



The mysterious glass transition

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Often, when we physicists ask the right questions, we realize that even the most commonplace parts of our world remain deeply puzzling. In its 125th anniversary issue, *Science* magazine asked many such questions.¹ My eye was caught by, “What is the nature of the glassy state? . . . Where and why does liquid end and glass begin?” I chuckled, partly because I knew the editors had made a perceptive choice, but also because I had just wandered inadvertently into that field of research and was beginning to appreciate its depth and subtlety. I also was learning that glass physics is a highly contentious subject—a sure sign that there is still a lot to learn about it.

My curiosity-driven excursion through glass physics started more than a decade ago with fracture and earthquake dynamics. I decided to look at amorphous solids because I thought their liquidlike structure would make them easier to understand than crystals; I would have no dislocations or grain boundaries to worry about. Then I moved from fracture to plasticity because I wanted to understand how molecules rearrange themselves near advancing crack tips; so I found myself in the mysterious world of glass dynamics.

A molten glass doesn’t suddenly solidify when cooled; it gradually becomes more and more viscous. If we put a drop of sufficiently hot molten glass on a flat surface, it quickly spreads like a liquid. A drop ten degrees or so cooler does the same thing but may take minutes or hours. If we cool it more, it will retain its shape for years or centuries, or perhaps for longer than the age of the universe. We ought to understand what is happening here—but we don’t. We don’t know what kind of transformation occurs when a liquid becomes a glass or even whether that familiar change of state is actually a thermodynamic phase transition like condensation or solidification, or something completely different.

Consider a supercooled, glass-forming liquid that somehow has es-

caped crystallization, and assume that this liquid consists of molecules interacting only via short-ranged forces. Those forces must be such that long-range crystalline order is frustrated; that is, the energetically preferred local arrangements of the molecules don’t fit neatly together to fill all space in a periodic array. As a result, the molecular structure of the system resembles a liquid even at low enough temperatures that the material behaves like a solid.

Now forget about complicated phenomena such as fracture. Instead, think about simple linear viscosity, in other words, the ratio of shear stress to shear flow in the limit of vanishingly small driving force. Irreversible motion of this kind, as opposed to reversible elastic deformation, requires molecules to change positions relative to one another. At low temperatures T , the rearrangements must be thermally activated. The energy barrier that they must overcome to move around each other, say ΔE , is larger than $k_B T$, where k_B is Boltzmann’s constant; thus the predicted viscosity has what is called an Arrhenius form, which means it is proportional to $\exp(\Delta E/k_B T)$ with a temperature-independent ΔE .

At yet lower temperatures, say T less than some T_A , an Arrhenius fit to the viscosity requires that ΔE grows with decreasing T and appears to become infinite at some nonzero temperature T_0 . Below T_0 , the material seems to be completely frozen, so much so that it is in a state of “broken ergodicity,” which means it violates Josiah Willard Gibbs’s assumption that such systems explore statistically significant fractions of their possible states on experimental time scales. Indeed, apart from the thermal jiggling of molecules in their local environments, the glassy molecular configurations seem to be stuck forever near just one of those configurational states. How can that happen? And what is happening at higher temperatures between T_0 and T_A ? Apparently, as T falls below T_A , increasingly large cooperative motions requiring increasing acti-

vation energies ΔE are needed to achieve local rearrangements. What are those motions? What features of the molecular dynamics are responsible for such behavior?

The mystery deepens

When one looks at the thermodynamic properties of supercooled glass-forming liquids, the mystery deepens. If the dramatic slowing of molecular rearrangements were just that—a slowing of all the motions in a way that didn’t affect the energies of interactions between the molecules—then the thermodynamics would be uninteresting. The systems might take longer and longer to equilibrate as T decreases toward T_0 , but ultimately, thermodynamic functions such as the specific heat would be unremarkable. That’s not at all what happens. Careful specific-heat measurements seem to indicate that the difference between the entropy of a glass-forming liquid and its crystalline phase extrapolates toward zero at a temperature T_K , named for Walter Kauzmann, who discovered the paradox experimentally in 1948. T_K is near and possibly equal to T_0 . Moreover, the corresponding jump in the specific heat near T_0 correlates well with Austen Angell’s dynamic fragility (a measure of how sharply the effective activation energy $\Delta E(T)$ grows near T_0). Thus there are strong relations between the dynamics and thermodynamics of glass-forming liquids—relations that demand to be understood, but which are difficult if not impossible to pin down precisely because of the extraordinarily slow behaviors of these systems near T_0 .

The thermodynamic signature of the glass transition near T_0 has led many investigators to conclude that something like a phase transition must be happening there. Theoretical models that show such transitions, however, do not look much like liquids with short-range interactions between their molecules. (I set aside the mode-coupling theories, which do start with realistic models of liquids but break down well above T_0 .)

Some of the most popular models of the glass transition are spin glasses. In such models, Ising-like spins sit on lattice sites, and random, very long-ranged, spin–spin interactions simulate glassy disorder. Models of this kind can show very interesting, glasslike, thermodynamic behavior, including collapse to a state of zero entropy at nonzero temperature. However, I do not think that they can be used to predict dynamic behavior such as the divergence of the viscosity at T_0 .

On the contrary, I think that the mechanisms that produce molecular rearrangements in glass-forming liquids must be localized and that long-ranged-force models inevitably fail to describe such mechanisms properly. For example, mean-field theories can adequately describe the thermodynamics of first-order phase transitions away from critical points, but they cannot deal with nucleation dynamics because the surface energies that determine critical droplet sizes are intrinsically short-ranged phenomena. In computing glassy relaxation rates, I do not think one can simply assume that unspecified transition mechanisms exist and then base analyses on densities of states or the like. Thus the classic 1965 formula of Gerold Adam and Julian Gibbs, which relates the vanishing entropy near T_0 to the diverging viscosity, should be understood as an intuitive success that still demands an explanation. In short, I think we must understand in detail which molecular configurations are accessible from which other configurations and how rapidly the transitions between the configurations can occur, and then we might learn how such dynamical mechanisms relate to thermodynamic observations.

Another approach to glass dynamics, based on so-called kinetically constrained models, is diametrically opposite to the mean-field, thermodynamic theories. The simplest example is a non-interacting Ising model in an external field that energetically favors the down spins. The equilibrium thermodynamics of this system is manifestly uninteresting. However, as discovered by Glenn Fredrickson and Hans C. Andersen in 1985, the system exhibits realistic glassy dynamics if one adds an artificial kinetic constraint by requiring that a spin can flip—up or down—only if at least two of its neighboring spins are up. Within that constraint, the transition rates can be chosen so that the system approaches a trivial thermal equilibrium. This model exhibits a rapidly increasing relaxation time and even anomalously

slow stretched-exponential decay of fluctuations at small T , but the relaxation time diverges only at $T = 0$. More sophisticated kinetically constrained models have more interesting properties. I find them to be useful examples of ways in which relaxation times in systems with short-range interactions can be extraordinarily sensitive to small changes in parameters such as density or temperature. In contrast to the mean-field theories, the kinetically constrained models seem to contain just the other half of the properties of real glasses; they have rich glasslike dynamics but no glassy thermodynamic behavior at all.

Hard facts from hard disks

A recent paper by Alexander Donev, Frank Stillinger, and Salvatore Torquato reinforces my bias toward short-ranged forces.² The authors describe a numerical study of a two-dimensional, binary mixture of hard disks that interact only through infinitely repulsive contact forces, which prevent them from overlapping with each other. When compressed and not allowed to crystallize, the system forms what looks like a glass. There is no energy scale, so there is no temperature, and the only control parameter is the density. Thus the system has some of the simplicity of the kinetically constrained models, but the kinetic constraints arise realistically from the requirement that, for one disk to move around another, its neighbors must collectively move out of the way. Such collective motions become more and more difficult as the density increases. There is a density at which the system becomes completely jammed in a state of maximum disorder, and it is tempting to guess that this maximally random jammed state is an ideal glass. But Donev and his collaborators find that this supposedly ideal state has nonzero entropy. They go further to show that there is a continuum of yet denser states in which the system achieves tighter packings by forming ordered regions of its two constituents, and that each of these states also has nonzero entropy. The only state of zero entropy is the densest, fully phase-separated crystal.

My interpretation, which I think is consistent with that of Donev and his collaborators, is that the mixture of hard disks encounters a transition of some kind at the jamming density, and that it is dynamically impossible for the mixture to find its way to the states of higher density and lower entropy. Something like this dynamic mechanism may happen in real glasses with energy scales

and temperature dependences. If so, glasses necessarily retain substantial residual entropies at low temperatures; there is no Kauzmann paradox or ideal glass transition; and the extrapolation of the configurational entropy to zero at T_K is unjustified. This interpretation, however, leaves us with no understanding of the mysterious relation between dynamics and thermodynamics at the glass transition, nor does it tell us whether some kind of thermodynamic phase transition occurs near T_K .

The reader will have guessed that I have my own ideas about molecular mechanisms that may produce both diverging relaxation times and rapidly varying entropies near the glass transition. I have suggested in recent papers how those mechanisms may induce correlations,³ and how those correlations may explain the thermodynamics. But my ideas are evolving as I write. In any case, this column may be an appropriate place for opinions and exhortations—but not for publishing my new research.

We can learn an important lesson from the glass mystery, no matter how it eventually will be resolved. Certainly, we must become more sophisticated about nonequilibrium statistical mechanics. For about a century, we have been accustomed to making a clean separation between equilibrium and far-from-equilibrium phenomena, constructing theories of the first by evaluating partition functions, and of the second by whatever means we can devise for dealing with a wide variety of thermally activated transitions and responses to external driving forces. The glassy state is surely not one of globally stable thermodynamic equilibrium, and the transition between a glass and a supercooled liquid, if sharply defined at all, seems highly unlikely to fit into any of our conventional categories of phase transformations. If glasses demand unconventional physics, then so must an enormous number of other important systems. The obvious examples are in biology, where nothing is in thermal equilibrium. How can we hope to understand the mechanical and thermodynamic behavior of biological substances if, after many decades of intense investigation, we still can't understand the properties of simple inorganic amorphous materials?

References

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3. J. S. Langer, *Phys. Rev. E* **73**, 041504 (2006); *Phys. Rev. Lett.* **97**, 115704 (2006). ■