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Nature of the glass transition

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We propose a picture whereby the kinetic glass transition observed in the laboratory is controlled by an underlying phase transition with unusual properties. We assume that the line of metastable liquid states below the freezing temperature ends in a fixed point, and show that this picture is in accord with a number of experimental observations, including the vanishing of the excess configurational entropy of the liquid and the Vogel-Fulcher law. Differences between this scenario and current theories of systems whose Hamiltonian possesses quenched disorder are discussed.

The nature of the glass transition is a perennial problem.[1] As observed in the laboratory, the crossover from liquid to glass is always purely kinetic; as temperature is lowered below the freezing point, response times in the liquid increase rapidly, eventually surpassing observational times scales. When this happens, large-scale flow processes cease and the material appears solid on human time scales. The liquid has fallen out of (metastable) equilibrium; the temperature T_g at which the relaxational and observational time scales cross depends on the observer, and does not represent any intrinsic temperature scale of the liquid itself.

Substantial debate has centered on whether an underlying intrinsic temperature *does* exist. In 1948, Kauzmann[2] pointed out that the excess configurational entropy of the metastable liquid, if extrapolated into the experimentally inaccessible region, appears to vanish at a finite temperature T_K, reminiscent of a second-order phase transition. Moreover, measurements of viscosity η and related relaxation times τ of large-scale flow processes seem to indicate, in the intermediate viscosity region, a non-Arrhenius behavior with an essential singularity at a finite temperature T_0,

$$\tau = \tau_0 e^{A/(T-T_0)} , \tag{1}$$

with A constant or weakly temperature dependent. Equation (1) is commonly referred to as the Vogel-Fulcher (VF) law. Of compelling interest is the observation for many materials that, to within experimental error, $T_0 \approx T_K$.[3-5] Since both quantities are obtained via extrapolation, the significance of their possible equality is unclear, though suggestive of an underlying singularity.

The description given above is considerably oversimplified and subject to a number of caveats. Among the most important are the following facts. (1) For some glass formers $T_K \approx T_0 \approx 0$. These include SiO_2, GeO_2, and BeF_2, among others. Angell and co-workers[3,4] refer to these as the "strong" liquids, as opposed to the "fragile" liquids (such as *o*-terphenyl) which obey Eq. (1). Strong liquids usually form a random covalently bonded network, while cohesive forces in fragile liquids are less directional in nature. (2) There often appears to be a crossover of τ to more Arrhenius-like behavior at higher viscosities (but still for $T > T_g$).[6] A crossover to pure Arrhenius behavior is also common at high temperature. (3) Diverging relaxation times in many glassy liquids may be equally well fit by a power-law singularity, or by some other functional form different from Eq. (1). (See the reviews[3,7-9] for further discussion of the experimental situation.)

In spite of the experimental uncertainty and complexity surrounding many of these issues, Kauzmann's observation and the VF law have led some theorists to propose that a singularity at T_K underlies the rather strange behavior of glassy liquids. There are three main theoretical points of view on the subject. (1) A true phase transition (usually proposed to be second order) exists at T_K, but diverging relaxation times prevent one from ever approaching it in equilibrium.[1,10-15] Proponents of this point of view have various ideas of the nature of the low-temperature state ($T < T_K$) of the true equilibrium glass. (2) A *kinetic* transition ($\tau \rightarrow \infty$ as $T \rightarrow T_0^+$) exists *without* an underlying equilibrium phase transition.[16-19] However, most of the theories which at first appeared to have such a transition were later found not to have one.[20,21] (3) Neither an equilibrium nor a kinetic transition exists. The behavior seen in Eq. (1) might be due simply to a crossover between two Arrhenius regimes, with the effective free-energy barrier for rearrangements at low T larger than that at high T. No true divergence would exist at any $T > 0$.

In cases (2) and (3), if one were to follow the liquid entropy curve into the experimentally inaccessible region $T < T_g$, it would eventually have to bend over to avoid crossing the crystal line, preventing the Kauzmann "paradox." No convincing mechanism for this is known.

The purpose of this note is to propose a possible scenario wherein the features of the glass transition as described here can be understood in terms of the fixed point structure of the Hamiltonian under appropriate renormalization-group transformations. Our proposals are speculative but testable. The central conclusion is that the

Kauzmann temperature corresponds to an underlying thermodynamic singularity that is the end of a line of metastable states, without there necessarily being *any* low-temperature equilibrium phase (besides the crystal) below T_K. The vanishing of the entropy and divergence of τ at T_K are natural consequences of this picture. Nonexponential (in time) relaxation is also implied, but will not be discussed herein.

Our starting point requires a modification of the usual renormalization-group picture of first-order transitions controlled by a *discontinuity fixed point.*[22] We suggest that a single discontinuity fixed point on the coexistence surface is not necessary, and, in at least some cases, is replaced by one on each branch of the free-energy surface. These fixed points lie within the metastable regions of each phase (i.e., the "cold" and "hot" phases) and each signifies the end of a line of metastable states in its phase (see Fig. 1). The first-order transition temperature T_f corresponds merely to the crossing of the two free-energy surfaces, not to a singularity of either phase. Renormalization flows are different in the two phases, as one might expect in a situation of broken ergodicity. Both fixed points might lie close to T_f, but in principle may lie anywhere within the metastable region. In the hot phase, trajectories flow under renormalization-group transformations to the infinite-temperature (disordered) fixed point, and in the cold phase to the zero-temperature (ordered) fixed point. Such behavior has in fact been claimed to have been seen recently in the ten-state Potts models in two dimensions.[23,24] While it is too early to tell whether the observations of Ref. 23 are correct, the two-lattice matching method within the Monte Carlo renormalization group described in that paper does provide a possible means of testing our picture on simple Hamiltonian models for dense liquids or glasses.

We shall hereafter assume that this picture describes the fixed-point structure of the Hamiltonian of a glass-forming liquid, and that the fixed point corresponding to the end of the line of metastable liquid states lies at a temperature $T_c < T_f$ well within the metastable liquid region. Upon remaining a liquid below the freezing temperature T_f, the system finds itself in one of a large number of metastable states.[25] Because renormalization trajectories flow into the liquid phase, the size dependence of the free-energy barriers vanishes as $L \rightarrow \infty$, where L is the size of the system; in other words, barrier heights remain of order unity. Hence, the thermodynamical and dynamical measurements taken over a sufficiently long time scale average over many metastable states and are thus history independent.

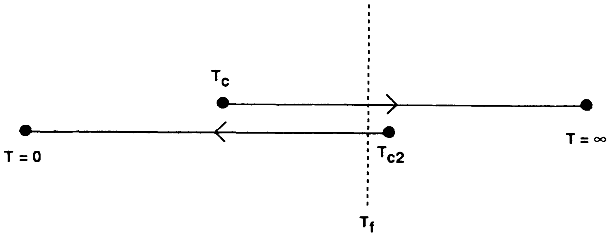

FIG. 1. Proposed fixed-point structure of the glass transition. Only the temperature axis is shown for clarity. Renormalization-group trajectories flow in different branches of parameter space corresponding to different branches of the free-energy surface.

As temperature is lowered, the barriers surrounding some of these states grow, while others may decrease. Because of the controlling fixed point, the linear size ξ of the average spatial region occupied by a typical metastable state will grow[26] according to

$$\xi \sim (T - T_c)^{-\nu} . \tag{2}$$

We use here the interpretation of ξ as a persistence length, rather than a correlation length.[27] The persistance length ξ corresponds to the size of domains of overlap with the different possible liquid phases associated with locally stable free-energy valleys. Because of the presence of multiple liquid phases as the fixed point, we must have[27,28]

$$\nu = 1/d ,$$

where d is the spatial dimension. This is consistent with the value of the relevant eigenvalues measured in Ref. 23.

The *configurational* part of the entropy can be written

$$S_c \sim (L/\xi)^d s_c , \tag{3}$$

where s_c is the subextensive configurational entropy of the confined region of configuration space corresponding to a particular metastable state. Equation (3) is reminiscent of the approach taken by Adam and Gibbs[11] (AG). Hence, in the region where the temperature dependence of ξ is governed by the critical point (which may extend even into the region above T_f), the excess configurational entropy (as $L \rightarrow \infty$) vanishes as

$$\Delta S_c \approx S_c \sim \xi^{-d} \sim (T - T_c)^{\nu d} = T - T_c , \tag{4}$$

which is well-obeyed experimentally and identifies T_c as the Kauzmann temperature T_K.

Equation (4) is consistent with the renormalization to *infinity* as $T \rightarrow T_c^+$ of some of the free-energy barriers between metastable states. Like the crystal, the system upon reaching T_c would become trapped, in the thermodynamic limit, in a small region of configuration space. Note that this is very different from a spinodal point, at which the barriers would renormalize to zero. It is not entirely clear what happens in principle in the inaccessible region below T_c, where the barriers would remain finite; multiple "ideal-glass" states are conceivable, but so is the absence of any equilibrium phase (besides the crystal) in this region. The free-energy surface corresponding to the liquid phase may simply cease to exist beyond the controlling fixed point.

Equation (4) implies that the complexity[29] vanishes at T_c as well. Kirkpatrick and Wolynes[14] (KW), in their study of many-field p state Potts glasses with $p > 4$, assert that the configurational entropy is equal to the complexity I,

$$I = -k_B \sum_s P_s \ln P_s , \tag{5}$$

where P_s is the Boltzmann weight, or canonical probability, of metastable state s. Hence, T_c can also be interpreted as the point where the complexity vanishes, or the logarithm of the number of deep metastable states become subextensive.[14] In general, it can be shown[29] that $I < S_c$. Hence, the vanishing of the configurational entropy implies the vanishing of the complexity as well.

There are several possible mechanisms by which barriers may renormalize to infinity as the fixed point is approached from above. All give non-Arrhenius behavior. The simplest is that proposed by AG.[11] Assuming that the free-energy barrier for cooperative rearrangement of a subregion scales with its size ξ^d, and that such subsystems are independent, AG show that the average relaxation rate τ^{-1} scales with the configurational entropy as

$$\tau^{-1} \sim \exp(-C/TS_c) , \qquad (6)$$

where C is a constant. We would point out, however, that a free-energy *barrier* need not scale with the size of the subsystem; AG's arguments are not convincing in this regard.

KW (Ref. 14) use a plausible Cahn-Hilliard-type argument[30] to find the rate of transitions above their T_K. The essential point is that transitions are entropy-driven; since the energy of any two states is roughly the same, nucleation of a new state occurs because there are many different states to escape to. Hence, the volume free energy of a nucleation seed of radius R is given by $F_{\text{bulk}} \sim -TS_cR^d$, while the surface free energy is $F_{\text{surface}} \sim \sigma R^{d-1}$, where σ is the effective surface tension between liquid states corresponding to different valleys. This is the simplest assumption for F_{surface}, but in fact $d-1$ is probably a lower bound for the exponent. This then leads[14] to a rate of transitions proportional to $\exp[\sigma^d/(TS_c)^{d-1}]$. More sophisticated arguments will change the power to which the exponent is raised, but the essential physics remains intact; the free-energy barriers governing transitions diverge as the excess configuration entropy vanishes.[31]

Within our picture, the KW argument makes sense as long as $R^* < \xi$, where R^* is the critical nucleation size. When R^* grows larger than ξ, it is reasonable to assume that the dynamics is governed instead by the motion of domain boundaries. Here the barriers are roughly proportional to the surface area of the domains, or ξ^{d_s}, where $d > d_s \geq d-1$, since the domain boundary may be fractal. For simplicity, we take $d_s = d-1$. This then implies a crossover in the dynamical behavior at the temperature where $R^* \sim \xi$. Using the KW approach, one expects $\log\tau \sim \sigma^d/(T-T_c)^{d-1}$ above the crossover temperature, and $\log\tau \sim \xi^{d-1}/T \sim 1/(T-T_c)^{(d-1)/d}$ below this temperature; the crossover is from a stronger divergence of the relaxation time at higher temperatures to a weaker divergence nearer the glass transition. This may be enough to explain the observed crossover towards Arrhenius behavior close to T_g.

In addition, one can qualitatively relate the surface-tension term to the "strength" or "fragility" of a given liquid.[3] If the molecular bonding in a liquid is highly directional or otherwise constrained, as in the strong liquids, it seems reasonable to expect that many bonds along a domain boundary will be strained or unsatisfied, leading to large values of σ in general. In the fragile liquids, where bonding is less directional, adjustment of bonds along a domain boundary should be easier, leading to lower values of σ. Resulting plots of τ vs T are in qualitative accord with experiment, where the amount of curvature in an Arrhenius plot can be approximately parametrized[15] by a single number D: $\log\tau \sim DT_0/(T-T_0)$. Strong liquids have larger values of D than fragile liquids, and, hence, less curvature in a plot of $\log\tau$ vs T_g/T.

While the precise algebraic form of the relaxation time as a function of temperature differs in these several approaches, they all have a pole in $\log\tau$ at T_c. All are in reasonable agreement with experimental results, from which it is difficult to tell the precise form beyond the pronounced curvature on an Arrhenius plot. The tendency towards a weaker divergence near to T_g may also be understood in terms of a crossover.

We also need to consider the rate of nucleation to the crystal state; this rate is energy driven rather than entropy driven. For a discussion of experimental results on this phenomenon, see Ref. 32. In general we should expect the surface tension between a metastable liquid phase and the crystal phase to be considerably larger than that between metastable liquid phases, by the same reasoning as that used for strong liquids. Therefore, the crystal nucleation time τ_{crystal} should be much longer than other relaxation times, as observed. Nevertheless, there is no clear mechanism to make τ_{crystal} diverge at T_c, and it is possible that it does not. In this case, τ will eventually exceed τ_{crystal} and the system will crystallize before coming to equilibrium, though probably not on human time scales. Note, however, that this mechanism is not an essential part of our scenario, and in particular is *not* needed to avoid the Kuazmann paradox.

The picture described here differs in an important respect from that of both the Potts glass and recent scaling theories of spin glasses,[33,34] both of which begin with a Hamiltonian containing quenched disorder. It has long been recognized that spin glasses differ from glasses in that the latter have no such disorder in their Hamiltonian, but there has been considerable uncertainty as to the significance of this fact.[35] However, according to the current picture of short-range spin glasses, the statics and dynamics of the low-temperature phase is controlled by a disordered zero-temperature fixed point.[34,36] We see no need for such a zero-temperature fixed point controlling a low temperature, "ideal glass" phase; in our picture, the line of metastable states simply ends at a (probably first-order) fixed point at some finite temperatures below T_f. Renormalized flows are always into the high-temperature phase; the fixed point can never be reached in equilibrium. Because of the rapid divergence of relaxation times [Eq. (1)], the system will always fall out of equilibrium above the fixed point; its presence is only felt at higher temperatures. The significance of the Kauzmann temperature is *not* that of a second-order transition from liquid to crystal; the system merely gets trapped in some small region of phase space.

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