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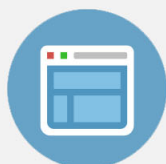Strong influence of supercooled liquid on crystallization of the Al 85 Ni 5 Y 4 Nd 4 Co 2 metallic glass
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Perspective: Supercooled liquids and glasses

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Supercooled liquids and glasses are important for current and developing technologies. Here we provide perspective on recent progress in this field. The interpretation of supercooled liquid and glass properties in terms of the potential energy landscape is discussed. We explore the connections between amorphous structure, high frequency motions, molecular motion, structural relaxation, stability against crystallization, and material properties. Recent developments that may lead to new materials or new applications of existing materials are described. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4747326]

I. INTRODUCTION

Glasses play a critical role in current and developing technologies. Metallic glasses, consisting of alloys of two or more components, enable modern power transmission[1] and are finding increasing use in applications calling for high strength or low shrinkage upon solidification.[2] Amorphous inorganic semiconductors have revolutionized optical disc technology and may play a critical role in non-volatile electronic memory.[3] Modern communication technology would be impossible without amorphous silicates for optical fibers. Organic glasses are the basis for organic light emitting diodes and other developments in organic electronics.[4,5] Polymer glasses are replacing metals in the fuselage of new commercial aircraft.[6] Glasses, and the supercooled liquids from which they are usually prepared, also provide a challenging array of fundamental questions that have been the subject of study for nearly 100 years. The last decade has seen significant advances in the microscopic characterization of these amorphous materials, driven by the development of innovative experimental strategies and increasing ingenuity in the use of computer simulations, often inspired by the perspectives and predictions of theoretical descriptions. Here we review some of these new developments and speculate about fruitful avenues for future work. Our coverage of recent work in the field is neither comprehensive nor systematic, but we endeavour to describe research that provides important physical insights and enables new developments in the application of amorphous materials.

Three physical features dominate much of the behavior of liquids as they are supercooled. The first is the massive increase in the shear viscosity (more than a factor of 10^{14}) that results in the continuous transition from a low viscosity fluid to a solid glass, characterized by the glass transition temperature T_g. This behavior is illustrated for SiO_2 and o-terphenyl in Figure 1. Liquids such as SiO_2 whose viscosity exhibits an Arrhenius temperature dependence are known as *strong* liquids.[7] The viscosity of o-terphenyl, in contrast, is quite non-Arrhenius, the defining characteristic of a *fragile* liquid.[7] The change of the effective activation energy with temperature for fragile liquids suggests an increasing de-

gree of cooperativity in the relaxation mechanism, a feature whose explanation has been the major focus of theoretical descriptions of the glass transition.[8] The structural relaxation time τ_α represents the time required for the liquid to return to equilibrium after a small perturbation. In practice, it is accessed via dielectric relaxation measurements or dynamic neutron scattering. As shown schematically in Figure 1, τ_α and the viscosity have similar temperature dependences, and both are frequently used to quantify the transition between liquid and glass.

The second key feature of supercooled liquids is the temperature dependence of the entropy. Since the heat capacity of a liquid is larger than that of the crystal, the liquid entropy decreases more rapidly on cooling than does the entropy of the ordered phase, as shown in Figure 2 for o-terphenyl. Were this trend to continue, the entropy of the supercooled liquid would equal the entropy of the crystal (at the *Kauzmann temperature* T_K[12]) and, ultimately, become negative and thus unphysical. The problem is avoided in practice as, on cooling, the structural relaxation time eventually exceeds the time scale defined by the cooling rate. (There is considerable interest in relating the loss of entropy in the liquid with the increasing cooperativity of relaxation,[13] a subject we shall return to in Sec. II.) At T_g, the sample falls out of equilibrium with a corresponding decrease in the measured heat capacity; below this temperature, properties become time-dependent as the sample slowly "ages." Kinetic arrest does not resolve the *conceptual* problem regarding the ultimate fate of the metastable liquid. (We can, after all, legitimately ask what we would expect to see for an observation time of arbitrary duration.) The two most likely fates of the liquid state are (i) the loss of metastability with respect to crystallization[12,14,15] and (ii) a transition to a (low heat capacity) disordered ground state.[16–18]

The third key feature is dynamic heterogeneity, a relatively recent addition to the phenomenology of supercooled liquids, but one that provides an explicit and quite general connection between spatial fluctuations and relaxation kinetics. The continuous transition from fluidity to rigidity on cooling points to some kind of coexistence of liquid-state and solid-state behavior. The discovery of *spatially heterogeneous*
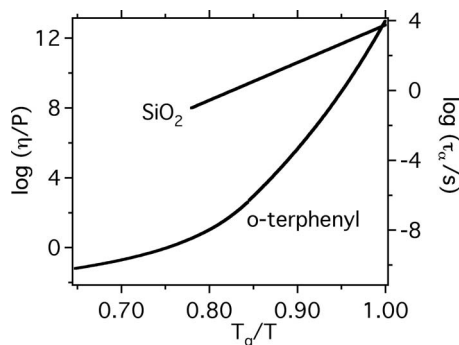
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FIG. 1. Viscosity as a function of inverse temperature for SiO_2 and o-terphenyl. Because the structural relaxation time τ_α has nearly the same temperature dependence as the viscosity, a single curve reasonably represents both functions. (Viscosity data from Refs. 9 and 10.)

dynamics or *dynamic heterogeneity* in supercooled liquids has provided an explicit physical picture of the form this coexistence takes.[19–22] Computer simulations have played a central role in establishing the existence of these transient fluctuations in dynamics.[23] As illustrated in Figure 3, in supercooled liquids, the rates of molecular rearrangements differ from one region of space to another.[25] Near T_g, these rates can vary by several orders of magnitude between points separated by only a few nanometers.[21,24] Dynamic heterogeneities, such as those depicted in Figure 3, evolve over time so that eventually all particles have sampled the fast and slow environments.

It is our view that the problems posed by supercooled liquids and the glass transition do not correspond to a single unified quest but, instead, are most usefully treated as multiple inter-related lines of inquiry. Reflecting this view, this perspective is organized around six themes: the energy landscape, vibrations, stress relaxation, diffusion and molecular reorientation, structure and crystallization, and finally, interfaces and thin films. The energy landscape, discussed in Sec. II, provides a useful framework for unifying the discussion of the diverse aspects of supercooled liquids. This unification comes, we admit, with a level of abstraction that might not interest all readers. As the sections of this article can be read in any order, we invite readers to skip ahead as their interest dictates.
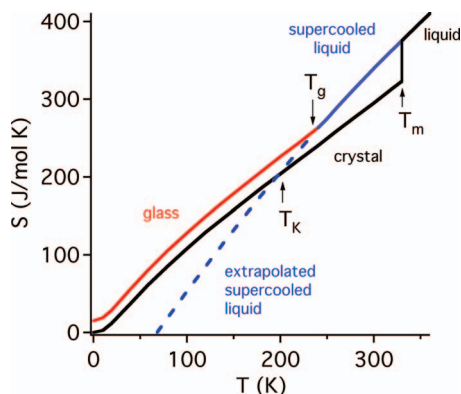

FIG. 2. Entropy as a function of temperature for o-terphenyl in the liquid, supercooled liquid, glass, and crystal. (Data from Ref. 11.)
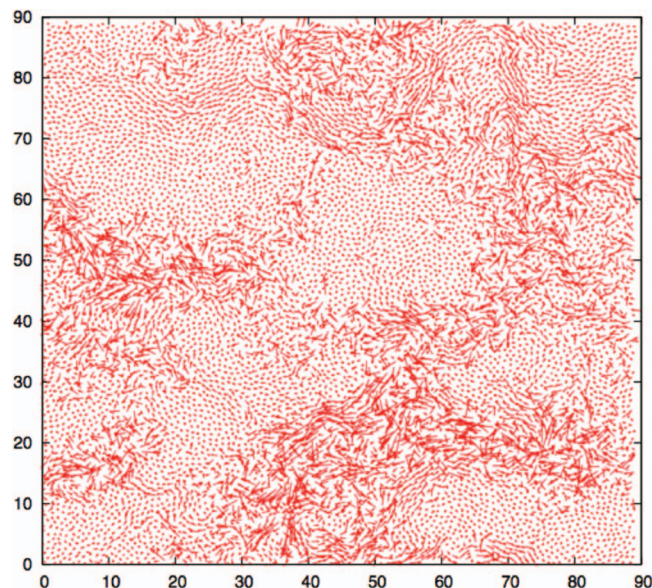

FIG. 3. The relative magnitudes of the displacements of particles in a 2D Lennard-Jones mixture over the timescale of structural relaxation are represented by the length of their displacement vectors. Reprinted with permission from L. Berthier, Phys. **4**, 42 (2011). Copyright © 2011 American Physical Society.

II. DYNAMICS AND LOCAL MINIMA IN THE POTENTIAL ENERGY LANDSCAPE

The instantaneous configuration of a collection of particles can, formally, be represented as a single point in a high dimensional space. The potential energy of a supercooled liquid or glass is a function of the positions of all the atoms in the system and so can be regarded as a complicated surface (the so-called potential energy *landscape*) over this high dimensional space of configurations. In the last decade, considerable progress has been made in transforming the potential energy landscape into a quantitative computational tool for understanding amorphous systems.[26] This work has been reviewed in Refs. 27 and 28.

The central insight of the landscape picture is that the equilibrium properties of a deeply supercooled liquid are dominated by the properties of the local potential energy minima (the *inherent structures*) while the kinetics of relaxation and transport are governed by the transitions between these local minima.[29]

A. The distribution of inherent structures as a function of energy

The number of local minima at a given energy is given by the density of states G(e). This quantity can be written as $G(e)$ = exp $[s_c(e)N]$ with $s_c(e)$ being the configurational entropy per particle for minima in the same energy range. The calculation of G(e) is a straightforward, if time consuming, computational problem. In Figure 4, we reproduce the distribution G(e) calculated for models of SiO_2[30] and a binary atomic alloy[31]—examples of a strong and fragile liquid, respectively. Both G(e)'s are well-fitted by a Gaussian (as shown) with the principal difference being that the density of states of SiO_2
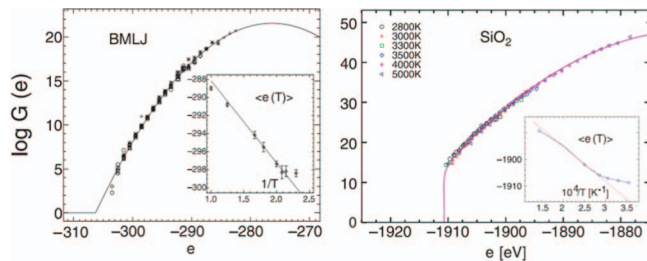
FIG. 4. The distribution G(e) of inherent structures as a function of energy in a binary Lennard-Jones mixture (BMLJ) and a model of SiO_2. The lines correspond to Gaussian fits, with a cutoff utilized in the right panel. The inserts show the temperature dependence of the average inherent structure energy. Reprinted with permission from A. Heuer, J. Phys.: Condens. Matter **20**, 373101 (2008). Copyright © 2008 Institute of Physics.

exhibits a well-defined low energy cutoff at an energy e_{cut}. The configurations associated with e_{cut} in SiO_2 correspond to a continuous random network in which every silicon atom is coordinated by 4 oxygens. In spite of sharing the same local topology as the crystalline state, there are a large number of such disordered networks[32] so that liquid silica can be cooled into these disordered ground states without a large loss of entropy. Once a liquid has been cooled to the point where almost all accessible states have a configurational energy near e_{cut}, further cooling cannot change the accessible configurations or the connectivity of the network and, hence, we would expect the dynamics below this temperature to exhibit only an Arrhenius temperature dependence, as is indeed observed in the case of SiO_2 (see Figure 1).

The density of states of the fragile glass former in Figure 4 (a mixture of Lennard-Jones spheres) has, in contrast, no obvious lower cutoff and so the number of accessible minima could, in principle, decrease continuously with temperature. There is some discussion concerning whether this trend continues smoothly to its ultimate end with the crystalline state[33] or if there is, even for the close-packed liquids, some abrupt decrease in the amorphous density of states.[34] One of the simpler realizations of this unresolved quandary is whether the random close-packed density of hard sphere mixtures is a robust property of the density of states[35,36] or if it depends upon the method of preparation.[37]

B. Trap models of landscape dynamics

To proceed beyond the qualitative connection between the density of states and the temperature dependence of the dynamics provided above, we need to consider, along with G(e), the connectivity of the pathways between the energy minima and the energy barriers along these paths. Trap models represent a simple but instructive treatment of this problem.[38–40] Let us assume that the hopping rate from minimum i to minimum j is given by $\Gamma_{i \rightarrow j} = \Gamma_o \exp[-\beta E_{ij}]$ where $E_{ij} = e_j - e_i + V_o$ for $e_i \leq e_j$ and $E_{ij} = V_o$ otherwise. Here e_i is the energy of the ith minimum, $\beta = 1/k_B T$ and V_o is the barrier height which, for simplicity, is assumed to be the same for all transitions. In the ideal Gaussian model,[41] the issue of connectivity is reduced to the assumption that once a threshold energy e* is reached, the local minima are

sufficiently connected that irreversible relaxation will occur. Transitions between energy minima still occur below e*, but these transitions are often reversed before new parts of the landscape are explored; a group of minima connected in this way are known as a *metabasin*. In contrast, transitions from metabasin to metabasin occur much less frequently and are essentially never reversed. The reader should note that it is irreversibility (as opposed to landscape topography) that represents the key concept in the definition of a metabasin. In the ideal Gaussian model, it is assumed that any site with an energy less than e* can make transitions to a number of metabasins that is proportional to G(e*)/G(e), the random mixing result. The rate of escape Γ(e) from a site of energy e is then given by

$$\Gamma(e) = \Gamma_o \frac{G(e^*)}{G(e)} \exp[-\beta(e^* - e)] \exp[-\beta V_o] \qquad \text{for e} \leq \text{e*}$$

$$\Gamma(e) = \Gamma_o \exp[-\beta V_o] \qquad \text{for e} > \text{e*}. \qquad (1)$$

The temperature dependent relaxation time $\langle \tau \rangle$ is obtained as the average over the equilibrium distribution of inherent structures $p_{eq}(e)$ of the rate of escape Γ(e) from individual minima by

$$\langle \tau \rangle^{-1} = \int_{e_{cut}}^{\infty} de \; p_{eq}(e) \Gamma(e). \qquad (2)$$

The ideal Gaussian model, as characterized by Eqs. (1) and (2), predicts that, as the temperature decreases, the effective activation energy increases from V_o to the low temperature limit, $V_o + e^* - e_{cut}$. Here is a rationalization of the super-Arrhenius temperature dependence that characterizes fragile liquids. In some liquids, such as SiO_2, that low temperature limit (i.e., at which $p_{eq}(e) \approx \delta(e_{cut} - e)$) is reached at sufficiently high temperature such that the relaxation rate is still high. The subsequent decrease in the relaxation rate below this temperature is Arrhenius with an activation energy of $V_o + e^* - e_{cut}$. The simple threshold treatment of the connectivity between inherent structures provided by the ideal Gaussian model avoids any explicit treatment of the topology of the landscape and, as a consequence, cannot tell us what value of the threshold e* to use, let alone whether such a threshold argument is adequate.

C. Reversals and connectivity in the landscape

As is evident from the previous discussion, the increasing fraction of transitions that return to their initial configuration with decreasing temperature is central to thinking about non-Arrhenius behavior. The probability of reversals represents a useful unifying perspective from which to compare various theoretical descriptions of the glass transition. As already discussed, reversals are explicitly invoked to identify metabasins, the basis of coarse-grained approaches to configuration space dynamics.[42–46] Relaxation kinetics has been described, in the context of the mosaic theory,[47] regarding the transition from one amorphous state to another as occurring via the appearance and subsequent growth of a "droplet" of the new configuration within the matrix of the old. If the droplet is too small,
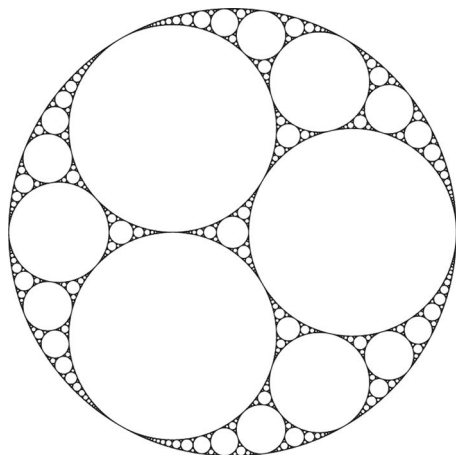
FIG. 5. An Apollonian packing model of the energy landscape. Imagine that the circles represent contours of a single value of energy so that the large circles correspond to low energy minima while the small circles are higher energy ones. The low energy minima (large circles) are highly connected and correspond to "hubs" in the landscape. Reprinted with permission from C. P. Massen, J. P. K. Doye, and R. W. Nash, Physica A **382**, 683 (2007). Copyright © 2007 Elsevier Ltd.

the transition is likely to be reversed. Relaxation kinetics are dominated by a "critical" droplet size corresponding to the minimum droplet size necessary to ensure that the probability of reversal is sufficiently small.[48] An alternate starting point is to model glassy relaxation as a consequence of explicit kinetic constraints.[49,50] These constraints generate a configuration space obstructed by a labyrinth of "walls." Irreversible escape from any given region requires a sampling of the local configurations sufficient to sort the exit routes from the dead ends.

The explicit topology of landscapes can be computed for clusters. An excellent review of this approach can be found in Ref. 27. In recent years, a number of authors[51] have used such calculations to explicitly correlate the deviation from Arrhenius behavior with the increase in the probability of reversals on cooling.[52] The details of these cluster networks are now providing us with something more than a generic one-dimensional sketch of the energy landscape. For simulations of small clusters of atoms, the distribution of connections per minimum exhibits a power law tail.[53] This means that most of the minima have relatively few connections but there are a small number of minima ("hubs") that have a large number of neighbours. Apollonian packings of discs show a similar connectivity to that found in the potential energy surface of small clusters and so provide a helpful visualization of these landscapes. In Fig. 5, the circles correspond to the potential energy basins, with the larger basins associated with lower energy minima.[54] The essential kinetic consequence of this topology is that the minimum sequence of transitions joining any two minima is small (thanks to the highly connected hubs) but these shortest routes involve traversing the deepest minima.

D. How does cooperativity emerge from the landscape?

The non-Arrhenius dynamics of fragile supercooled liquids have often been rationalized in terms of an increase in cooperativity of relaxation on cooling. "Cooperativity" is gen-

erally defined, somewhat loosely, in terms of the minimum number of particles that must move in some sort of concert in order for an elementary relaxation event to occur. (Defined this way, cooperativity might arise from explicit mechanical constraints to motion or, alternatively, in a statistical sense with regards to the probability of fluctuations between configurations.) Adam and Gibbs[13] introduced the idea of a "cooperatively rearranging region" involved in an irreversible reorganization and proposed that the number of particles in this region was inversely proportional to the configurational entropy. The mosaic theory[16] provides an explicit argument (analogous to that used in classical nucleation theory) connecting the minimum size of the rearranging region and the configurational entropy.

It is not clear whether the explanation of non-Arrhenius behavior based on cooperativity is consistent with that provided above by the trap model or if it is, in fact, a distinct alternative. A simulation study[55] has identified a threshold inherent structure energy above which excitations no longer require the "nucleation-like" character described in the mosaic theory. Establishing whether or not a connection exists between this threshold energy and the energy e*, invoked in the trap model, would go some way to clarifying the relationship between the two approaches to non-Arrhenius behavior. Progress in the mosaic theory has been the subject of a number of excellent reviews.[8,28,56,57]

III. SOFT MODES IN AMORPHOUS SOLIDS

The vibrational modes provide a detailed description of the energetics and kinetics of the response of a material to small perturbations of the equilibrium configuration. In disordered materials, these modes also provide a direct connection between the structural disorder and the collective dynamics and so represent a conceptual "stepping stone" between structure and properties.

The vibrational modes in a harmonic crystal obey the Debye dispersion relation $\omega \propto k^2$, where ω and k are the frequency and the magnitude of the wavevector, respectively. The essential feature of the Debye crystal is that low frequency motions are uniquely associated with long wavelength modes. In contrast, disordered solids exhibit low frequency modes in excess of this Debye relation, with particle participation far less than expected for plane wave modes, an indication of localization. We call the normal modes whose frequency and spatial extent (typically measured as a participation fraction) fall below suitable threshold values *localized soft modes*. The localized soft modes of the energy landscape can be regarded as an *in situ* measure of the degree of local mechanical constraint between particles.[58] Over the last decade, we have come to appreciate the central role these localized soft modes play in the collective dynamics of supercooled liquids and glasses.

A. The structural origin of dynamic heterogeneities

The obvious question posed by the existence of dynamic heterogeneities (Figure 3) is what causes them? This question

is unlikely to have a universal answer. While there has been some significant progress, the issue of the structural origin of dynamic heterogeneities remains open for many systems. Utilizing the isoconfigurational ensemble in computer simulations, it is possible to quantify the likelihood of each particle in a given configuration subsequently exhibiting high mobility.[58] The close correspondence between the spatial distribution of this propensity for motion and that of the dynamic heterogeneities themselves has established that, to a significant extent, dynamic heterogeneities are determined by local features of a configuration of particles.[59] While the local free volume shows little correlation with local mobility,[60] the short-time mean-squared displacement per particle provides a good indicator of where larger amplitude motions will later occur.[61] Taking this latter observation further, the regions of high mobility have been shown to be strongly correlated in space with the localized soft modes.[62–64] The liquid state heterogeneities are, in this sense, more reminiscent of solid state defects than a fluctuation of purely kinetic origin. What is the structural origin of these "defects"? Here our understanding ends. When strong fluctuations in composition[65] or structure[66] are present, explicit connections between liquid structure and liquid dynamics can be established. In many model liquids, however, no such strong fluctuations have been identified and we are left with some fascinating questions. What determines the characteristic average length scales associated with the soft modes? To what degree does the density of such modes fluctuate in time (to produce intermittent bursts of more rapid particle reorganization interspersed with dormant periods)?[67,68] What are the barriers specifically associated with movement along these soft mode eigenvectors? Is there any general relationship between fragility and the degree of dynamic heterogeneity? (A growing length scale of dynamic heterogeneities, on cooling, has been observed for strong as well as fragile liquids.[69–71]) Work on these questions has only just begun. The very fact that we can now pose such well-defined questions is itself a mark of progress. A recent monograph[72] provides an extensive review on the research on dynamic heterogeneities.

B. Phonons in amorphous materials and the boson peak

An amorphous solid exhibits an excess density of modes over that predicted by the Debye picture of plane waves, with the excess typically falling in the THz frequency range. This excess has been well known for decades from inelastic scattering of light and neutrons and is conventionally characterized as a peak in $D(\omega)/\omega^2$ known as the boson peak; here $D(\omega)$ is the vibrational density of states. This peak, despite its complex connection with the rest of the glass phenomenology, is probably the single most intensively studied feature of amorphous materials. While the localized modes described above look like obvious candidates for this excess density of states, simulations indicate that the boson peak occurs at a frequency lower than those of the localized modes.[73–75] There appears to be a growing consensus that the frequency of the boson peak corresponds to the maximum frequency at which transverse phonons can propagate in the disordered material,[76,77] i.e.,

the Ioffe-Regel limit. Above this frequency, scattering from the disorder becomes so efficient that transport of particle momenta no longer occurs via propagating plane waves.[73–75] The peak height reflects the statistical fluctuations in the density[78] and is found to be correlated with the Poisson's ratio.[78,79] A variety of theoretical and computational models have successfully generated a boson peak: binary mixtures undergoing transitions over saddle points,[77,80,81] disordered network solids with fixed bond connectivity,[82] soft spheres at T = 0 near the (un)jamming transition,[83] an elastic continuum with spatial fluctuations in the modulus,[84–86] excitations of the domain walls in mosaic-like configurations,[87] and crystalline lattices of springs whose stiffness is randomly assigned.[88] Boson peaks have been observed in disordered crystals[89] and a recent study[90] of a sodium silicate glass has presented evidence suggesting that, at high pressures, the boson peak becomes equivalent to the van Hove singularity[91,92] in the corresponding crystal, the latter feature being associated with purely harmonic behavior.

The ubiquity of the boson peak feature in disordered systems has rendered the identification of the physical origin of the peak difficult since, in any real material, a number of features listed above may contribute. Studies of the temperature and pressure dependence of the excess vibrational modes will help differentiate the various physical pictures. A simulation study of a Lennard-Jones glass[93] has reported that the frequency and height of the boson peak scale with the pressure P as P^{α} and $P^{-3\alpha}$, respectively. This result is consistent with a scaling arising from behavior dominated by power-law repulsions.[93] The observed decrease in the boson peak frequency on heating vitreous germania[94] resembles the singularity of a critical phenomena, an observation interpreted as indicative of a transition from behavior dominated by the inherent structure to that dominated by saddle points on the energy landscape.[80]

C. Non-affine deformation in amorphous solids and the onset of plastic flow

The nonlinear mechanical response of a disordered material—whether it fractures or flows under stress—is critical to any application involving applied loads.[95] An excellent review of this area has recently appeared.[96] The spatial distribution of particle displacements in response to a global strain has proven to be an informative probe into the inhomogeneity of the mechanical response of an amorphous material. Deviations from uniformly distributed strain are referred to as non-affine deformations. In amorphous materials a crossover length has been identified below which marked deviations from affine deformations are observed. This length represents an important property of the disorder. In simulations of atomic mixtures in 3D (Ref. 97) and 2D (Ref. 98), the crossover length has been found to be ~30 diameters (a length significantly greater than that associated with the dynamic heterogeneities[98]). The non-affine displacements can be regarded as reflecting a mechanical "noise" introduced by the structural disorder. Extensive simulation studies of T = 0 systems of particles undergoing shear (i.e., quasistatic flows) have explored how this "noise" breaks the symmetry of the

amorphous material and eventually results in an instability of one of the normal modes to produce a yield event.

Just as in the case of equilibrium dynamic heterogeneities, the spatial location of a yield event is strongly correlated with localized soft modes[99] or a low value of a locally defined elastic modulus.[100,101] The local yield event is a saddle-node instability,[102] characterized by an energy barrier that vanishes as $(\gamma_c - \gamma)^{3/2}$ where γ is the shear strain and γ_c is the critical yield value.[103–105] These yield events consist of a plastic core surrounded by a region of elastic strain, the separation of which is an important and non-trivial problem[106] and have been associated with the shear-driven escape from a metabasin.[96] With increasing shear rate, the yield events couple to trigger system-spanning plastic events known as avalanches[107–109] that eventually coalesce into shear bands and, hence, the macroscopic fracture of the material.

The effect of thermal fluctuations on shear driven instabilities[103,110–112] and the eventual connection with nonlinear rheology[105,113,114] are problems that are currently being actively pursued. At a coarse-grained level, nonlinear deformation can be interpreted to accelerate mobility in glasses by many orders of magnitude and thus transiently lower the viscosity enough to enable flow.[95,115–120] Unexpectedly, glasses become more dynamically homogeneous during plastic flow and the microscopic origin of this is not yet clear.[121]

IV. STRESS RELAXATION AND THE TEMPERATURE DEPENDENCE OF VISCOSITY

A number of recent papers have made the case that a divergence in the value of the viscosity as the temperature is lowered, a central feature of the popular Vogel-Fulcher-Tammann expression $\eta \sim \exp[E/(T-T_o)]$, is not required to fit experimental data.[122–126] While the differences between the various proposed expressions are modest throughout most of the experimentally attainable temperature range, the reality (or otherwise) of the divergence of the viscosity above $T = 0$ is of some significance since the empirical correlation between T_o and T_K is an important starting point for theories of the glass transition that are based on an underlying thermodynamic singularity.[57]

A. How does viscosity get to be so large?

Unlike a fluctuation in chemical composition or molecular orientation, a fluctuation in shear stress in an amorphous material will generally relax quickly through the action of transverse phonons. For the stress relaxation to be slow (the reason for the viscosity becoming large), it is necessary that some component of the stress cannot be relaxed by vibrations and so, instead, must relax via an activated reorganization of particles. How activation comes to dominate stress relaxation is a question we are only beginning to address. An important piece of the puzzle is the fact that the inherent structures have non-zero shear stresses.[127–132] It follows directly from this observation that this residual stress can only be relaxed through transitions between inherent structures, an activated process by definition. In simulations of glass forming mixtures, the entire long time tail of the shear stress autocorrelation function is found to be accounted for by the relaxation of this residual stress of the inherent structures.[131,132] The relationship between the particle reorganizations required for transitions between inherent structures and the magnitude of stress change they produce has only begun to be studied in detail.[133] A characteristic temperature has been identified, significantly higher than most of the characteristic temperatures associated with supercooled liquids, which marks the crossover from stress relaxations dominated by gas-like fluctuations to those dominated by solid state behavior.[134]

The problem of large viscosities then comes down to answering two questions: How did the inherent structures come to be stressed? What is the apparent activation energy controlling the time scale of the transitions between inherent structures in the landscape? The answer to the first question is straightforward. Inherent structures are rigid solids and so will be stressed by the imposition of any arbitrary static boundary condition.[132] The essential point here is that even above T_g, a liquid samples these amorphous solids (i.e., the inherent structures) and so the liquid also samples their associated residual stress. This picture of viscous liquids as a sequence of transient solids, with each solid spanning the entire sample, warrants further study. As to the second question, we have already considered some aspects of activation energy in Sec. II. Here we note the striking scaling that has been reported of the temperature dependence of the viscosity with high frequency modulus G_∞ (Ref. 135) and, more recently, the relaxed modulus.[127–130,136,137] In metallic glasses, for example, T_g has been found to be roughly proportional to the Young's modulus of the glass.[138] A correlation has been reported between the fragility of a liquid and its high frequency Poisson ratio.[79] That a property such as G_∞, related to perturbations about the local energy minima, can provide useful information about activation barriers is remarkable and is the focus of a number of theoretical treatments.[135,136,139]

V. DIFFUSION, MOLECULAR REORIENTATION AND STRUCTURAL RELAXATION

The simplest picture of the dynamics of a supercooled liquid is that it is characterized by a single time scale and that all transport and relaxation processes are, in turn, governed by that time. This idea (as represented in Figure 1) successfully accounts for the similar temperature dependences of the average relaxation times associated with a variety of molecular motions: rotational relaxation, dielectric relaxation, shear viscosity and structural relaxation.[140–142] This "single time scale" picture fails dramatically, however, in the case of translational diffusion. This breakdown of time scaling was first demonstrated experimentally in 1992 when the translational diffusion coefficient D of a probe molecule in o-terphenyl was shown to exhibit a significantly weaker temperature dependence than that of either molecular reorientation or η for the host liquid.[143]

A. Translational diffusion

In the last decade, a great deal of progress has been made towards understanding translational diffusion in deeply

supercooled liquids. The initial challenge was to measure the self-diffusion coefficient close to T_g where roughly a minute is required for a molecule to diffuse its own diameter. These measurements were achieved for four molecular glass-formers all the way down to T_g.[142,144–146] In contrast to the simple proportionality $D \sim \eta^{-1}$ postulated in the "single time scale" picture, the self-diffusion coefficient for o-terphenyl scales as $D \sim \eta^{-0.8}$.[144] As a consequence, D exceeds the postulated value by two orders of magnitude at T_g. In polymeric hosts, the failure of the "single time scale" picture is even more stark with the diffusion of a probe molecule "enhanced" over its postulated value at T_g by more than 10^4,[147] a result of considerable relevance for the performance of low molecular weight additives such as plasticizers and antioxidants.

The existence of spatially heterogeneous dynamics is the starting point for understanding why the "single time scale" proposal fails for translational diffusion while apparently working for other relaxation and transport processes. Initially, it was suggested that the difference in temperature dependence between diffusion and structural relaxation, for example, arose as a result of the difference in how the respective observables averaged over the distribution of time scales. This view is now seen as inconsistent with experiments[142,144,145] and simulations.[148,149] The difference between the temperature dependence of D and the structural relaxation time τ_α has been particularly informative since these two quantities refer to the same physical property (single particle displacements) and differ only in terms of the relevant wavelength, long and short, respectively. Using simulations of a binary atomic mixture, it was shown that the wavelength dependence of the product $\tau_\alpha D$ was completely determined by the length scale of spatially heterogeneous dynamics.[150,151] Subsequent simulations of a liquid of diatomic molecules[149] showed that the difference in the temperature dependence of the translational and rotational diffusion constants can be similarly understood by a growing length scale associated with heterogeneous dynamics. The breakdown of the "single time scale" picture for translational diffusion arises, it appears, whenever a liquid exhibits spatial fluctuations in dynamics.[152] These conclusions are subject to the standard qualification that computer simulations are restricted to short relaxation times and, hence, are limited to small supercoolings. It is possible that other physics dominates the kinetics at lower temperatures.

In more highly structured liquids, such as water, this heterogeneity can appear well above T_g.[153] This effect in water is presumably related to a change in the average structure of liquid water as the temperature is lowered, associated with the increasing fraction of four-coordinated water molecules.[154] In polymer melts, spatially heterogeneous dynamics leads to the failure of the "single time scale" picture in an additional manner, with the temperature dependence of segmental and large scale chain motions being dissimilar for fragile systems.[155] In glass forming mixtures, the intrinsic properties of different chemical species will impose their own heterogeneity. This chemically induced heterogeneity can combine with dynamic heterogeneity to produce average mobilities for different species that have different temperature dependences.[156–160]

B. Molecular reorientation

Molecular reorientation provides insight into structural relaxation and can be observed by dielectric relaxation, nuclear magnetic resonance (NMR), and optical methods. The advent of optical experiments capable of tracking the reorientation of individual probe molecules has provided the tantalizing prospect of answering fundamental questions about heterogeneous dynamics near T_g. For example, how long does a slower-than-average molecule remain slower-than-average? In practice, given the finite number of photons received from any given molecule prior to photobleaching, answering such questions requires a careful statistical analysis. Various studies have established that individual probe molecules do exhibit distinct dynamics.[161–164] Very recent work has shown that some averaging over the total distribution of reorientation rates apparently takes place on the time scale of the probe reorientation.[162,165] Further averaging takes place over times on the order of 30 probe reorientation times, which is hundreds of times longer than the structural relaxation time of the host molecules (glycerol).[162] The observation that some molecules have not randomized their reorientation rates after 100 τ_α is challenging as it indicates that a relaxation time longer than the "structural relaxation time" may play a fundamental role in deeply supercooled liquids. A critical advance in single molecule experiments would be measurements on a probe that is comparable to the size of the host molecules.

Computer simulations have contributed significantly to our understanding of molecular reorientation processes,[149,166,167] albeit in a regime where dynamics are 10^8 faster than at the laboratory T_g. From simulations, a key insight concerning spatially heterogeneous dynamics is the strong correlation between the reorientational and the translational mobility of individual molecules, i.e., unusually fast rotators are also unusually fast translators.[149,167] This correlation strengthens as the temperature is lowered. (A related observation, due to solid state NMR experiments, is that molecules that contribute to the slow side of the β relaxation process also contribute to the slow side of the α relaxation process.[168]) The choice of words in the literature on this point is somewhat confusing. The increasing difference in the time scales for translational and rotational motions with cooling is widely referred to as an example of "decoupling," in spite of the evidence from simulations that, at a molecular level, the coupling between translational and rotational motion of individual molecules actually increases on cooling.

C. Influence of pressure on dynamics

The last decade has seen a significant upsurge in experiments that measure how pressure influences molecular motion in supercooled liquids. For a recent review, see Ref. 169. A key question can be answered by these experiments: When a supercooled liquid is cooled at constant pressure, is the slowdown of molecular motion a result of the temperature decrease or does it result from the increase in density ρ?[170,171] The answer is important because it provides model-independent information as to whether molecular motion is limited more by energy barriers or by the "jamming" (lack of

"free volume") that would occur even for hard spheres. For many liquids, the observed dynamics can be represented over some range of temperature and pressures as a function of a single variable ρ^γ/T, where γ is a material specific constant. Small values of γ are found for hydrogen-bonding liquids (such as glycerol and sorbitol), indicating that temperature is the dominant factor for these systems and that density plays a minor role.[169] Larger values of γ are found for van der Waals liquids (e.g., o-terphenyl); for these systems, the slowdown in dynamics with decreasing temperature at 1 bar typically has roughly equal contributions from temperature and density changes.[169] Starting from a model in which relaxation involves a distribution of activation energies,[172] an explicit expression has been proposed for the scaling exponent γ in terms of thermodynamic properties of the liquid.[173, 174]

Simulations have recently provided insight into the dependence of the dynamics upon the combined variable ρ^γ/T. For systems with a certain class of interaction potentials (inverse power law), this scaling is exact. Such systems have been described as "strongly correlating liquids" and van der Waals liquids are thought to fall into this category (to a good approximation).[175] For such systems, a single parameter controls structure and dynamics everywhere on the temperature-density plane, even if the system is not in an equilibrium state; this latter feature may allow a simplified description of physical aging of glasses. Other liquids (such as water) have been shown not to be "strongly correlating" and it appears that a single control parameter does not exist in such cases.[176]

VI. AMORPHOUS STRUCTURE AND STABILITY WITH RESPECT TO CRYSTALLIZATION

The atomic structure of a material serves to link global properties of the material with the specific details of the particle interactions. Amorphous materials present a twofold challenge in this regard: defining and measuring the structure and then establishing its connection to material properties. In this section we shall look at some recent progress on both of these challenges.

A. Examples of structure in liquids

The description of structure in the low valence networks of oxide and chalcogenide glasses has been reviewed extensively.[177–179] Constraint theory has been successfully employed to rationalize the dependence of T_g on composition of chalcogenide glasses.[180] There has also been recent progress in understanding the structure of amorphous silicon.[181] These descriptions are greatly simplified by the fact that the amorphous ground states of the network materials are dominated by the same local topology as found in the crystal. In contrast, the analysis of local structure in close-packed liquids has proved a greater challenge. Statistical information about the amorphous structure has been obtained by scattering (x-ray and neutron), x-ray absorption fine structure, transmission electron microscopy and fluctuation electron microscopy.[182] These techniques have been augmented by reverse Monte Carlo analysis in which the atomic structure is varied to optimise the reproduction of in-

formation from these experimental techniques.[181–183] Reference 184 provides a comprehensive review of this approach with respect to metallic glasses. A number of structural motifs have been identified. In metal-nonmetal alloys (e.g., NiP) the structure reflects the strong chemical ordering associated with the preference of the non-metal to be fully coordinated by metals.[185, 186] In a number of alloys, this coordination has been characterized by a trigonal prism arrangement.[187, 188] *Ab initio* calculations[189] have clearly established the importance of the directional character of the metal-P bond—a feature omitted from a widely used Lennard-Jones model inspired by the Ni-P alloy.[190] Alloys of more than one metal typically involve larger coordination shells, with icosahedra (distorted away from the regular Platonic geometry due to the compositional variations) a common motif.[184] As first described in the Frank-Kasper crystal phases,[191] the medium range order in these amorphous states consists of overlapping coordination shells with the associated rapid growth in structural diversity as the radial extent increases. In cases where the unit cell of the crystalline state extends further than the first coordination shell, it is possible that the liquid can "use" the same local coordination as the crystal while retaining global disorder through a variety of medium range arrangements.[66] The concept of geometric frustration, reviewed in Ref. 192, offers up one general condition by which a difference in the length scales of local and crystalline order can occur. Descriptions of the low temperature structure of molecular liquids, with the huge variety of molecular shapes and flexibility, remain an important open challenge.

We look for structure because it is an accessible signature of stability. "Accessibility," here, relies on the stable structures being simple enough to be recognizable by inspection or, failing that, enumerable by computer. Since there is no general reason why amorphous structure should be so simple, it may be more fruitful to measure structure by probing the stability it represents. One such approach is the "point-to-set correlation."[193, 194] This computational strategy, inspired by the random first order transition theory,[195, 196] considers how effective "walls" of frozen amorphous material are at reducing the number of accessible configurations in the adjacent liquid. The greater the length scale over which a wall's influence extends, the greater the length scale of the (implicit) structure of that liquid. This approach has established structural correlation lengths of up to ~4 particle diameters.[197]

B. Structure, dynamics and the limits of the liquid state

One local measure of stability in an amorphous material is the local relaxation time. In this sense, dynamic heterogeneities can be interpreted as a spatial map of structural stability. A number of simulation studies have reported correlations between the presence of a specific local structural feature and slower than average relaxation.[66, 198, 199] In a study of a binary Lennard-Jones mixture without strong chemical order, clusters linked by sixfold "bonds" were shown to have significantly longer relaxation times than the average.[66] These clusters resembled fragments of the large unit cell structure of the crystal. The density of these clusters was shown to

increase rapidly on cooling and to contribute significantly to the liquid heat capacity. Examples of significant structure in a liquid such as described in Ref. 66 require a word of qualification. The Lennard-Jones mixture, along with a number of other popular models of glass formers, has recently[200, 201] been shown to crystallize during extended simulation runs at a modest supercooling, indicating that they are not as good glass formers as previously assumed. More realistic models of metal alloys do not, to date, exhibit the same preponderance of a single local structural motif.[202]

How much structure can a liquid accumulate and still go on being a liquid? Simple models of a liquid characterized by a favored local structure have demonstrated that the liquid can accommodate a substantial fraction of the favored structure as long as this structure is of low symmetry.[203–205] Eventually, such liquids become unstable with respect to crystallization. The accumulation of order in a liquid might, in itself, involve sufficient cooperative character to result in a phase transition between low and high ordered liquid states. Just such a scenario has been intensively studied in the case of supercooled water where considerable evidence supports the existence of two metastable liquids.[206–209] Exactly where the crystallization instability lies with respect to the liquid-liquid transition in water remains a point of debate. Recent simulations have either located the instability coincident with the proposed liquid-liquid transition[154, 210] or have relegated any such instability to a temperature well below that of the phase transition.[211–214]

C. Glass-forming ability and the stability of glasses to crystallization

A liquid is referred to as glass forming when its fastest rate of crystallization is still slow enough to be exceeded by the cooling rate. This means that the glass forming ability of a liquid can be quantified by this maximum crystallization rate. The maximum rate, which reflects the competition on cooling between the growing thermodynamic driving force and the decreasing mobility in the liquid, occurs at temperature T_{max} well above T_g (e.g., $T_{max} = 0.95T_m$ for o-terphenyl[215] and $0.82T_m$ for a Pd-based bulk metallic glass[216]). Glass forming ability, in other words, is quite distinct from the glass transition.

In fields as diverse as metallic glasses and pharmaceuticals, the chemical design of good glass formers is a more important question than that concerning the nature of the glass transition. Two general options for increasing glass forming ability are to either increase the stability of the liquid or decrease that of the crystal. The former approach is widely employed in the development of metallic glasses where the optimal concentrations are typically close to eutectic points. In the latter strategy, the thermodynamic driving force for crystallization is lowered by increasing the free energy of the crystal. This point was nicely illustrated in a recent study investigating the glass forming ability of an homologous series of molecules that are structurally similar to o-terphenyl;[215] the molecule with the highest melting point was the poorest glass former. The crystal engineering community has shown that design rules for crystal formation can be systematically vi-

olated to prepare good glass formers.[217] In one case, hydrogen bonding motifs inconsistent with dense crystals both decreased the thermodynamic driving force for crystallization and increased the kinetic barrier by slowing molecular rearrangements in the supercooled liquid.[217] This can be viewed as engineering the preferred liquid packing to be different than the preferred crystalline packing.

For most applications of amorphous materials, glasses need to stay glassy. An important example is amorphous pharmaceuticals.[218] Promising drug candidates often have crystalline forms that are too insoluble to allow oral administration. Glasses have higher free energies than crystals and have been observed to dissolve faster and to higher concentrations (in some cases, by more than a factor of 10).[219] There is interest in administering these drugs in the amorphous state but this is only possible if such states are highly stable against crystallization. Alternately, controlled partial crystallization can create materials with superior mechanical properties, for example, in nanocrystalline aluminum alloys.[220]

Some progress has been made in understanding the kinetic barriers to crystal growth. For a deeply supercooled liquid, the standard view is that crystal growth is completely limited by the rate of molecular rearrangements in the liquid, since these rearrangements are needed for liquid molecules at the crystal interface to join the crystal.[221] While the viscosity has typically been used to predict the rate of crystal growth, recent work has shown that this is only accurate for strong glass formers such as SiO_2 and GeO_2.[221–223] A typical organic liquid is moderately or highly fragile and the viscosity does not provide an adequate prediction of the crystal growth rates.[222] For these systems, the self-diffusion coefficient is a better predictor of crystal growth rates.[142]

For a number of organic and metallic materials, the rate of crystal growth near T_g is surprisingly rapid, significantly faster than that predicted from the diffusion coefficient or the viscosity. An interesting ratio is the number of crystal layers added in one structural relaxation time τ_α of the liquid. Standard models place an upper bound of 1 on this ratio and supercooled organic liquids typically obey this sensible speed limit. On the other hand, for some organic liquids, this ratio jumps to 1000 molecular layers per τ_α just above T_g and remains at a high value in the glass.[224–228] For binary and ternary metallic glass formers, rapid crystal growth appears to be common in both the supercooled liquid and the glass.[229] There are indications of similar behavior for crystallizing hard sphere glasses.[230] While many aspects of this behavior are not understood, one interesting proposition is that such rapid crystal growth is possible only when the amorphous structure and the local crystal structure are similar.[228]

VII. THIN FILMS, INTERFACES, AND NEW GLASSES

A. Thin film properties

Recently there has been tremendous interest in the properties of nanometer thick polymer films and particularly in the glass transition temperature T_g as a function of film thickness.[231–234] Such films are important technologically and also hold promise for revealing fundamental features of the
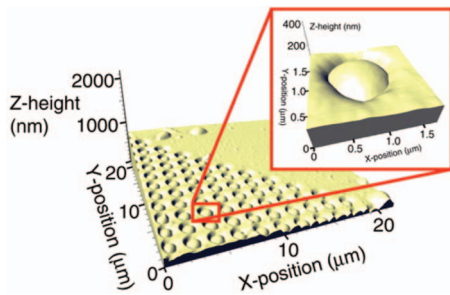
FIG. 6. AFM image of a 27 nm thick free-standing polyvinylacetate film, pressurized from below to provide controlled deformation. Reprinted with permission from P. A. O'Connell and G. B. McKenna, Science **307**, 1760 (2005). Copyright © 2005 AAAS.

behavior of glass forming materials near surfaces and interfaces. T_g for thin films has been widely determined by measuring the film thickness as a function of temperature (using ellipsometry for example); a change in the temperature dependence is interpreted as T_g. For polystyrene supported by silicon with a native oxide coating, such measurements from many labs show roughly comparable behavior, with T_g *decreasing* 10–30 K for a 10 nm film.[231,232,235,236] (Others have argued that thoroughly annealed samples of this type show no T_g change.[233,234]) Depending upon the polymer and the substrate, T_g can decrease or increase with decreasing film thickness, with increases of up to 40 K being reported.[237–242] T_g decreases are generally interpreted in terms of enhanced mobility at the free surface while increases in T_g are interpreted as reduced mobility near the substrate interface.

Even bigger decreases in T_g (up to 70 K) have been reported for freestanding polymer films in the nanometer regime.[231,243,244] A nano-bubble inflation technique (as shown in Figure 6) has been used to directly study the deformation properties of freestanding films down to 3 nm in thickness.[245] T_g shifts as large as 100 K have been reported with this technique,[246] along with equally striking qualitative changes in the response of larger length scale polymer motions. T_g shifts in freestanding films have been reported to depend upon molecular weight for very long chains,[231,243,244] which is surprising since the glass transition in polymers has been understood to reflect structural relaxation on the scale of a few segments. Very recent measurements on freestanding polystyrene films indicate that such systems may show two thickness-vs.-temperature transitions (interpreted as two glass transitions), with the dominant transition being molecular weight independent and within 20 K of the bulk T_g.[247] Another surprising result is that physical aging in thin polymer films can depend upon film thickness even beyond the one micron scale.[248]

Let us put these results into perspective. For bulk polymers, a 10 K change in T_g is typically associated with a 1000-fold change in molecular mobility. Thus the results described above have the potential to very significantly modify polymer properties in applications where mobility near an interface is important, including sensors and battery materials. Reports that film thicknesses of 100 nm significantly influence the glass transition properties of polymer films[248,249] challenge our understanding of structural relaxation in bulk glass for-

mers which is thought to be localized on the scale of a few nanometers.

B. Interface influence on mobility

Motivated by the T_g measurements described above, many methods have been utilized in an attempt to directly measure dynamics at the free surface of polymer glasses. Several papers have reported that roughened or patterned surfaces of polymer glasses smooth to some extent below T_g, consistent with the idea of fast surface dynamics.[250,251] The sub-T_g relaxation of orientation of the rubbed surface of a polymer glass also supports this view.[252] Nanoparticles can embed rapidly (up to a few nanometers) into polymer glass surfaces below T_g, and if the particles are removed, the resulting nanoholes also fill rapidly below T_g.[253,254] The rotational mobility of probe molecules in thin films indicates both "bulk" and "near interface" populations with mobilities differing by orders of magnitude.[255,256] "Local T_g" measurements performed by monitoring the temperature-dependent emission properties of chromophores in layered polymer films have been reported to indicate very fast surface dynamics that penetrates more than 10 nm into a thick film.[257,258]

Enhanced surface mobility is also important for low molecular weight organic glasses. Experiments in porous materials and emulsions indicate enhanced mobility near a soft interface and diminished mobility near a hard surface.[259] Ion embedding experiments on supercooled 3-methylpentane indicate a low viscosity surface layer that extends a few monolayers into the film.[260] Neutron reflectivity measurements on trisnaphthylbenzene glasses are consistent with this view and both of these experiments indicate enhanced mobility of a few orders of magnitude at a free surface.[261] Even larger effects have been reported in a study of surface grating relaxation on indomethacin glasses.[262] Using a methodology established to study diffusion on crystals, surface diffusion was determined to be 10^6 times faster than bulk diffusion at T_g. This high surface mobility is roughly consistent with a recent theoretical model for surface mobility,[263] and may be responsible for fast crystal growth on glass surfaces.[264]

Many studies of surface mobility are consistent with these features: (1) mobility at free surfaces can exceed bulk mobility by many orders of magnitude; (2) interfacial effects extend into the bulk at least a few monolayers in molecular glasses and at least a few nanometers in polymer glasses; (3) near-surface mobility has a weaker temperature dependence than bulk mobility and thus surface mobility becomes more enhanced relative to the bulk at low temperature. Simulation studies[265–270] generally support this picture. Over the modest range of supercoolings available to molecular dynamics simulations, kinetics at the surface of films comprised of a glass-forming liquid are enhanced by two orders of magnitude[266,268] and exhibit a significantly lower fragility than the bulk.[270]

Nevertheless, this is an area with some significant controversies that are not yet resolved. For example, some experiments have been interpreted to indicate that dynamics are not faster at the free surface than in the bulk material.[233,234]

New experimental methods that measure both bulk and near-interface mobility would be particularly useful as the field turns its attention to understanding the range of behaviors shown by various molecular and polymeric glass formers.

C. Enhanced surface mobility as a route to new glasses

While physical vapor deposition has been used to prepare glasses for decades, it was only recently discovered that this method can produce organic glasses with remarkably high density and stability.[261,271–273] When the substrate is held near 0.85 T_g, molecules arriving from the vapor phase can utilize enhanced surface mobility to efficiently sample various packing arrangements and thus nearly achieve the equilibrium structure at the deposition temperature.[261] It has been estimated that an ordinary glass formed by cooling the liquid would have to be aged for 10^3–10^9 years in order to achieve the kinetic stability and density of these vapor-deposited glasses.[274]

Highly stable vapor-deposited glasses allow the lower reaches of the energy landscape to be probed for the first time. In terms of energy, such glasses are roughly halfway to the bottom of the amorphous part of the landscape, relative to ordinary, unaged glasses.[274] These glasses have lower thermal expansivities[275] and heat capacities[276] than ordinary glasses, indicating that potential energy minima lower in the landscape are more nearly harmonic and are characterized by higher vibrational frequencies. The packing in such stable glasses is so efficient that when submicron films are heated above T_g, the glass melts like an ice cube, with the supercooled liquid forming first at the free surface and growing into the center of the sample[277] (see Figure 7). Evidently, molecules in the center of such a film are jammed so tightly that mobility arrives from somewhere else before the molecules can unpack themselves. This front-like annealing has been described as a macroscopic manifestation of dynamic heterogeneity and successfully reproduced by a model based on this perspective.[278] A front-like solution for the dynamics of a local mobility parameter has also been demonstrated for a theoretical description based on mode coupling equations of motion and the mosaic theory.[279] Innovations in simulation algorithms[278,280,281] hold the promise, analogous to that of the vapor-deposited films, of reaching configurations substantially lower in the energy landscape than has been possible up to now.

Low energy vapor-deposited glasses may also provide insights into fundamental aspects of amorphous systems, including the boson peak and the Kauzmann entropy crisis. Vapor-deposition provides a more efficient path to low energy and high stability organic glasses than was previously thought possible. This raises the possibility that low energy glasses of other types of materials might be prepared by this route and that other efficient paths to low energy glasses might be discovered.

Vapor-deposited organic glasses form the electron- and hole-transport layers in many organic electronics devices (e.g., OLEDS).[4] They may also play a role in higher resolution, next-generation photoresists.[282] Given that vapor-deposition in model systems has been shown to produce
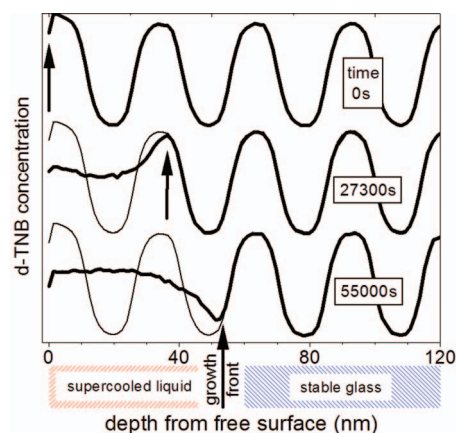

FIG. 7. Mobility enters highly stable glasses from the free surface (located at the left of the figure). The top panel shows the initial composition profile of a highly stable vapor-deposited glass with alternating layers of deuterio- and protio-trisnaphthylbenzene (TNB). With annealing, isotopic mixing initially occurs only near the free surface. At long times, the packing in the interior of the film is finally disrupted. Adapted from Fig. 3 of Ref. 285.

glasses with a wide and interesting range of physical properties, it seems likely that this new level of understanding can translate into better materials for these and other applications. Some vapor-deposited organic glasses exhibit anisotropic packing not characteristic of liquid-cooled glasses,[283] and this anisotropy may be beneficial in maximizing charge carrier efficiency as it should lead to better overlap between π orbital systems of neighbouring molecules.[284]

VIII. CONCLUSION

The study of the onset of glassy behavior in supercooled liquids and the properties of the resulting amorphous solids represents nothing less than the re-working (and, in many cases, re-invention) of materials science, along with the chemistry and physics that underpins it, for those cases where neither crystal structures nor their associated defects can be invoked. Viewed this way, the ambitious scale of the task becomes evident, the more so because the structural distinction between solid and liquid is removed and the study of viscous liquids merges with that of soft solids. Progress in this field is best measured in terms of the degree to which we can provide molecular-level accounts of the energies, structures, and time scales that characterize the low temperature properties of each amorphous substance. Prosaic as these questions may appear, answering them is anything but; they demand the full range of ideas, insights and methodologies we have tried to describe in this brief essay. There is no real value in attempting to conclude this perspective with some sort of scorecard as to how we are doing, save, perhaps, to acknowledge that, given the great scope of the task, progress will inevitably be distributed heterogeneously across such a broad range of topics.

Where might a complete understanding of supercooled liquids and glasses take us? Amorphous materials have already established their value in applications where crystal features—facets, grain boundaries, or defects—are unwanted. With increasing understanding and experimental

access to molecular detail, we increase our capability to control amorphous states at nanoscales. Tougher glasses,[286] electronic phase change memory,[3,223] biomineralization via amorphous intermediates[287,288] and nonlinear rheology in microfluidics[289] are just some of the possible directions that will benefit from our growing insight into glasses and the glass transition.

ACKNOWLEDGMENTS

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