Understanding Slow and Heterogeneous Dynamics in Model Supercooled Glass-Forming Liquids

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ABSTRACT: Glasses are ubiquitous in nature. Many common items such as ketchups, cosmetic products, toothpaste, etc. and metallic glasses are examples of such glassy materials whose dynamical and rheological properties matter in our daily life. The dynamics of these glass-forming systems are known to be very sluggish and heterogeneous, but a detailed understanding of the origin of such slowing down is still lacking. Slow heterogeneous dynamics occur in a wide variety of systems at scales ranging from microscopic to macroscopic. Polymeric liquids, granular material, such as powder and sand, gels, and foams and also metallic alloys show such complex glassy dynamics at appropriate conditions. Recently, the existence of dynamical heterogeneity has also been found in biological systems starting from collective cell migration in a monolayer of cells to embryonic morphogenesis, cancer invasion, and wound healing. Extensive research in the past decade or so lead to the understanding that there are growing dynamic and static correlation lengths associated with the observed dynamical heterogeneity and rapid rise in viscosity. In this review, we have highlighted the recent developments on measuring these correlation lengths in glass-forming liquids and their possible implications in the physics of the glass transition.

INTRODUCTION

Appearance of rigidity in a phase of matter is believed to be a direct manifestation of long-range spatial order. Crystals are rigid because of long-range translational order. In a ferromagnet, to flip a single spin one has to flip a whole bunch of them, precisely due to long-range magnetic ordering. Glasses are also rigid but without the presence of any immediately obvious long-range order. Static configurations of a glass look very similar to that of a liquid (Figure:1) with all symmetries present; then an answer to the question of emergence of rigidity or rapid slowing down of dynamics or the increase in viscosity while approaching the glass transition requires a notion of a new definition of static order in disordered systems. This so-called static order in disordered systems is often referred as “Amorphous order”. The existence of such a static order was proposed by Adam and Gibbs1 in terms of cooperatively rearranging regions to rationalize the apparent entropy crisis noted by Kauzmann. Following the success of the mean field spin glass model, Kirkpatrick and Thirumalai3 proposed a new theory, known as “random first-order transition theory” (RFOT) which predicts the presence of a growing static length scale that governs the dramatic rise in viscosity with decreasing temperature or increasing density. Subsequently, the Point-to-Set (PTS) correlation function was proposed to measure the growth of such a static correlation length, \( \xi_s \), which became well-known as the PTS length scale. In spite of the success, these different methods remained mostly applicable to computer simulations of modeling glass-forming liquids and colloidal glasses primarily due to the complexity of the method. Experimental validation in molecular liquids remains a handful.

On the other hand, with decreasing temperature yet another growing length scale associated with the dynamics of the constituent particles emerges. This is well-known as the dynamic heterogeneity length scale \( \xi_d \). Physically it is the typical length scale over which local relaxation processes in the system are correlated. This manifests itself by forming clusters of different mobility particles (see Figure:1) and also leads to nonexponential relaxation, violation of the Stokes–Einstein relation, non-Gaussianity in the van Hove function, etc. In the literature this phenomenon is referred to as dynamic heterogeneity (DH). This is the phenomenon of spatiotemporal dynamical fluctuations in the system. The existence of dynamical heterogeneity in glass-forming liquids is so ubiquitous that it is believed to be one of the major hallmarks of glassy dynamics. Dynamical heterogeneity is observed in a wide variety of systems ranging from molecular glass-forming liquids to colloidal glasses,
bubble rafts, gels, foams, and driven granular media. Recently, many studies in dense biological tissues have also revealed the presence of dynamical heterogeneity (including caging and viscoelastic behavior). The motion of the cells becomes collective and depends strongly on their neighborhood during organ regeneration, embryonic morphogenesis, and wound healing. During these processes, the cells exhibit remarkable behavior of heterogeneity from rigid like a solid to flowing like a liquid across different time scales. Cancer tumors are also known to be a mixture of rigid and soft cells that have a different degree of active contractility. Also, it is believed that soft cells in cancer tumors are more mobile and proceed in the direction of the boundary of a primary tumor much more easily than their rigid counterparts. Thus, the time evolution of heterogeneity in cancer tumors or in biological tissues may also become important to understand the progression of the disease. Thus, understanding of the evolution of dynamical heterogeneity in such disordered systems will also be important along with an understanding of the growth of the static and dynamic lengths.

The first theoretical attempt to explain this complex dynamical behavior came from the Mode Coupling theory (MCT) by Götze and co-workers in the 1980s. The theory tried to predict the full microscopic dynamics from the static structure factor, $S(k)$, where $k$ is the scattering wave vector. Although it failed to anticipate the glass transition temperature which probably occurs at much lower temperature (higher density) than the predicted mode coupling transition temperature, $T_c$ (density, $\rho_c$), but it is the only microscopic theory of the glass transition so far that correctly predicts the two step stretched exponential relaxation of the two-point density–density correlation function or the self-intermediate scattering function, $F_s(k, t)$ (defined later). Extension of this theory to understand the dynamic heterogeneity via four-point susceptibility, $\chi_4(t)$ (defined later), is also quite successful. It correctly predicts the overall shape of the correlation function with a peak at a time scale close to the $\alpha$-relaxation time. MCT also predicts the divergence of the peak height of $\chi_4(t)$ with increasing supercooling. Although the divergence of the peak height of $\chi_4(t)$ is not observed in simulations and experiments, one does discover the power law growth of the peak height with decreasing temperature in moderately supercooled liquids. Thus, although the theory does not work deep in the supercooled temperature regime, it predicts the observed dynamical features of the liquids faithfully at moderate supercooling. Another extension of MCT theory, known as Inhomogeneous Mode Coupling Theory (IMCT), also
predicts a growing dynamical correlation length as discussed later in detail. On the other hand, RFOT theory, being a thermodynamic theory of glass transition, has reasonable success predicting the right kind of ergodicity breaking at temperature \( T_f \) (corresponds to \( T_G \) in MCT), known as the dynamical transition temperature. The thermodynamic behavior below \( T_f \) is controlled by an exponentially large number of metastable states that are statistically similar to each other and would result in extensive “configurational entropy (S_c)” or “complexity”. A naive extrapolation of the configurational entropy to lower temperature results in vanishing of this entropy at a temperature, \( T_0 \), known as the Kauzmann temperature where a thermodynamic transition is predicted to take place. In the temperature regime \( T_K < T < T_f \), the system fragments itself in a mosaic state with linear length, \( \xi_s \), representing the typical size of a correlated patch. Dynamical heterogeneity in the context of RFOT theory is argued to be coming basically from the emergence of frozen particle clusters that have time scales longer than the average relaxation time leading to spatially heterogeneous relaxations in the system.

Another question of significance in this context is the mutual relation between the static and dynamic length scales but a clear consensus is still lacking. Although the existence of two growing length scales is not contested, there are systems in which these two length scales grow hand in hand\(^{12}\) and systems where these length scales are decoupled. Although the two types of glass forming liquids show very similar dynamics, only the length scales are decoupled. Although the existence of two growing heterogeneities in the system,\(^{3}\) the emergence of frozen in particle clusters that have time scales size of a correlated patch. Dynamical heterogeneity in the eventual state reached by a glass former if it is allowed to settle at a temperature, \( T_f \), the system fragments itself in a mosaic state with linear length, \( \xi_s \), representing the typical size of a correlated patch. Dynamical heterogeneity in the context of RFOT theory is argued to be coming basically from the emergence of frozen particle clusters that have time scales longer than the average relaxation time leading to spatially heterogeneous relaxations in the system.

The questions related to the existence of locally favored structural motifs or medium range crystalline order (MRCO) or Locally Favorated Structures (LFS). The related questions to the existence of locally favored structural motifs or medium range crystalline order and their role in the vitrification of supercooled liquids are important because they appear in a wide variety of glass forming systems including metallic glasses. Thus, their role in the slowing down of the dynamics in supercooled liquids becomes interesting due to their industrial applications. On the other hand, growth of MRCO or LFS also raises questions about the eventual state reached by a glass former if it is allowed to relax for sufficiently long times. Is a slowly growing locally favored structure responsible for slow dynamics? Are the molecular mechanisms for glass transition in liquids with and without MRCO the same? If yes, glass-formers with MRCO would then provide a paradigm for understanding glassy behavior generically. If not, systems with MRCO form a special class of glass forming materials whose molecular mechanism for slow dynamics may be easier to understand in terms of growing local structural order and should be approached in that manner, even while they may not provide generic insights. The static and dynamic properties of glasses with MRCO are found to be different from those of other generic glass-formers with no predominant local order.

In the rest of the review we will be touching upon the recent advances made to understand and compute static and dynamic length scales in glass forming liquids as well as the current understanding of glass forming systems with local structural order. Finally, we will also briefly discuss the temporal evolution of dynamic heterogeneity and its implications in understanding the physics of slow dynamics.

**Quantifying Dynamic Heterogeneity and Amorphous Order.** Earlier many experimental\(^{5}\) and numerical studies have shown the presence of dynamical heterogeneity where the particles with similar mobility (long-lived populations of slow or fast particles) formed clusters and the spatial extent of the clusters grows while approaching the glass transition. These observations suggest that one might be able to extract the dynamic heterogeneity length scales from the cluster size distribution. As a consequence, different methods has been proposed to measure this important length scale of the system. However, each method has its own limitation and that is why it is necessary to come up with a novel method that can be used in a wide variety of systems both in numerical studies and in experiments.

We start by briefly discussing the different methods to measure the dynamical length scale. As a definition of slow and fast particles depends crucially on an arbitrary cutoff parameter, it is desirable to remove such arbitrariness. This can be achieved by measuring the length scale via a four-point correlation function\(^{13}\) with an analogy to spin glass physics. The function is defined as

\[
g_s(r, t) = \langle \delta \rho(0,0) \delta \rho(0, t) \delta \rho(r, 0) \delta \rho(r, t) \rangle - \langle \delta \rho(0,0) \delta \rho(0, t) \rangle \langle \delta \rho(r, 0) \delta \rho(r, t) \rangle
\]

(1)

\( \delta \rho(r, t) \) is the deviation of local density \( \rho(r, t) \) from its average value at a distance \( r \) from the origin and time \( t \). This function measures the spatiotemporal correlation between two space points which are separated by a distance \( r \) over time \( t \). The volume integral of \( g_s(r, t) \) gives the four point susceptibility, \( \chi_4(t) \), and Fourier transform of \( g_s(r, t) \) is known as the 4-point structure factor, \( S_4(0, t) \). \( \chi_4(t) \) can be written as the variance of two point density correlation functions or the self-intermediate scattering function, defined as

\[
F_s(q, t) = \frac{1}{N} \sum_{j=1}^{N} e^{-i q \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))}
\]

(2)

where \( \mathbf{r}_j(t) \) is the position of the \( j \)th particle at time \( t \) and \( q \) is the scattering wave vector. A popular variant of the two point density correlation is the overlap function \( Q(t) \) which measures the alikeness in two configurations separated by time interval "\( t \)" and is defined as

\[
Q(t) = \frac{1}{N} \sum_{j=1}^{N} \theta(a - |\mathbf{r}_j(t) - \mathbf{r}_j(0)|)
\]

(3)

where \( \theta(x) \) is the usual step function and value of \( a \) is chosen to neglect the small decorrelation because of vibration of particles/molecules in their respective cages. Structural relaxation time, \( \tau_{ar} \) is defined as \( Q(\tau_{ar}) = \exp(-1) \). The \( \chi_4(t) \) is then defined as

\[
\chi_4(t) = N [\langle Q^2(t) \rangle - \langle Q(t) \rangle^2]
\]

(4)

\( \langle \cdots \rangle \) refers to ensemble and time average. \( \chi_4(t) \) shows a peak at time close to the structural relaxation time, \( \tau_{ar} \) as can be seen in Figure 2(b). Also, both the magnitude and lifetime of the dynamical heterogeneity increase with decreasing temperature which corresponds to the growth of the dynamical correlation length. Later, Biroli et al.\(^{11}\) proposed another way to obtain dynamical susceptibility by applying an external field in the system. This theory is known as Inhomogeneous mode coupling theory (IMCT). The obtained susceptibility is akin to a three point density correlation function, \( \chi_3(t) \). IMCT showed that \( \chi_3(t) \) behaves in a similar way as the four point susceptibility, \( \chi_4(t) \). Note that \( \chi_4(t) \) is directly measurable in experiments\(^{14}\).
and this gives an indirect way to measure $\chi'_s(t)$ and the growth of dynamic heterogeneity in the system. It is worth mentioning that the peak value of dynamical susceptibility, $\chi'_s(t)$, is directly related to the dynamic heterogeneity length scale, $\xi_{ds}$ as $\xi_{ds} \sim \xi^H_{T4} t^{-\eta}$ with a priori unknown exponent $\eta$.

The static correlation length on the other hand is generally measured via the Point-To-Set (PTS) correlation function, and the corresponding length is referred as the PTS length, $\xi_{PTS}$. As discussed earlier, it is the typical length scale of a correlated volume which can remain confined to a particular metastable state if the outside of the volume is kept in a frozen state. It is measured by systematically increasing the probe volume while keeping particles outside the probe volume stationary as a boundary condition. The largest linear length at which the overlap computed for the correlated volume between its long time equilibrated states and the initial state is significantly large and would give us the PTS length scale. Various other measures of the static length scale include finite size scaling (FSS) analysis of the structural relaxation time, $\tau_{\alpha}$, and FSS of the minimum eigenvalue of Hessian matrix, computed for energy minimized configurations with Inherent structures sampled from a given temperature.

Efforts to measure these length scales in experiments are still challenging since it is not yet possible to spatially and temporally resolve the individual molecules in molecular glass-formers. Although for colloidal glasses and granular glasses the cluster of mobile particles has been directly observed, in ref 17 it has been shown that a suitable dynamical response function $\chi'_s(t)$ to an induced perturbation field “$x$”, like density fluctuation in colloidal glasses or temperature fluctuation in molecular glasses, is related to $\chi'_s(t)$ via fluctuation theory and linear response formalism. Thus, $\chi'_s(t)$ will be indirectly related to $\chi'_s(t)$ as suggested in IMCT, although obtaining the dynamic heterogeneity length scale remains indirect due to the unknown exponent. Similarly, experimental measures of the growing static length scale in glassy systems are also very limited again due to the lack of methods that are accessible to experiments. One such direct measure comes from the calculation of fifth-order dielectric susceptibility, $\chi''_s(t)$, in supercooled glycerol and propylene carbonate. Wall pinning via holographic optical tweezers in colloidal glasses also gave a direct measure of this length scale. The level of complexity in these experiments itself suggests the need for a viable experimental procedure to measure the dynamic and static correlations about which this review would surely give ideas for future experiments and simulations.

**Block Analysis: An Elegant Finite Size Scaling Method.**

The Critical phenomenon finite size scaling hypothesis predicts that in a finite system (with linear dimension $L$) near a critical point where the microscopic length scale becomes irrelevant, the relevant physical quantities are expected to be a function of the underlying growing length scale, $\xi$, as $f\left(\frac{L}{\xi}\right)$. The functional $f(x)$ goes to a constant as $x \rightarrow \infty$, and it increases with $x$ for $x > 0$. This leads to an excellent route to extract the temperature dependence of the correlation length, $\xi(T)$, since for different temperatures one can choose an appropriate $\xi(T)$ which gives a master curve between the relevant physical observable measured in various sized systems and $L/\xi(T)$. This leads Karmakar et al. to use the FSS arguments on the system size dependence of the peak of four point dynamic susceptibility, $\chi''_s(T,L)$, which was found to vary systematically with decreasing temperature (shown in Figure 2(b)) and increasing system size, indicating a growing length scale, and the following scaling function was found to describe the data quite well,

$$\chi''_s(L, T) = \chi''_s(L \rightarrow \infty, T) f\left(\frac{L}{\xi_{ds}}\right)$$  

(5)

where $\chi''_s(L \rightarrow \infty, T)$ is the asymptotic value of $\chi''_s(L, T)$. By performing the data collapse to a master curve, the dynamic length scale of the system, $\xi_{ds}(T)$, was extracted very reliably.

However, the above finite size scaling (FSS) technique suffers from some drawbacks. First would be that it requires equilibrium configurations with different system sizes of which some might be very close to the relevant length scales of the system. Also in simulations, the periodic boundary condition (PBC) suppresses some of the important contributions to $\chi'_s(t)$ coming from density and composition fluctuations. Moreover, one would also need extensive averaging to get reliable results in small system sizes. Experimentally also it will be very difficult to implement as it require studies of different system sizes. It is therefore necessary to have an alternative FSS methods to extract length scales from numerical simulations and more importantly from experiments where the above problems can be inherently avoided. In ref 19 a novel method named the block analysis method was introduced. The major problems of conventional FSS analysis are avoided leading to an excellent scaling technique. Figure 2(a) shows a schematic representation of block analysis methods. In this method an equilibrium molecular dynamics simulation is performed on a large system and then the whole simulation box is systematically divided into blocks of varying sizes. A different block size here would imitate different system sizes in the conventional FSS argument, but the problem of density and composition fluctuations will not arise as the subsystem or the blocks can be thought of as immersed in a bigger bath mimicking a grand canonical ensemble. The appropriate physical quantities, such as $\chi'_s$ and $\alpha$ relaxation time, $\tau_{\alpha}$, for an individual block are then calculated and averaged over different blocks and different ensembles. The dynamical susceptibility for an individual block ($L_B$) is then redefined as

$$\chi'_s(L_B, t) = \frac{NL^4}{L_B^4} \left(\langle Q(L_B, t) \rangle - \langle Q(L_B, t) \rangle^2\right)$$  

(6)

Its peak value ($\chi''_s(L_B, T)$) as expected shows a strong block size and temperature dependence. Thus, obtaining the dynamical length scale using the FSS scaling form (eq 5) immediately becomes an obvious choice.

In the inset of Figure 2(d) the block size and temperature dependence of $\chi'_s$ are shown, and the main panel displays the scaling collapse following the scaling ansatz (eq 5). The obtained scaling collapse is indeed very good as compared to the scaling collapse obtained from conventional FSS of $\chi'_s(N, T)$ at different system sizes as shown in Figure 2(c). The obtained length scale is validated using other methods (shown in Figure 2(f)) and is found to grow substantially with increasing supercooling. A similar route of obtaining the dynamic length scale was presented in the work of Bhowmik et al. by analyzing the van Hove correlation function. The Van Hove correlation function, $G_s(x, t)$, is the probability of finding a number of particles with displacement $x$ over a time interval $t$. For normal liquids without the presence of dynamic heterogeneity, the van Hove function will be Gaussian in nature. In ref 20, the van Hove function is computed over a coarse-grained length scale similar to Block Analysis (shown in Figure 2(e)) but instead of getting the van Hove function of the individual block, each block is...
Figure 2. (a) Schematic diagram for the block analysis method. (b) Time evolution of four point susceptibility \( \chi(t, T) \) (see text for definition) for a binary Lennard-Jones system in three dimensions. The appearance of a peak in \( \chi(t) \) at time closer to the structural relaxation time \( \tau_s \) indicates the presence of maximal dynamic correlations at that time scale, and an increase in peak height \( \chi(t) \) with decreasing temperature indicates the growth of dynamic correlations. (c) Finite size scaling done on \( \chi(N, T) \) to obtain the dynamic heterogeneity length scale \( \xi^\text{fl} \). The system size variation of \( \chi(N, T) \) for the system at different temperatures is plotted in the inset (adapted with permission from ref 13. Copyright 2009 Proceedings of the National Academy of Sciences of the United States of America). (d) Scaling collapse obtained for \( \chi(L_B, T) / \chi(\infty, T) \) on rescaling the block length \( L_B \) with an appropriate system length scale \( \xi^\text{fl} \). Also, the block size variation of \( \chi(L_B, T) / \chi(\infty, T) \) for different temperatures is shown in the inset (adapted with permission from ref 19. Copyright 2017 American Physical Society). (e) Self-part of the van-Hove function, \( G(x, \tau_a) \), calculated for a composite particle made of particles present in a block of linear length \( L_B \) at \( \tau_a \) time. The non-Gaussianity of \( G(x, \tau_a) \) for a smaller block size indicates the presence of different mobility clusters at the length scale of the block size (adapted with permission from ref 20. Copyright 2018 American Physical Society). (f) Comparison of the temperature dependence of the dynamic length scale obtained from FSS of \( \chi(N, T) \), i.e. \( \xi^\text{fl} \), block length scaling of \( \chi(L_B, T) \), i.e. \( \xi^\text{fl}_{LB} \) and block length scaling the non-Gaussian parameter of the self-part of the van-Hove function of a composite particle, i.e. \( \xi^\text{fl}_{LB} \).

To compute static correlations using the same method, the block size dependence of the distribution of \( \tau_a(L_B) \) is examined. The mean \( \langle \tau_a(L_B) \rangle \) and the variance \( (\Delta \tau_a(L_B))^2 \) of \( \tau_a \) of a block of particular length are used to compute the following scaling function.

\[
\chi(L_B, T) = L_B^{-1} \left[ \frac{(\Delta \tau_a(L_B))^2}{\langle \tau_a(L_B) \rangle^2} \right]
\]  

where \( \Delta x = x - \bar{x} \) overline represents the average over different blocks and the outer angular bracket stands for ensemble and time origin average. Thus, \( \chi(L_B, T) \) measures the normalized spatial fluctuations in \( \tau_a \) at the length scale of the block size; hence, it probes the presence of mosaics. For block size comparable to or smaller than the typical mosaic size, \( \chi(L_B, T) \) should be small because of the fact that almost all particles in a block would be structurally correlated; thus, \( \chi(L_B, T) \) should not vary much spatially. On increasing the block size, the number of particles out of the mosaic in a particular block starts to increase, hence the spatial fluctuation. Eventually for large enough block size these fluctuations would saturate. A similar finite size scaling analysis of \( \chi(L_B, T) / \chi(\infty, T) \) as a function of \( L_B / \xi^\text{fl} \) will lead to extraction of the underlying static length scale. The scaling collapse indeed was found to be very good, and the extracted length scale compares very well with other conventional methods such as PTS as shown in the inset of Figure 3(f).

To reiterate once more, the usual finite size scaling requires equilibrium systems with periodic boundary conditions and different system sizes that are small or comparable to the relevant length scale. Even in colloidal experiments, this will be very difficult to execute since the trajectories of all the particles in the entire system need to be imaged. Now, in the block analysis method, one can easily image a smaller section of the sample and then vary the imaging volume. One can also image a slightly larger sized region using a confocal microscope and then do the rest of the block analysis as done in simulations. Blocks of different sizes would imitate different system sizes in the conventional FSS method. Thus, it will not be difficult to extract the dynamic length scale in colloidal glasses experimentally by doing finite size scaling of dynamic susceptibility for individual blocks. The largest block that is needed to have a good range of sizes for doing finite size scaling is around 2000–4000 particles.

The mean \( \langle \chi(t) \rangle \) at time closer to the structural relaxation time \( \tau_s \) indicates the presence of maximal dynamic correlations at that time scale, and an increase in peak height \( \chi(t) \) with decreasing temperature indicates the growth of dynamic correlations. (c) Finite size scaling done on \( \chi(N, T) \) to obtain the dynamic heterogeneity length scale \( \xi^\text{fl} \). The system size variation of \( \chi(N, T) \) for the system at different temperatures is plotted in the inset (adapted with permission from ref 13. Copyright 2009 Proceedings of the National Academy of Sciences of the United States of America). (d) Scaling collapse obtained for \( \chi(L_B, T) / \chi(\infty, T) \) on rescaling the block length \( L_B \) with an appropriate system length scale \( \xi^\text{fl} \). Also, the block size variation of \( \chi(L_B, T) / \chi(\infty, T) \) for different temperatures is shown in the inset (adapted with permission from ref 19. Copyright 2017 American Physical Society). (e) Self-part of the van-Hove function, \( G(x, \tau_a) \), calculated for a composite particle made of particles present in a block of linear length \( L_B \) at \( \tau_a \) time. The non-Gaussianity of \( G(x, \tau_a) \) for a smaller block size indicates the presence of different mobility clusters at the length scale of the block size (adapted with permission from ref 20. Copyright 2018 American Physical Society). (f) Comparison of the temperature dependence of the dynamic length scale obtained from FSS of \( \chi(N, T) \), i.e. \( \xi^\text{fl} \), block length scaling of \( \chi(L_B, T) \), i.e. \( \xi^\text{fl}_{LB} \) and block length scaling the non-Gaussian parameter of the self-part of the van-Hove function of a composite particle, i.e. \( \xi^\text{fl}_{LB} \).
and in colloidal experiments. So block analysis will not have a significant limitation for colloidal glasses. Implementing the same for molecular liquids will be nearly impossible; thus, block analysis will not be useful for extracting the same dynamical length scale in molecular glasses. The limitation of block analysis can be largely overcome via the method that we are going to discuss in the next section. This method can be directly implemented in experiments to extract these length scales in molecular glass-forming liquids using rod-like particles as a probe.

**Rods: The Measuring Tape for Different Length Scales.**

Probing microscopic properties of liquids using rod-like probe molecules is not new in experiments. Rotational-translation decoupling, rotational relaxation times, single molecule dynamical studies, etc. are the usual quantities that are measured using fluorescence and phosphorescence depolarization, a photobleaching technique, nuclear magnetic resonance (NMR) spectroscopy, and dielectric relaxation methods. Probe rods of the size of a single dye molecule (∼1 nm) to gold nanorods (∼20 nm) have been used in molecular glass-formers to study dynamic heterogeneity in previous studies. In ref broadening in the distribution $P(\log(\tau_R))$ is observed with increasing supercooling where $\tau_R$ is the decorrelation time for dye molecules/gold nanorods immersed in supercooled glycerol. This observation clearly indicates the increase in dynamic and static correlations in the supercooled liquid glycerol at the length scale of respective probe length with increasing supercooling. It was also claimed that the distribution $P(\log(\tau_R))$ is log-normal in nature. But the extraction of the associated length scale was lacking along with an understanding of the log-normal nature of the distribution of decorrelation times. These results certainly call for a proper theoretical explanation, and in ref both the dynamic and static length scale are obtained by studying the rotational dynamics of hard rods immersed in model glass-formers (see Figure 3(a) for a schematic) along with an analytical derivation of the asymptotic form of the distribution of rotational decorrelation time. The proposed methodology is thus very interesting and will not be difficult to implement in experiments to extract both dynamic and static length scales of molecular glass-formers as well as colloidal glasses and granular media. The key concept behind this method is similar to that of block analysis explained earlier, but this method is immediately realizable in experiments to study the growth of the dynamic and static correlation in molecular glass-formers.

[Figure 3.](#) (a) Schematic of a rod-like particle as probe in a glassy environment. (b) Rod length variation of the peak value of non-normal parameter $\langle \sigma_3^2 \rangle$, a parameter which quantifies the fluctuation in the rotation diffusion constant of the rod in a glassy environment modeled by the 3dKA system. The time evolution of $\tau_{\chi\ell}$ for a rod of length $L = 2.5$ immersed in the same model system is presented in the inset. (c) Collapse obtained for $\tau_{\chi\ell}(T)$ on scaling the rod length with an appropriate system length scale, $\xi_\ell(T)$. The quality of collapse and the comparison of the obtained length scale with the dynamic length scale measured by traditional methods in the inset confirms the robustness of the method. (d) Distribution of log of scaled first passage time (FPT) distribution (scaled with moment of inertia) for rods of various lengths in the 3dKA system at temperature $T = 2.0$ (high temperature) with the absorbing boundary at $\phi = \pi/8$. (e) Same distribution but at temperature $T = 0.5$ (low temperature). The emergence of supercooling effects can be seen clearly as a shoulder build up in a small time regime indicating the cooperative motion because of emerging local structure. (f) Rod length scaling the rod length with an appropriate system length scale, $D_{\chi\ell}$ for a rod of length $L$. The emergence of supercooling effects can be seen clearly as a shoulder build up in a small time regime indicating the cooperative motion because of emerging local structure. (g) Same distribution but at temperature $T = 0.5$ (low temperature). The emergence of supercooling effects can be seen clearly as a shoulder build up in a small time regime indicating the cooperative motion because of emerging local structure.
To measure the spatial fluctuation of diffusion constants in a system, one measures the deviation of the self-part of the van Hove function, $G_s(r, t)$, from its Gaussian form for a system with homogeneous diffusion. This quantity is called the non-Gaussian parameter, $\alpha_s(t)$. Appearance of exponential fat tails in $G_s(r, t)$ (see Figure 2(e)) is known to be universal across various systems encompassing granular as well as biological systems. Thus, a nonzero value of the non-Gaussian parameter, $\alpha_s(t)$, is considered a good measure for quantifying the dynamic heterogeneity in the system, and works presented in ref 20 suggest that extraction of the underlying heterogeneity length scale is possible from this information using suitable finite size scaling analysis. Similarly, for rotational dynamics of the rod one can solve the rotational diffusion equation to get the distribution of angular displacement for Brownian rods immersed in a dynamically homogeneous medium in both two (2D) and three dimensions (3D) analytically. Deviation from that distribution would then be a measure in fluctuation of the rotational diffusion constant provided by a dynamically inhomogeneous medium. From the exact solutions in ref 23 one can easily verify the following to be the non-normal parameters (NNPs) for the rotational dynamics of the rod in 2D and 3D,

$$\alpha_{rot,2D}(t) = \frac{1}{3} \left( \langle \hat{u}(t) - \hat{u}_0 \rangle^2 \right)^2 - \frac{1}{24} \left( \langle \hat{u}(t) - \hat{u}_0 \rangle^2 \right)^3 \times \left( \langle \hat{u}(t) - \hat{u}_0 \rangle^2 \right) - 8 - 1$$

(8)

$$\alpha_{rot,3D}(t) = \frac{1}{2} \left( \langle \hat{u}(t) - \hat{u}_0 \rangle^2 \right)^2 + \frac{1}{6} \left( \langle \hat{u}(t) - \hat{u}_0 \rangle^2 \right) - 1$$

(9)

where $\hat{u}(t)$ is the orientation vector of the rod at time $t$ and $\hat{u}_0$ is the initial orientation of the rod. The NNP should be zero for a rod immersed in a homogeneous medium, so one should expect the same for rods in high temperature (or low density) liquid at all times independent of the rod lengths. But in a supercooled environment this NNP shows a peak at time $\tau_{ss}$ (see the inset of Figure 3(b)) similar to $\chi_4(t, T)$. Thus, the peak height would be a very good measure of the dynamic heterogeneity present in the system at that time probed by the rod. Also the peak height ($\alpha_{rot,2D}$ and $\alpha_{rot,3D}$) decreases with increasing rod length (see Figure 3(b)) as a rod of larger length sees the dynamical response of the surrounding medium averaged over the typical volume of the linear dimension that is proportional to the rod length. A length scale $\xi_{rod}(T)$ is obtained by scaling the rod length with an appropriate system length scale to obtain a master curve between $\alpha_{rot,2D}(T)$ or $\alpha_{rot,3D}(T)$ and $I_{rod}/\xi_{rod}(T)$ (see Figure 3(c)). The equivalence of the temperature dependence of the length scale obtained with the traditional methods and the quality of the collapse suggest that it is indeed a robust method to extract the dynamical length scale of the system.

Similarly, an appropriate finite size scaling analysis of the rotational decorrelation time of rods in supercooled liquids yields a static length scale as discussed below. Thus, a probing rod picks up both the static and dynamic length scales from the same experiments or simulation study, very similar to the block analysis method discussed in the previous section. In experiments, rotational decorrelation times ($\tau_{ss}$) of hard rods are usually measured and are defined as the time ($\tau_{ss}$) when $\cos \theta = \hat{u}(t) \cdot \hat{n}_0$ crosses some predefined value ($\cos \theta = \cos \theta_0$). So in 2D the distribution of $\tau_{ss}$ is the first-passage-time (FPT) of the rod which measures the time taken for the rod to rotate to $\theta = \pm \theta_0$ starting from $\theta = 0$, and in 3D it is the FPT of the rod on a cone defined by $\theta = \theta_0$, with the initial condition of the rod along the z-axis. One can solve the rotational diffusion equation with appropriate boundary and initial conditions to find out the distributions of FPT as given in ref 21. Any deviation in observed rotational decorrelation time distribution from these exact expressions would simply mean the emergence of a structural correlation in the system. The rotational diffusion constant of rods ($D_\phi$) in liquids grows inversely with the moment of inertia of rods $I_{rod}$ so for rods of different length in liquid (high temperature or low density liquid) at the same temperature, the distribution of the scaled time, $P(y = \log(t_{ss})/I_{rod})$ should be a master curve as shown in the bottom left panel of Figure 3 (see ref 21 for detailed theoretical arguments). On increasing supercooling this distribution tends to form a shoulder in the small time region (see Figure 3(e)) for smaller rods which is a clear indication of cooperative motion of local structure formed at the length scale comparable to the rod length. The skewness ($\chi_{FPT}$) of $P(y = \log(t_{ss})/I_{rod})$ would thus be a good parameter to measure the emerging static correlations. Figure 3(f) shows the collapse generated by scaling $\chi_{FPT}(T, I_{rod})$ with the appropriate system length scale $\xi_{rod}^n$. The quality of collapse and the comparison of the obtain length scale with traditional methods and block analysis in the inset suggest that rod-like molecules can be an excellent probe of complex dynamics of glass-forming liquids. Future studies along this direction will certainly be very useful for establishing the robustness of this method for a wide variety of systems in both simulations and experiments.

**Medium Range Crystalline Order (MRCO).** Another question that has bothered researchers for an extended time is the potential origin of dynamic heterogeneity being hidden in its local structure. If the answer is affirmative, then the search for an appropriate structural quantity may lead to better understanding of the physics of glass formation. Different structural motifs including the icosahedral have been identified in colloids and granular experiments and in computational studies. These structural motifs are often referred to as locally favored structure (LFS) (see Figure 4(a)–(d)) which fails to span the whole system due to frustration arising from the incommensurate nature of the structural motifs. However, there are glass forming liquids which do not present any apparent local structural order, or at least the essence of local structural symmetry is not understood but shows rather comparable dynamics with the LFS glass forming liquids. Such findings raise the question of whether the mechanism of glass transition in systems with or without LFS is the same or not. A few studies have been carried out recently to link the local order to slow structural relaxation and fragility. Recently Tah et al. analyzed a special category of glass formers, whose properties are dominated by growing structural order, which are different from generic glass formers. This local order is measured in terms of the hexatic order parameter ($\psi_6$) for 2d systems,

$$\psi_6 = \frac{1}{N} \sum_{i=1}^{N} \psi_6', \quad \text{with} \quad \psi_6' = \frac{1}{n_i} \sum_{k=1}^{n_i} \exp(16\theta_{jk})$$

(10)

where $\theta_{jk}$ is the angle made by the vector from particle $j$ to its neighbor $k$ with the axis $x$ and $n_i$ is the number of neighbors of particle $j$ (in two dimensions). The associated length scale, $\xi_{rod}(T, I_{rod})$ calculated from the spatial correlation of $\psi_6$. An obvious question that comes up from this study is whether local structural order will form eventually at very low temperatures for all glass forming liquids or this class of glass-formers belongs to a
special category. In Figure 4(b) a snapshot of such local order, also known as medium range crystalline order (MRCO), is shown for one of the model glass forming liquids. The authors clearly showed that the dynamical slowing down is strongly correlated with growing structural order associated with MRCO. These results are in complete agreement with other previous results. The authors have established that the dynamic length scale is strongly coupled to the structural or the static length scale (shown in Figure 4(c)). Analogous experimental results at the deep supercooled regime were presented by Hallett et al.\textsuperscript{24} for the colloidal system (rendered coordinates of defective icosahedra and full icosahedra for colloids are shown in Figure 4(a)) and reveal a strong correlation between structural order to dynamics, and they found that domains of local structure have a characteristic time scale of the system. Most of the studies on dynamical heterogeneity have focused on the $\alpha$-relaxation time, whereas very few studies were done at other time scales although it has important implications in the dynamics at various other time scales as well. In ref 28 it was shown for the colloidal system that characterizes the local structure of different types of structural ordering (between short-range localized ordering (denoted by particle size $a$), medium-range crystal ordering (denoted by MRCO), and particular bond orientational ordering (denoted by icosahedral LFS)) for 2d spin liquids and 3d polydisperse colloids (adapted with permission from ref 25. Copyright 2013 Royal Society of Chemistry). (d) Molecular snapshot for generic glass formers close to $T_g$ (adapted with permission from ref 12. Copyright 2018 American Physical Society). (e) Growth of dynamic ($S_q(q,\tau)$, $S_q(q,\tau_b)$, BC) and static length scales ($\xi_{\text{stat}}$, $\xi_{\text{max}}$) for molecular liquid in the presence of medium range crystalline order (MRCO), and $\xi_{\text{bc}}$ is the structural length scale, which emerges from local structural order (adapted with permission from ref 12. Copyright 2018 American Physical Society). (f) Growth of dynamic and static length scales for generic glass forming liquid (adapted with permission from ref 12. Copyright 2018 American Physical Society).

Temporal Evolution of Dynamic Heterogeneity. After characterizing dynamic heterogeneity, one might wonder whether this heterogeneous nature of the dynamics persists over a wide range of time scales or it is mostly significant at some characteristic time scale of the system. Most of the studies on dynamical heterogeneity have focused on the $\alpha$-relaxation time, whereas very few studies were done at other time scales although it has important implications in the dynamics at various other time scales as well. In ref 28 it was shown for the first time that the dynamic heterogeneity length scale is intimately connected with the $\beta$-relaxation time, $\tau_\beta$ and suggested that it is quite possible that dynamic heterogeneity is well developed at a time scale as short as $\tau_\beta$. In a recent work Tah et al.\textsuperscript{29} have explicitly shown that displacement of particles is correlated over a larger length scale at the time scale $\tau_\beta$ leading to a very strong system size dependence which is very unusual as $\beta$-relaxation is generally believed to be a local process and not cooperative in nature. Moreover, the obtained correlation length has been found to have the same temperature dependence as that of the dynamical heterogeneity length scale computed at the $\alpha$-relaxation time. This observation supports the previous findings of ref 28. It is interesting to also note that some of these results are in fact in good agreement with some of the predictions from inhomogeneous mode coupling theory (IMCT). IMCT states that there exists a unique diverging “dynamical correlation
length” that grows as $\xi_d \sim |T - T_d|^{\alpha}$ and the temperature dependence of this length scale is the same in both the $\alpha$ and $\beta$ relaxation regimes. This observation is found to be robust across different model systems. Note that it is quite possible that dynamic heterogeneity developed at the $\beta$-relaxation time may act as a precursor for the dynamic heterogeneity observed in the $\alpha$-relaxation time. This may then give us clues of why the temperature dependence of the length scale remains the same across different time scales. Detailed studies are necessary to elucidate this issue in the near future.

In ref 29 it was found that $\xi_d(t)$ obtained from the wave vector dependence of $S_d(q, t)$ grows up to $\tau_\alpha$ and decreases at a later time. It was also found that a power law $\chi(t) \sim t$, holds well and near to the $\alpha$-relaxation time and the correlation length $\xi_d$ grows with time as $\xi_d \sim \log(t)$. However, at later time scales $\xi_d$ was found to remain constant up to the time at which the correlation length can be measured accurately. The time dependence of dynamics heterogeneity seemed to be different for hard sphere and soft sphere systems. To examine the time dependence of the heterogeneity length scale for soft sphere and hard sphere glass forming liquids, further studies have been done in ref 29 using a different model system (referred here as 3dHP), in which the softness $\delta$ of the interaction potential, $V(r) = \frac{C}{\delta}(1 - \left(\frac{r}{\delta}\right))^5$ has been tuned systematically. This model system is widely used in the literature as a prototypical model to study the jamming transition. The interaction potential becomes softer with increasing $\delta$, and the nature of the heterogeneity is found to be different with increasing $\delta$. It was observed that for the softness parameter $\delta = 2$ the heterogeneity length $\xi_d$ reaches a peak at time scale close to $t = 4\tau_\alpha$ and it shifts toward the lower time scale $t \sim \tau_\alpha$ for softness parameter $\delta = 3$. This suggests that the nature of dynamic heterogeneity in soft sphere models may be qualitatively different from other generic molecular glass-former liquids. However, the length scale computed from the particle displacements correlation (measurement of translational and directional correlation, called vectorial displacement—displacement correlation) shows a completely different behavior; it remains the same in magnitude over all the time window from $\tau_\beta$ to $\tau_\alpha$. This result is very puzzling and a resolution to this remains unclear at this moment.

CONCLUSIONS

Finally, we end this review by briefly summarizing the recent progress that enabled us to gain a better understanding of the microscopic reasons behind the slow and heterogeneous dynamics of glass forming liquids and highlighting some outstanding issues that still need to be resolved. It is now universally accepted that heterogeneity in the dynamics of glass-forming liquids is a hallmark nature of the glass transition, and there is a growing dynamical correlation length associated with it. Thus, a better understanding of the growth of the heterogeneity length scale will definitely have a wider impact as glass-like dynamical behavior is observed in many other systems including biologically relevant systems. At the same time it is also important to emphasize that the growth of the dynamical length scale may not be directly related to the slowing down in the dynamics at least in generic glass forming liquids. The existence of a static length scale that directly couples to a drastic rise in viscosity is now believed to be central for solving glass transition problem, and various numerical and experimental attempts to measure such a length scale are indeed very encouraging. Although a lack of simpler but elegant methods to probe both these important length scales is still crippling the major progress in this field, most of the studies in this direction are still restricted to model glass forming systems in computer simulation and there are only a handful of experimental studies. The current review highlights some of the issues and also presents some methods that might encourage more future experimental studies. This review also highlights the possible existence of a separate class of glass-forming liquids whose dynamical behavior can be distinct from other generic glass-formers. This new category of glass-formers has predominant local structures (MRCO or LFS) which lead to strong coupling of static and dynamic length scales leading to one single length scale that controls both the dynamics and thermodynamics of the system. It is quite possible that the physics of the glass transition may be easier to understand in these systems thermodynamically but that mechanisms may not be applicable to generic glass-formers. It implies that there is no unified thermodynamic theory that can explain the glass transition physics for all types of glass-forming systems, and the dynamic description of the glass transition cannot be ruled out. The LFS systems are distinct from other generic glass formers, and it is important to address the physical mechanism of the glass transition separately for these systems even though it may not be the generic mechanism of the glass transition in all glass-forming liquids. A better understanding of the microscopic origin of the glass transition in systems with local ordering may still have implications in realistic glass-formers like metallic glasses which poses local ordering at a scale of a few tens of nanometers.30

Finally, temporal evolution of dynamic heterogeneity in glass-forming liquids also turns out to be nontrivial, and a better understanding of this phenomena may help us improve the dynamical and rheological properties of many glassy materials for design of better materials.

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