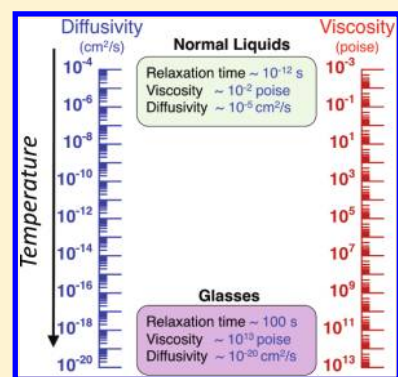


Breaking Through the Glass Ceiling: Recent Experimental Approaches to Probe the Properties of Supercooled Liquids near the Glass Transition

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ABSTRACT: Experimental measurements of the properties of supercooled liquids at temperatures near their glass transition temperatures, T_g , are requisite for understanding the behavior of glasses and amorphous solids. Unfortunately, many supercooled molecular liquids rapidly crystallize at temperatures far above their T_g , making such measurements difficult to nearly impossible. In this Perspective, we discuss some recent alternative approaches to obtain experimental data in the temperature regime near T_g . These new approaches may yield the additional experimental data necessary to test current theoretical models of the dynamical slowdown that occurs in supercooled liquids approaching the glass transition.



Amorphous materials are ubiquitous in many fields including pharmaceuticals, polymer chemistry, optical and material science, biology, and food science, to list just a few.¹ As such, there is great interest in obtaining molecular-level insight into the behavior of amorphous/glassy materials and supercooled liquids near their glass transition temperatures.^{1–6} This insight may lead to the ability to control the properties of glassy materials and also increase our fundamental understanding of the liquid phase itself. One difficulty in studying deeply supercooled liquids is that their lifetimes are often limited by the inherent metastability with respect to crystallization.

Figure 1 is a schematic for the formation of supercooled liquids that illustrates the problem. Supercooled liquids are formed when a liquid is cooled below its melting point (T_{Melt}), and yet, it does not transform to the thermodynamically favorable crystalline phase. Instead, the liquid remains in a metastable state until a kinetic pathway to the lower free-energy crystalline phase is found. As the temperature is further decreased below T_{Melt} , the thermodynamic driving force to crystallize increases, thus decreasing the lifetime of the metastable supercooled liquid. In fact, to cool most supercooled liquids to temperatures far below their melting points usually requires either rapid cooling or emulsion techniques to circumvent the crystallization kinetics.¹ Even with such techniques, it is often difficult to cool most molecular liquids directly from the liquid phase to temperatures near T_g .

However, if one could continue to cool the supercooled liquid without it crystallizing, the time for the system to sample the entire available energy landscape (i.e., stay in equilibrium) would increase as the temperature decreases. At some point, this time becomes long compared to the laboratory time scale (say 100–1000 s), and the system is said to be out of thermal

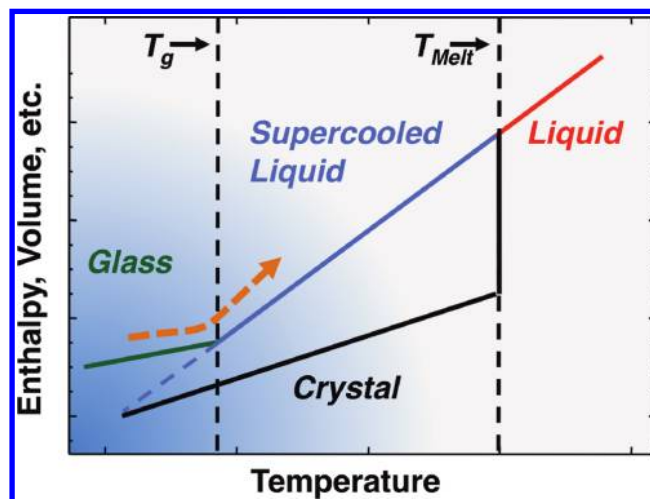


Figure 1. Schematic illustrating the relative thermodynamic values between the liquid, supercooled liquid, and crystalline phases. The vertical dashed lines demarcate the melting, T_{Melt} , and the glass transition, T_g , temperatures. The dashed arrow indicates the pathway to form a supercooled liquid from an amorphous solid.

equilibrium and nonergodic. This temperature is known as the glass transition temperature and is labeled T_g in Figure 1. A glass (or amorphous solid) has the disorder of a liquid but has the mechanical properties of a solid. In this sense, a glass can be thought of as a “frozen liquid”. The glass transition can also be

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defined as the temperature where the viscosity has a value of $\sim 10^{13}$ poise.^{2,5,6} This value is about 10^{15} times lower than that of room temperature liquid water, which has a viscosity of $\sim 10^{-2}$ poise. Correspondingly, assuming the Stokes–Einstein relationship, $D = RT/6\pi\eta r$, where r is the radius of the diffusing particle and the viscosity, η , and diffusivity, D , are inversely proportional, the diffusivity at T_g would be about 10^{-20} cm²/s (room-temperature water diffusivity is $\sim 10^{-5}$ cm²/s).

As stated above, cooling a supercooled liquid to temperatures near T_g directly from the liquid phase is difficult because of the inherent tendency toward crystallization. However, an alternative approach to create supercooled liquids at temperatures near T_g is illustrated by the dashed arrow in Figure 1. In this case, an existing amorphous solid is heated above its T_g whereupon it transforms into a highly viscous supercooled liquid. As a result of this extremely high viscosity and corresponding low diffusivity, the crystallization rate can be dramatically reduced, and hence, the lifetime of the highly viscous metastable liquid can be longer than that at temperatures just below the melting point. The extended lifetime provides the opportunity to probe the properties of the supercooled liquid at T_g . Fortunately, amorphous solids for many materials can be made by vapor deposition onto a cold substrate, and therefore, the approach is applicable to a large number of substances.

The experimental approach incorporating this idea is illustrated in Figure 2. In the first step, molecular beams are used to vapor

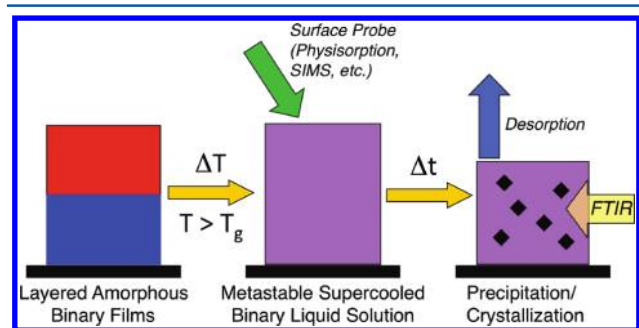


Figure 2. Cartoon of the experimental approach to creating deeply supercooled liquids near their T_g . Initially, nanoscale amorphous films are created by vapor deposition at low temperature (left). The film (or composite film) is heated above its T_g , whereupon it transforms into a supercooled liquid. Prior to crystallization, the properties of the supercooled liquid can be probed with a variety of techniques (middle). Eventually, the metastable supercooled liquid will transform to the lower-energy crystalline phase (right).

deposit material on a low-temperature (below T_g) substrate to create amorphous nanoscale films consisting of either single component or composite layers. In step two, the amorphous film is heated above T_g , where it transforms into a supercooled liquid. At this point, the properties of the deeply supercooled liquid can be explored, at least until the onset of crystallization. For example, the desorption rate (which is directly related to the vapor pressure when the sticking coefficient is unity) from the supercooled liquid melt can be used to determine its excess free energy when compared to the desorption rate from the crystalline phase. We have done this for water and have shown that there is thermodynamic continuity in the free energy and entropy between the melt of amorphous solid water (ASW) at 150 K and normal supercooled water near its melting point.^{7,8} In addition, one can use a variety of techniques such as desorption, infrared spectroscopy, physisorption, and so forth to study the crystallization kinetics as the

metastable supercooled liquid transforms to the lower-energy crystalline configuration.^{9–13}

The transport properties of supercooled liquids near T_g can also be studied in this way. In this case, nanoscale amorphous films are constructed by sequential dosing of two isotopic components. As the film is heated to temperatures near T_g , the diffusivity increases, and the initially separated layers can begin to intermix. The time evolution of the intermixing can be determined by monitoring the isotopic composition of the outer layer. We have previously used isotopically labeled (H_2O/D_2O and $H_2^{16}O/H_2^{18}O$) ASW films to study the diffusivity transport properties of deeply supercooled liquid water.^{9,13–16} In that work, the diffusivity of layers was determined using the isotopic composition of the film's outer layer as determined from the molecular desorption rate of the two components. McClure et al. have studied diffusion in ASW films using a similar approach to ours, and their findings suggest that the diffusion kinetics are more complicated than indicated in our earlier studies^{9,13–16} and that vapor transport along cracks may play an important role.^{17,18}

Ediger et al. have used a similar approach to study the properties of supercooled *o*-terphenyl at temperatures above its T_g , where the diffusivities ranged from 10^{-15} to 10^{-12} cm²/s.^{19,20} Vapor-deposited isotopically labeled layers of tris-naphthylbenzene were also used to obtain its self-diffusion by annealing and subsequent depth profiling using secondary ion mass spectrometry (SIMS).^{21,22} Similarly, the approach can be used to probe the properties of supercooled liquid solutions by using amorphous films composed of different molecular species. For example, films composed of amorphous layers of methanol and ethanol have been used to probe the desorption properties of the deeply supercooled liquid solutions created upon heating above T_g .^{23,24} In that particular case, the desorption properties could be quantitatively described by a kinetic model for desorption from an ideal binary liquid solution.

At a diffusivity of 10^{-18} cm²/s, molecular motion in a macroscopic sample (say 1 cm) would take about 3.2×10^{10} years! Clearly, this time scale is well beyond the graduate student or postdoctoral tenure.

It is important to note that the use of nanoscale films is essential to study the extremely low diffusivities (10^{-18} – 10^{-12} cm²/s) that exist at temperatures near and just above T_g . For example, it takes ~ 1000 s to move an average of one molecular diameter (say ~ 3 Å for water) at a diffusivity of 10^{-18} cm²/s. At this diffusivity (10^{-18} cm²/s), molecular motion in a macroscopic sample (say 1 cm) would take about 3.2×10^{10} years! Clearly, this time scale is well beyond the graduate student or postdoctoral tenure.

Despite the successes of this approach, there are a few limitations. Specifically, if one is monitoring the intermixing using desorption from the film's outer layer, the species of interest must have an experimentally measurable desorption

rate prior to the intermixing of the composite layers and crystallization. This is not necessarily the case for all systems. Of course, other surface probes such as inert gas physisorption or SIMS could work but are not as convenient as direct desorption measurements. However, even if one could measure the surface composition, the mobility of the individual species in any binary system, be it different substances or isotopes, can be different. Thus, the intermixing kinetics of the two disparate layers is actually measuring an averaged diffusivity. Finally, the diffusivity in a binary system often depends on molar composition. In the layered experiments, the system is sweeping through a range of compositions as the film is mixed. As a result, the apparent diffusivity is an averaged value over a range of molar compositions.

We have recently developed a new approach that addresses some of these limitations. The technique uses the permeation of rare gas atoms through overlayers of the supercooled liquid to determine its diffusivity.^{25–29} The technique is illustrated in Figure 3. Initially, a

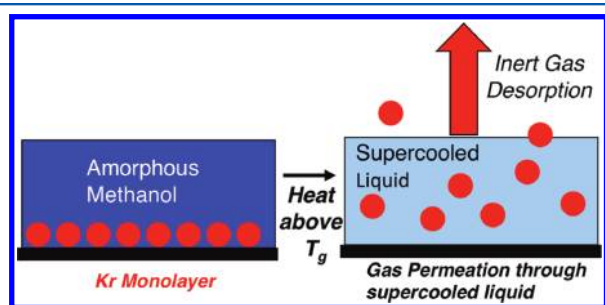


Figure 3. Schematic of the inert gas permeation technique. A monolayer thick layer of an inert gas (e.g., krypton) is covered by a vapor-deposited amorphous film. The film is heated above its T_g , whereupon it transforms into a supercooled liquid, allowing the inert gas to permeate through the film. The temperature and rate of permeation is used to determine the diffusivity of the supercooled liquid itself.

monolayer of an inert gas (e.g., Kr) is deposited onto a substrate and then covered by an amorphous film. The amorphous film is heated to temperatures near its T_g , whereupon it transforms into a supercooled liquid, and the inert gas can begin to diffuse through the overlayer. The hypothesis is that the transport of the inert gas is directly related to the diffusivity of the supercooled liquid overlayer itself. Because the gas permeation technique measures the desorption of the probe gas and not the overlayer of interest, the problems described above are avoided. The diffusivity can be extracted from permeation experiments from numerical simulations using a one-dimensional kinetic model in which the inert gas diffusion is represented by a series of discrete hops between potential minima between adjacent overlayers.^{25–28} However, we have also shown that based on diffusion scaling laws, the diffusivity can be obtained simply by using the overlayer thickness, the heating rate, and the desorption peak temperature.²⁸ Our recent measurements have shown that the diffusivity for methanol, ethanol, and its mixtures is highly non-Arrhenius.²⁹

It is fair to ask if the inert gas permeation through the supercooled liquid overlayer would be in any way related to the diffusivity of the liquid itself. Some insight comes from the permeation of various gases (e.g., N_2 , O_2 , Ar, CH_4 , C_2H_6 , etc.) through room-temperature liquid water.³⁰ For the most part, the gas permeation rates have about the same temperature dependence and differ in absolute value by less than a factor of 2. The similarity in the temperature dependence suggests a common diffusion mechanism that must be related to the motion of the liquid itself. The factor of 2 differences between the gases is relatively small when compared

to the factor of 10^{15} change in the diffusivity of the liquid near the melting point and the supercooled liquid near T_g . Given this, the permeation of inert gases through deeply supercooled liquids should provide a good value for the activation energy and reasonable estimate of the diffusivity itself.

Figure 4 displays an Arrhenius plot of the diffusivity of deeply supercooled methanol obtained from Kr permeation experiments

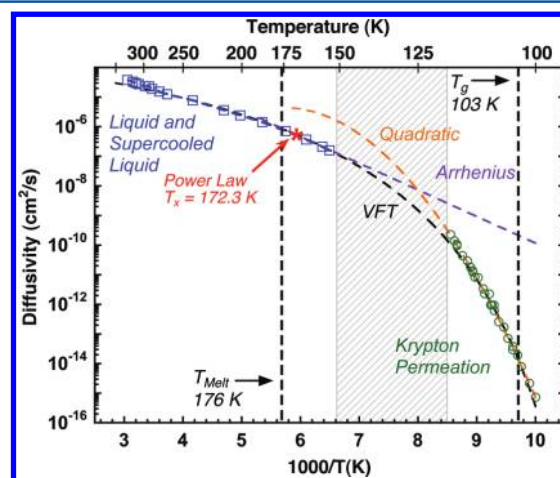


Figure 4. Arrhenius plot of liquid and supercooled liquid diffusivity^{31,32} (open squares) and the diffusivity from Kr permeation (open circles).^{25,26,29} Also displayed are fits (dashed lines) using various models. The VFT fit was to the liquid, supercooled liquid, and Kr permeation data. The VFT parameters were $D_0 = 2.11 \times 10^{-4} \text{ cm}^2/\text{s}$, $B = 525.7 \text{ K}$, and $T_0 = 80.6 \text{ K}$. The quadratic equation was fit to the Kr permeation data only yielding the fit parameters $D_0 = 4.5 \times 10^{-6} \text{ cm}^2/\text{s}$, $J = 727.7 \text{ K}$, and $T_0 = 175.4 \text{ K}$. The asterisk (red) demarks the value of $T_x = 172.3 \text{ K}$ reported by Mallamace et al. below which an Arrhenius curve (dashed purple line) is used to fit the data ($D_0 = 1.15 \times 10^{-1} \text{ cm}^2/\text{s}$ and $E_a = 17.2 \text{ kJ/mol}$).³³ The gray hatched box marks the temperature region where there currently is no experimental data, a so-called “no-man’s land”.

(open circles)^{25,26,29} along with the liquid and supercooled liquid methanol diffusivities (open squares).^{31,32} The Kr permeation data range from ~ 100 to 120 K , which is near and just below methanol’s T_g of 103 K . The data vary smoothly through T_g , indicating no dramatic change in the diffusion dynamics or divergence, which is consistent with the observations of others.³³ The combined data sets clearly cannot be fit by a single Arrhenius function (a straight line on this plot), and even the Kr permeation alone displays curvature indicative of non-Arrhenius behavior. Note that the diffusion activation energy (the slope of the tangent to the data) dramatically increases from a value of $\sim 12 \text{ kJ/mol}$ for liquid methanol to a value of $\sim 80 \text{ kJ/mol}$ at temperatures near T_g .²⁵ The behavior of supercooled liquids approaching T_g is of great interest as it provides insight into the physical processes extant in this regime. The dashed lines in Figure 4 are fits to several different mathematical models that we describe below.

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Supercooled liquids are often classified as being either “fragile” or “strong”, depending on the temperature dependence of the transport properties (e.g., diffusivity, viscosity).^{1,2,5,6,34,35} For example, a non-Arrhenius temperature dependence approaching T_g is characteristic of fragile liquids. This behavior indicates that the activation energy for the process is continually changing, which suggests that diffusion is occurring as part of a complex collective motion on a rugged energy landscape.^{1,2,5,6,34,35} Conversely, Arrhenius behavior is indicative of strong liquids where the diffusion mechanism is due to the physical crossing of a single barrier. The rapidly diverging decrease in the diffusivity, characteristic of fragile liquids, is often well-described by the empirical Vogel–Fulcher–Tammann (VFT) equation, $D(T) = D_0 \exp(-B/(T - T_0))$, where D is the diffusivity, T is the temperature, and D_0 , B , and T_0 are fitting parameters. While initially used as an empirical fitting equation, it has been argued that the thermodynamic basis for the VFT equation is the decreasing configurational entropy of the system as it approaches T_g .³⁶

An alternative mathematical description for the super-Arrhenius temperature dependence comes from kinetic constrained motion models.^{37,38} In this case, the low-temperature transport properties are described by the quadratic equation, $\log_{10}(D/D_0) = J^2(1/T - 1/T_0)^2$, where D is the transport property of interest (viscosity, diffusion, relaxation), J is a scale parameter, and T_0 is the temperature below which constrained mobility turns on. A key feature of this approach is that, unlike the VFT equation, there is not a singularity at very low temperature. Instead, the model predicts a transition back to strong behavior, which is referred to as the fragile-to-strong transition. However, these authors argue that, as yet, there is no system where enough experimental data exist to confirm the low-temperature transition back to Arrhenius behavior.^{37–39}

Recently, Malamace et al. have proposed the power law description, $D = D_0((T - T_x)/T_x)^{-\theta}$ (shown here for diffusivity), where D_0 and θ are fit parameters and T_x is called the crossover temperature.^{33,40} The temperature dependence is described by the power law above T_x and by an Arrhenius equation below T_x . The authors have shown that more than 80 glass-forming liquids are well-described by this method and that rescaling by T_x collapses the data onto a single master curve. Contrary to the assessment of the advocates of the quadratic equation, these authors state that T_x demarks the onset of the fragile-to-strong transition.^{33,40} In most cases, the value of T_x is well above T_g .

Figure 4 displays VFT, quadratic, and Arrhenius equation fits to the diffusivity data. The VFT curve (black dashed line) does a reasonably good job of fitting both the high-temperature methanol diffusivity and low-temperature Kr permeation data. The quadratic function fits the low-temperature data very well and yields $T_0 \approx 175$ K, which is near the temperature of the lowest of the supercooled liquid measurements. Above T_0 , the quadratic equation is not applicable because the transport mechanism there is not based on restrictive, correlated motion for which it was derived, but instead, the mechanism is that of a simple liquid. As mentioned above, Malamace et al. have recently reported the transition from super-Arrhenius to Arrhenius behavior at a temperature, T_x , for many supercooled liquids including methanol.³³ For many substances, the value T_x is within the available data; however, for methanol, only a few diffusivity data points are below the reported T_x of ~ 172 K (marked by an asterisk in Figure 4).³³ Below T_x , an Arrhenius function is used to fit the data (purple dashed line in Figure 4). We have applied the power law equation ourselves and find that

a good fit to the high temperature can be obtained, but the power law does not simultaneously fit both the high-temperature and low-temperature data sets well. To summarize, the quadratic equation fits the low-temperature Kr permeation data well, the power law fits the high-temperature diffusivity data well, and the VFT provides a reasonable fit to both sets of data.

Our intention is not to cast any aspersions on the validity of any of the models based on the results in Figure 4 but instead to point out that for many small molecular systems, there is a lack of experimental data at temperatures near T_g . For example, the experimental data used for determining T_x for the self-diffusivity of supercooled liquid methanol extend only to a temperature of ~ 154 K, which is well above methanol's T_g of ~ 103 K. The temperature region between 120 and 154 K (gray hatched area) is also void of experimental diffusivity data, a so-called “no-man's land”.⁴ The problem is that attempts to enter the region either by supercooling the liquid or by heating the amorphous solid are thwarted by the onset of crystallization of the metastable supercooled liquid.

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In a recent experiment, we have observed a potential approach that may allow one to push into the no-man's land regime using the permeation technique. The experimental permeation technique is displayed in Figure 5 for a series of films where 1 monolayer (ML) of Kr was deposited on a graphene-covered Pt(111) crystal at 25 K and then capped with various alcohol overlayer thicknesses. The initially amorphous films consisted of pure ethanol (top set), pure methanol (bottom set), and a 50/50 mixture of ethanol and methanol (middle set). The films were heated (0.1 K/s), and the desorption of krypton through the overlayer was detected via a quadrupole mass spectrometer.²⁹ The plots show that for a given overlayer composition, the Kr desorption peak shifts to higher temperature with increasing thickness. For the 50/50 ethanol/methanol mixture, the desorption spectra for all overlayer thicknesses have a Gaussian-like shape that broadens as the capping layer gets thicker. This is the expected behavior for diffusion through a homogeneous overlayer. In contrast, for the pure methanol and ethanol films, the desorption spectra for some of the thicker overlayers are clearly not Gaussian-like. In pure methanol and ethanol overlayers, we have shown previously using infrared spectroscopy that these effects are the result of crystallization of the supercooled liquid. When the overlayer crystallizes, the mobility of the Kr ceases, and it remains trapped until the film itself desorbs.²⁷ However, there is no evidence for crystallization in the desorption spectra or in the infrared spectra (not shown) for the mixtures.²⁹ This is consistent with our previous

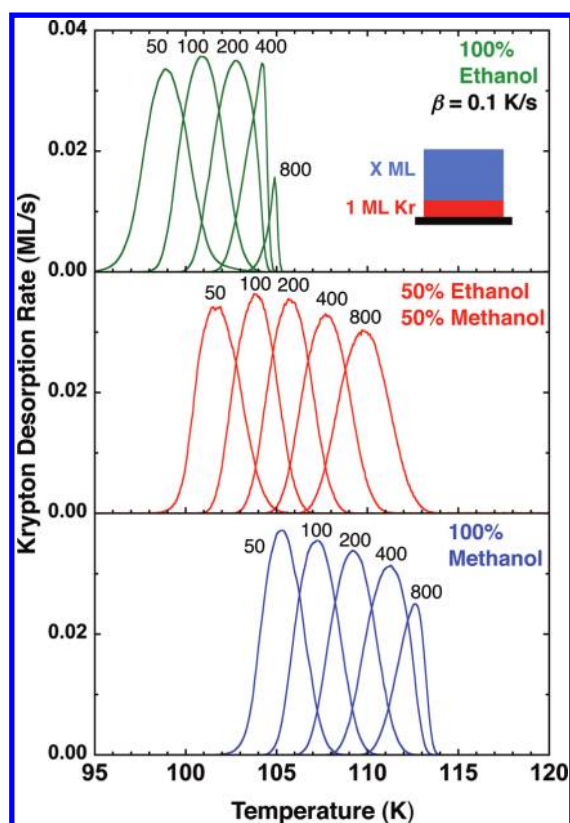


Figure 5. Desorption spectra of 1 ML of Kr capped with 50–800 ML films. The films consisted of pure ethanol (upper), pure methanol (lower), and 50/50 mixtures of ethanol and methanol (middle). The Kr and amorphous overlayers were deposited at ~ 25 K, and the ramp rate was 0.1 K/s. Some of the thicker pure films show signs of crystallization, whereas none of the mixed films do.

work that found that the crystallization is suppressed in ethanol/methanol mixtures.^{23,24} Thus, the use of mixtures may provide a method to extend the temperature range beyond where information about the pure supercooled liquids can be acquired.²⁹

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Clearly, much more work is needed to help to resolve these competing theoretical explanations for the dramatic slowdown in transport properties at temperatures approaching T_g . In this Perspective, we have shown how the use of nanoscale amorphous films and the associated surface science techniques may provide a productive scheme to probe the physical and chemical properties of supercooled liquids in the experimentally challenging temperature regime near the glass transition. These data may provide a stringent test for the various proposed theoretical models and lead to a deeper understanding of the supercooled liquids and amorphous solids.

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Notes

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