mu_i(\Delta t)$ is the scalar displacement of particle i in $[0, \Delta t]$. We defined a corresponding generalized dynamic susceptibility, $\chi_U(\Delta t)$, which is proportional both to the volume integral of $G_u(\mathbf{r}, \Delta t)$ and to the fluctuations $\langle U^2(\Delta t) \rangle - \langle U(\Delta t) \rangle^2$ in the total displacement $U(\Delta t) = \int d\mathbf{r} u(\mathbf{r}, \Delta t)$ of all particles in the system in a time window, Δt . The quantities, $G(\mathbf{r}, \Delta t)$ and $\chi_U(\Delta t)$, were constructed so as to reproduce the usual static van Hove correlation function, $G(\mathbf{r})$, and isothermal compressibility, κ_T , when the particle displacements are uncorrelated. We calculated these quantities in two different Lennard–Jones mixtures [40–42] and a polymer liquid [44] approaching the mode-coupling temperature. In all systems, the susceptibility, $\chi_U(\Delta t)$, increases and decreases in time as shown in Fig. 6, due to the increasing and decreasing size of clusters of mobile

particles (or monomers) in the liquid. Moreover, χ_U is a maximum at a time Δt^* , and both $\chi_U(\Delta t^*)$ and Δt^* increase as T_c is approached, with an apparent power law divergence of both quantities in all three systems at T_c [41,44]. Of course, a precise determination of the functional dependence of these quantities requires further simulations close to and below T_c , and thus our proposal of power law dependence is only preliminary. Nevertheless, the increase in $\chi_U(\Delta t^*)$ demonstrates that $G_u(\mathbf{r}, \Delta t^*)$ is becoming increasingly long-ranged as $T \rightarrow T_c^+$. Thus, despite the fact that density fluctuations remain small as T_c is approached, *mobility* fluctuations increase with decreasing T , having the type of dependence (albeit in a different order parameter) normally associated with critical phenomena.

4.2. Four-point, time-dependent density correlation function

Density correlation functions and dynamical heterogeneity – the need for four points; the Parisi overlap order parameter in liquids; spatial correlations of localized particles; rapid growth of overlap fluctuations on approaching T_c .

Quantifying dynamical heterogeneity and correlated particle motion in liquids requires four ‘points’ of information: the location of two different particles at one time, and their location at a later time. Thus *two*-point, time-dependent density correlation functions are insufficient to describe spatially heterogeneous dynamics, and one must consider the next non-trivial, higher order function; namely, a *four*-point, time-dependent density correlation function [42,69,70]

$$G_4(\mathbf{r}_1, \mathbf{r}_2, t) = \langle \Delta\rho(\mathbf{r}_1, 0) \Delta\rho(\mathbf{r}_1, t) \Delta\rho(\mathbf{r}_2, 0) \Delta\rho(\mathbf{r}_2, t) \rangle - \langle \Delta\rho(\mathbf{r}_1, 0) \Delta\rho(\mathbf{r}_1, t) \rangle \langle \Delta\rho(\mathbf{r}_2, 0) \Delta\rho(\mathbf{r}_2, t) \rangle. \quad (2)$$

Here $\Delta\rho \equiv \rho(\mathbf{r}, t) - \langle \rho \rangle$, $\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i(t))$, and $\langle \rho \rangle \equiv N/V$ where N is the total number of particles in the volume V . This correlation function was first studied in the context of supercooled liquids by Dasgupta, et al. [69]. Its volume integral yields a generalized dynamical susceptibility, $\chi_4(t)$, which is proportional to the fluctuations $\langle Q^2(t) \rangle -$

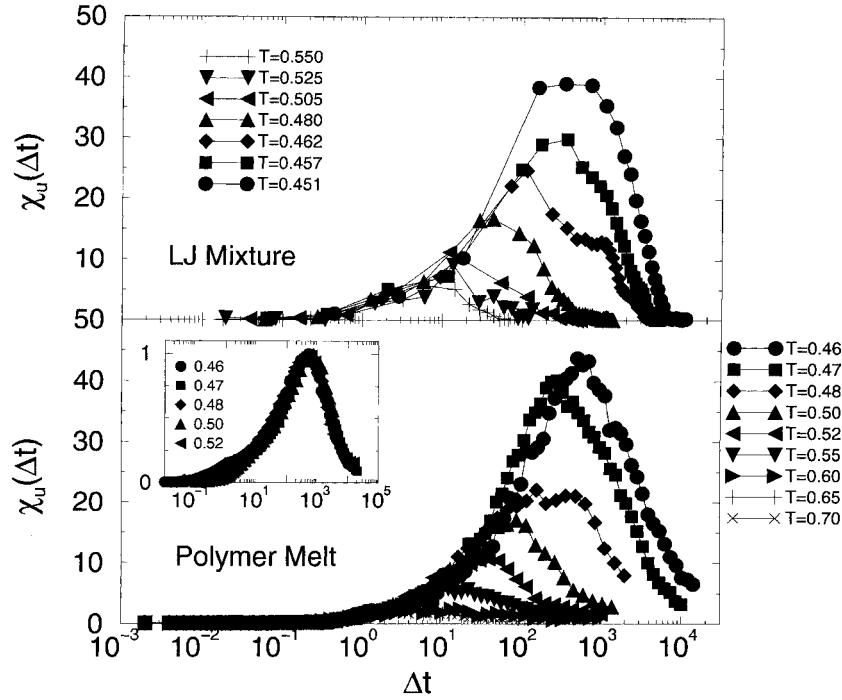


Fig. 6. Generalized dynamic susceptibility $\chi_U(\Delta t)$ of correlated particle displacements vs. time window Δt for several temperatures, for (a) 80:20 LJ binary mixture and (b) polymer melt. Inset in (b): Data collapse of the curves in (b) obtained by dividing Δt by Δt^* and $\chi_U(\Delta t)$ by $\chi_U(\Delta t^*)$. Data from [41,44]. Lines are drawn between symbols of each type.

$\langle Q(t) \rangle^2$ in a time-dependent order parameter, $Q(t)$, representing the ‘overlap’ between two liquid configurations separated by a time, t [70,71]

$$Q(t) = \sum_{i=1}^N \sum_{j=1}^N w(|\mathbf{r}_i(0) - \mathbf{r}_j(t)|). \quad (3)$$

Here w is an overlap function that is unity inside a region of size a and 0 otherwise, where a is taken on the order of a particle diameter. With this definition, $Q(t)$ is simply the total number of particles that, in a time t , have either been replaced by another particle, or have not moved beyond their own radius.

In the particular case of the mean-field, p -spin model [72–77], the time dependence of $\chi_4(t)$ was solved analytically in Ref. [70]. The dynamics of the p -spin model, which shares a number of gross common features with real glass-forming liquids, are described exactly by the ideal mode-coupling equations, and exhibits a sharp dynamical transi-

tion at T_c [72–75]. Franz and Parisi showed that, in this model, T_c is coincident with a spinodal temperature, such that below T_c there is an effective ergodicity breaking and the appearance of a secondary minimum in the effective potential [78–82]. It was shown in [70] by numerically solving the analytical dynamical equations for the p -spin model [83] that $\chi_4(t)$ is a maximum at an intermediate time, t_4^* , in the late- β /early- α relaxation regime, and both the position and height of this maximum increase as $T \rightarrow T_c^+$. Below T_c , $\chi_4(t)$ is independent of time and equivalent to the static generalized susceptibility, χ_4 , which has been calculated analytically in Ref. [70] within the effective potential theory both for the p -spin model and for a simple liquid in the hypernetted chain approximation. As T approaches T_c from below, χ_4 diverges as a power law with mean-field exponent 1/2 [70]. These calculations provide the first analytical prediction of the growth and possible divergence of a generalized dynamical susceptibility

and (by inference) the corresponding dynamical correlation length in a model glass-forming system. Calculations of $\chi_4(t)$ in MD simulations of two different LJ mixtures above T_c have qualitatively similar dependence to that predicted by the theory [42,70], with exponents consistent with the mean-field prediction. The predictions below T_c remain to be determined by simulation.

It was shown in Ref. [42] for a 50:50 LJ mixture that $\chi_4(t)$ is dominated by spatial correlations between *localized* particles, i.e., particles that do not move outside the cage formed by their neighbors in a time, t . Thus the increase of $\chi_4(t_4^*)$ with decreasing T and apparent power law divergence at T_c implies a growing range of spatial correlations between localized particles on the time scale t_4^* , which itself increases as T_c is approached. Evidence for an increasing length scale associated with solid-like properties in supercooled liquids has been reported in Refs. [36,84,85]. Of course, by trivially substituting w by $1 - w$ in the expression for $Q(t)$, the particles that dominate the order parameter become the *non-localized* ones; thus it is important to remember that this approach measures the correlations within a subset of particles, where the subset is chosen according to whether or not the particles are localized in a time interval $[0, t]$.

The displacement correlation function described in the previous section measures the extent to which the (scalar) displacements of a pair of particles initially separated by a distance r are spatially correlated. This function is similar to the static, two-point correlation function, $g(r)$, but with each particle's contribution to $g(r)$ weighted by its subsequent displacement over a time interval $[0, t]$. In contrast, the four-point function G_4 just described measures the extent to which overlapping particles within a time interval $[0, t]$ are correlated. Although these two correlation functions differ by definition (and thus, e.g., the exponents describing the T -dependence of the generalized susceptibilities, χ_4 and χ_U , will differ), the length scale associated with G_4 may underly the increasing range of correlated particle displacements. However, it is important to remember that the geometry of the clusters of mobile particles and that of the immobile particles is not the same; mobile particle clusters are ramified and – in the

case of LJ liquids studied – composed of strings, while immobile particle clusters are more compact [39]. Thus, the specific relationships between the different quantities that have been proposed to describe dynamical heterogeneity still remain to be explored.

5. Dynamical heterogeneity and ‘decoupling’ in supercooled liquids

Decoupling of diffusion and relaxation above T_c ; characteristic time scales for dynamical heterogeneity; relation between dynamical heterogeneity and decoupling.

At temperatures and/or moderate densities at which there is no particle aging, transport coefficients in liquids obey the Stokes–Einstein–Debye (SED) relation in which diffusion and viscosity vary inversely to one another [86,87]. Near the glass transition, however, this relation breaks down, and measured diffusion coefficients can be several orders of magnitude larger than would be predicted from the SED relation and the measured viscosity. Experimentally, this breakdown of the SED relation, or decoupling of diffusion and structural relaxation, is observed to occur at and below the mode-coupling temperature [88–92]. In simulations, however, decoupling is detected at much higher temperatures, starting essentially at the onset of caging and transient particle localization [55–57,93–97]. In these model liquids, the inverse diffusion coefficient, D^{-1} , and α -relaxation time, τ_α , (for the wave-vector corresponding to the main peak in the static structure factor) scale *differently* with temperature, thereby violating one prediction of the ideal mode-coupling theory. It is likely that more sensitive experimental measurements may detect the onset of decoupling in real liquids at temperatures higher than T_c , as predicted by simulations. However, there is the possibility that the simulated model liquids are simply different from real liquids in this respect, for reasons not presently understood.

Many authors have noted the probable connection between decoupling and dynamical heterogeneity, suggesting that domains of fast particles should dominate diffusion, while domains of slow

particles should dominate structural relaxation or viscosity [88–91,93,94,98–101]. In [42], we recently demonstrated via the four-point, time-dependent density correlation function in Eq. (2) that the time scale on which overlapping particles are most correlated *differs* from the time scale on which the (squared) particle displacements are most correlated; moreover, these two characteristic times scale *differently* with temperature (see Fig. 7), which has important implications for the decoupling of transport processes in dense liquids described above. In particular, we showed in the 50:50 LJ mixture that the time scale, t_4^* , on which overlapping particles are most spatially correlated coincides within numerical error with τ_α (see Fig. 7), while the time scale on which the squared displacements of particles are most spatially correlated scales with temperature like the inverse diffusion coefficient. In this way, the decoupling of diffusion and structural relaxation is seen to arise naturally from spatially heterogeneous dynamics.

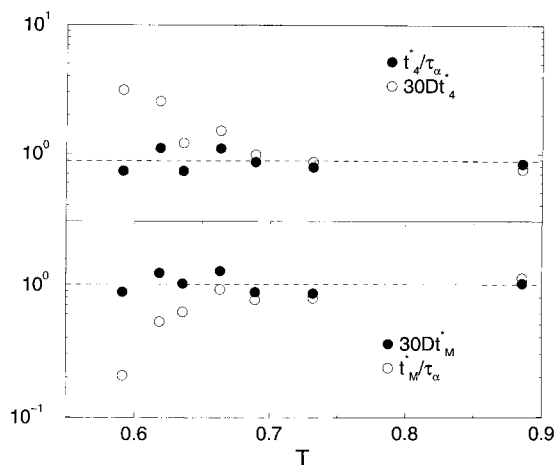


Fig. 7. Decoupling of diffusion and relaxation in the 50:50 LJ mixture above T_c , and relation to dynamical heterogeneity. (a) Comparison of the time t_4^* at which $\chi_4(t)$ exhibits a maximum, with both D^{-1} and τ_α . As plotted, a line of zero slope indicates proportionality. (b) Comparison of the time t_M^* at which the generalized dynamic susceptibility $\chi_M(t)$ corresponding to a correlation function of *squared* particle displacements exhibits a maximum, with both D^{-1} and τ_α . As plotted, a line of zero slope indicates proportionality. For this system, $T_c \approx 0.59$. Data from [42].

6. Conclusions

In each attempt to quantify dynamical heterogeneity in simulations of equilibrium, supercooled, glass-forming liquids, using either a cluster analysis of mobile particles, a correlation function of particle scalar displacements, or a four-point dynamical density correlation function, we have discovered quantities such as the mean cluster size, generalized dynamic susceptibilities, or even characteristic time scales, which all increase with decreasing T as T_c is approached from above. Although MCT as yet makes no specific predictions concerning any of these quantities, we have attempted to fit power laws to the data with T_c fixed to the critical temperatures found previously in separate investigations of the same systems. In all cases, a power law fit to the data was found to be as good as or better than the power law fits of other more traditional ‘mode-coupling’ quantities. While this statement does not imply that other functional forms such as the Vogel–Fulcher expression can be ruled out, it is at least suggestive that there is in fact some sort of dynamical transition occurring in the vicinity of the mode-coupling temperature, at temperature much greater than the glass transition.

Indeed, the analytical calculation [70] of $\chi_4(t)$ in the p -spin model supports this idea. That said, it is unlikely that there is any *true* divergence of the generalized dynamical susceptibilities, $\chi_U(t)$ and $\chi_4(t)$, and corresponding range of the displacement–displacement correlation function and four-point time-dependent density correlation function, respectively, in real and simulated liquids at T_c . Likewise, it is unlikely that there is a true percolation transition of mobile particles at T_c . Instead, the apparent divergence may be rounded, but more simulations on larger systems, closer to T_c , are needed to resolve these issues. Nevertheless, the increase and rich structure of transient mobility fluctuations inherent in the three glass-forming liquids we have studied is striking, and we have shown that the spatial correlation within these fluctuations controls such key features as the decoupling of diffusion and structural relaxation.

Based on the correlation function analysis described in Section 4, there is the *possibility* that

dynamical heterogeneity, at least above T_c , represents some unusual type of dynamical critical phenomenon [102]. Are the growing mobility fluctuations some type of critical fluctuations? In the Franz–Parisi mean field, effective potential theory of glass formation, the mode-coupling transition is coincident with a spinodal point. If we suppose that in real liquids, that relationship persists to some degree (perhaps the actual transition is ‘avoided’), this persistence might suggest the novel possibility that the increasing fluctuations in the time-dependent overlap of two snapshots of the system, and more generally the increasing fluctuations in mobility, are actually critical fluctuations associated with the approach to a spinodal. Of course this proposal is a speculation at this point, but simulations should be able to test this conjecture.

The importance of the string-like collective particle motion that we have observed in our simulations is yet to be fully explored or explained. Do these strings represent the fundamental, collective motion described in mean field by the mode-coupling theory [103]? Are they the elementary, cooperatively rearranging regions of Adam and Gibbs [63], Donth [104–112], and others? In a recent paper, Schröder, et al. reported that transitions between local minima on the potential energy landscape (‘inherent structures’ [113]) near and below T_c in a 50:50 LJ mixture involve collective rearrangements of particles in a single, long string [114]. However, the particles in these inherent strings move much less than the interparticle diameter moved by their equilibrium counterparts. Finally, what is the relation, if any, between our high temperature strings and the collective excitations that make up the Boson peak at lower T ?

The current state of our (still incomplete) understanding of correlated particle motion in the glass-forming liquids we have studied can be briefly summarized as follows. Above T_c , caging begins and, to break out of these cages, particles begin moving collectively, in quasi-one-dimensional strings. The mean size of these elementary, cooperatively rearranging groups of particles increases with decreasing temperature. At the same time, the strings ‘aggregate’ into larger, more

ramified clusters whose mean size increases more rapidly with decreasing T , and appears to diverge at the ideal mode-coupling temperature. The corresponding sample-to-sample fluctuations in the mobility increase and appear to diverge as well, as described by such correlation functions as the displacement–displacement correlation function and the time-dependent four-point, density correlation function. The apparent diverging dynamical correlation length characterizing the mean size of clusters of strings underlies the increasingly collective motion described by MCT, and thus underlies the ideal mode-coupling transition and the corresponding apparent divergence of relaxation times. Below T_c , it may be that the strings continue to increase with decreasing T , possibly following the predictions of Adam and Gibbs, but this statement remains to be confirmed in future simulations.

We note that the distinction between strings and clusters of strings raises interesting questions in the case of hard-sphere colloids, where the glass transition and ideal mode-coupling transition are identical. Weeks et al. [47,115] have shown that the cluster distribution is power law, but will the string length distribution still be exponential? Will the mean string length and mean cluster size ‘diverge’ at the same density in this system?

Besides the obvious fundamental interest in dynamical heterogeneity in glass-forming liquids, the presence of large, transient, correlated domains of mobile and immobile particles should have important, practical ramifications for a number of applications. For example, there are important implications for glass-forming liquids and polymers confined to small nanometer-sized pores or layers, since confinement on those length scales may interfere with the characteristic length scale of correlated motion, which is estimated to be several nanometers just above the glass transition [116–128]. In analogy with ordinary critical phenomena, this interference should shift the glass transition temperature up or down depending upon the boundary conditions at the surface, and indeed such shifts are observed, and even used by several researchers to extract a dynamical correlation length [116–128]. Such shifts have also been observed in polymer/clay nanocomposites and filled

polymer melts, and thus dynamical heterogeneity may play an interesting role in these systems as well. Another important implication of dynamical heterogeneity in supercooled, glass-forming liquids lies in the open question concerning its importance in nucleation and growth of the crystal phase in supercooled liquids. Some supercooled liquids having dynamical heterogeneity, such as the colloids studied by Weeks et al. [47], eventually crystallize. However, current theories of nucleation and growth ignore the possibility of spatially heterogeneous dynamics. A simulation study of the effect of dynamical heterogeneity in suppressing or accelerating the formation of critical nuclei in supercooled liquids could be extremely interesting. Finally, correlated particle motion and dynamical heterogeneity in the glass state may be related to aging phenomena, as well as to shear banding in metallic glasses.

Acknowledgements

The work described here was performed in a series of fruitful and enjoyable collaborations with P. Allegrini, J. Baschnagel, C. Bennemann, C. Donati, J.F. Douglas, S. Franz, W. Kob, V. Novikov, G. Parisi, P.H. Poole, and T.B. Schröder. I am especially grateful to E. Weeks and D. Weitz for sharing their experimental results prior to publication, and to many colleagues, too numerous to name here, for valuable and enlightening discussions.

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