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entropy, can be assuaged by noting that the entropy at T_K does not have to be zero, just very small.

Langer briefly mentions the success of the simplistic Adam–Gibbs (AG) model in describing the dynamics of supercooled liquids. Its nonlinear extension into the glass-transition region and glassy state (NLAG) is also surprisingly successful.[1] That extension is based on concepts introduced by several researchers over several decades: Simon Rekhson in 1994, George Scherer in 1984, Cornelius Moynihan in 1976, O. S. Narayanaswamy in 1971, and others. The successes of the NLAG model go far beyond expectations, and raise issues of their own. The resolution of these issues might provide important clues to a theoretical understanding of the glass transition.

▶ As noted by Langer, the experimentally observed effective activation energy $E(T)$ increases rapidly with decreasing temperature down to the glass-transition temperature T_g, but it then *decreases* through the T_g range until it reaches a constant value $E(T_g)$, so that glassy-state relaxation exhibits Arrhenius behavior. The singularity at T_0 noted by Langer only occurs in the equilibrium supercooled liquid state and not in the experimentally observed nonequilibrium glassy state. The change from non-Arrhenius to Arrhenius behavior at T_g is well described by the NLAG model and its precursor, the Tool-Narayanaswamy-Moynihan model.

▶ NLAG predicts a simple relation between the ratio T_K/T_g and an empirical constant that parameterizes the nonlinearity of the glass transition and glassy-state kinetics. This intriguing prediction needs to be independently confirmed or unambiguously refuted.

▶ The NLAG model, together with the plausible assumption that smaller localized activation energies $\Delta\mu$ enable the kinetic T_g to get closer to the thermodynamic T_K, generates many of the correlations captured by Angell's fragility. In fact, the ratio T_K/T_g is an excellent metric that allows fragility to be applied to the glassy state.

▶ Estimated values of $\Delta\mu$ for canonical glasses are often comparable with rotational energy barriers in polymers, and ionic, covalent, and hydrogen bond strengths. In these cases the NLAG model is almost quantitatively accurate.

▶ Incorporation of a distribution in $\Delta\mu$ yields a respectable account[2,3] of thermal manifestations of motions in hydrated proteins and B-DNA.[2,4] The mean value for $\Delta\mu$ is comparable with hydrogen bond strengths, albeit with a large uncertainty, and the large standard deviation—30% of the average—is consistent with the insightful but qualitative analysis of Jennifer Green and coworkers.[4] The fact that NLAG gives a decent account of annealing in hydrated proteins and B-DNA strongly supports Austen Angell's suggestion that the glass transition and protein dynamics have much in common.[5]

I share Langer's belief that short-range interactions are probably the key. Since the current models accommodate a wide range of interactions, such as covalent, hydrogen, and ionic bonding, the glass-transition phenomenon is evidently insensitive to the details of those interactions. This generality is missing from too many theoretical attempts at explaining the problem. Perhaps the averaging of details is why the simplistic NLAG model is so successful.

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I do not see any mystery in James Langer's "mysterious glass transition," at least with respect to inorganic glasses of one-component systems like silicon dioxide, boron oxide, and so on. To understand the glass transition of inorganic materials, one first has to understand why crystals melt. Near the melting temperature, electrons occupy more and more excited states as temperatures increase. Electrons in excited states possess wavefunctions different from those in their low-energy or ground states. Different wavefunctions mean that the probability distribution of the electrons in space changes. The core ions will be driven to new places as they interact with the excited electrons. However, the electrons will change again and again to other states with different wavefunctions. The arbitrary time series of sufficient electrons in their excited states will cause the core ions to continuously change position. That scenario corresponds to a melt.

As the melt cools, the electrons will occupy more and more low-energy states. If the forces of the electrons in their low-energy states are not strong enough to induce a regular order of the core ions, the transition to a glass occurs. Thus melting of chemically bonded solids, and glass formation from their melts, is basically an electronic effect generally neglected in publications dealing with properties of melts and glasses.[1] Glass formation from the melt depends on the strength and sufficiently large number of directed bonds (to stabilize the noncrystalline order) and on the melting entropy ΔS_m (that is, melting enthalpy ΔH_m, divided by melting temperature T_m). If ΔS_m is small, only a little entropy is released and produced once a bond closes, and the temperature increases locally by just a small amount. This implies that neighboring directed bonds of the undercooled melt can be broken only within a relatively small temperature range below T_m. This interval has to be passed fast enough for glass formation. If ΔS_m is large, the temperature interval of recalescence is relatively large to reach T_m and the undercooled melt has enough time to rearrange to crystals during cooling.[2]

Now it is easy to understand the "mystery" of the glass transition or what occurs in the glass-transition range. (Imagine that the temperature is rising.) In that range, bonding electrons start to occupy excited states. This causes an additional mechanism for the thermal expansion, an additional contribution of the specific heat capacities (not causing a "jump," however), and an increase of the damping of resonances of many kinds in glasses. The worldwide standard procedure to determine T_g in glass science is based on the change of the slope of dilatometer curves, not mentioned by Langer. As a consequence of the scenario described here, there is no phase transition at T_g, just an exponential freezing out of electrons from higher to lower energy levels with decreasing temperature.

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With the very noncrystalline nature of the state labeled "glass," the use of terms like "lattice sites" by some physicists is misleading if not erroneous. Having spent nearly 40 years researching solid-state chemistry using diffraction

methods, I can say that the glass state is not just limited to glass—that amorphous state of polymeric silicon oxide with doping of other oxides, including boron oxide. In fact, all polymers, including those extensively used in daily life starting with organic monomers, show the "mysterious" glass transition.

A study of the glass transition in any polymeric material is necessarily dictated by complex variations in the motions of the polymeric chain segments, which form as sheets, coils, helices, and the like. The glass transition in the case of doped silicon oxides may be ascribed to the conformational changes in the vicinity of the tetrahedral silicon, while in polymers it involves oxygen atoms in the polymeric helices or sheets.

One can draw inferences from the crystal structures of pure silicon oxides such as quartz in that even those crystals enter the glass state upon heating.[1] Then it is very difficult to recover the original crystal with the same characteristics.

When melted, even crystals of sucrose, a simple everyday compound, lead to a glassy state that is far more mysterious than the glass itself.

To understand the underlying principles of the behavior of the glass state, we must use radial distribution functions from diffraction data to study these mysterious glass transitions, particularly in regard to their structural details at the molecular level.

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Many thanks to the authors for their comments about my Reference Frame column. I have just a few remarks in reply.

Ian Hodge and I agree that we still need a deep, first-principles understanding of the remarkably successful Adam–Gibbs formula, in both its original and extended nonlinear versions. It will be interesting to see whether the physical mechanisms underlying the two related phenomenologies are actually the same in their respective regions of validity.

Jeppe Dyre remarks that some basic features of the glass transition are captured by the simple asymmetric double-well model. He clearly understands that there is a great deal more to the mystery than that, and I think he is making his point in an interesting way. Viscous relaxation rates near the glass transition are about 15 orders of magnitude slower than molecular vibration