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Mysteries of the glass transition

In his intriguing Reference Frame "The Mysterious Glass Transition" (PHYSICS TODAY, February 2007, page 8), James Langer discussed the challenges of glass science. This interdisciplinary field between physics and chemistry has increasingly important applications that now even include the pharmaceutical and food industries.

I like to picture the liquid–glass transition via the following model. Consider a Langevin particle in one dimension moving in an asymmetric double-well potential. The system has a finite relaxation time that diverges as temperature goes to zero, because the relaxation time is related to the barrier to be overcome in the usual Boltzmann expression characterizing rate theory. Consequently, when the system is cooled at a finite rate, it eventually falls out of equilibrium. That process exhibits most of the properties associated with the liquid–glass transition:[1–4] The liquid–glass transition is gradual rather than sharp, its transition temperature is lower for slower cooling, and the liquid–glass transition is associated with various nonlinear and hysteresis effects.

What happens in the glass transition of the asymmetric double-well potential is that jumps between the two energy minima cease and the system freezes into one minimum or the other.[5] A glass transition occurs whenever a system doesn't have enough time to equilibrate. Computer simulations confirm that picture for realistic liquids also. The non-Arrhenius behavior usually observed in supercooled liquids is not reflected in the simple model I described but is easily modeled by assuming that the activation energy increases as the temperature decreases.

If that simple model accurately reflects the basics of the liquid–glass transition, then the transition is also just a freezing into an energy minimum.[5] (Although the distribution of frozen-in energies may deviate from the equilibrium distribution,[4] it is a minor effect, and to zeroth order the system just freezes configurationally.) Does that eliminate the mystery? Not at all; an enormous challenge still lies in understanding the fairly universal properties of the ultraviscous liquid phase above the glass transition where the viscosity becomes almost 10^{15} times larger than that of ambient water. Everything is exceedingly slow in that phase, right? Well, most molecular motion is vibrational, and transitions between different minima are indeed rare. But the diffusion of transverse momentum is actually extremely fast because the exceedingly large kinematic viscosity of the Navier–Stokes equations is the transverse momentum diffusion constant. Thus the ratio between the particle diffusion constant and the transverse-momentum diffusion constant goes from roughly 1 in the less viscous phase to a number of order 10^{-30} just above the liquid–glass transition.

Such small dimensionless numbers are rare in condensed-matter physics; they appear to signal that an ultraviscous liquid is more accurately thought of as a solid that "flows." Researchers are not certain, but the existence of a very small dimensionless number characterizing such liquids gives hope that a fairly simple universal theory exists.

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As someone who has long been interested in the glass transition and glassy-state kinetics, I would like to comment on some of the issues raised by James Langer in his Reference Frame column.

I affirm Langer's statement about healthy contentiousness. Whether or not the glass transition has thermodynamic roots definitely makes for exciting science. The reason some of us think thermodynamics is important is that we find it difficult to dismiss as coincidences the similarities in the values of the kinetic temperature T_0 and the thermodynamic Kauzmann temperature T_K. One common objection to the Kauzmann analysis, that an amorphous solid should not have zero

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