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Scaling theory for the glass transition

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The technologically important viscoelastic structural properties of glasses are largely determined at the glass transition, where the supercooled liquid falls out of equilibrium. We examine recent experimental evidence that there is a thermodynamic critical point underlying this transition. We argue that the behavior of glasses can be understood using static and dynamical scaling about this critical point. We propose a scaling theory of the glass-transition critical point.

I. INTRODUCTION

Why are glasses solid? Crystals are solid because they have a regular lattice of atoms; crystalline lattices cannot rearrange except through motions of line dislocations, which are not present in thermal equilibrium. Glasses have no obvious long-range order; structurally they appear much closer to the corresponding liquid phase than to the crystal. Why they respond rigidly to external shear remains one of the profound mysteries in condensed-matter physics.

Glasses respond to external stresses differently then crystals do. In a crystal, a small external force induces an elastic response on an acoustic time scale; larger forces on a crystal produces plastic deformations mediated by line dislocations nucleated at defects. Glasses appear to have no plastic flow regime:[1] since line dislocations have no meaning in glasses, this is not terribly surprising. On the other hand, glasses respond elastically on an enormous range of time scales. How rigid a glass is depends drastically on the frequency of the experimental probe. It has been known since the middle of the past century[2] that glasses under load continue to stretch (roughly logarithmically in time) for years, and slowly return to their original size when the load is removed. There are similar responses to temperature shifts and dielectric probes:[3] unlike liquids and crystals, glasses have internal rearrangements occurring on time scales ranging from the microscopic to the cosmic.

It is becoming clear that explaining the dynamical relaxation in glasses will also involve answering the fundamental question of why glasses are solid. There will be two main elements of the final theory. First, and the subject of this paper, will be understanding the equilibrium properties of the supercooled liquid.[4] Many of the dynamical response properties of glasses have their precursors in the supercooled liquids: the melt looks like a glass when measured at high frequencies. The second element will be a quantitative theory of how glass-formers fall out of equilibrium as they are cooled. While it is no longer believed that the glass has the same properties as the liquid at a single "fictive temperature," the properties are largely set by the history of the glass in a narrow region of temperature. We are working on the fall from equilibrium separately.[5,6] Understanding the glass transition—the point where the liquid melt falls out of equilibrium and becomes glassy—demands understanding why the liquid becomes sticky in equilibrium as well as how it falls out of equilibrium. The glass transition should provide the key to the dynamic and history-dependent behavior throughout the glassy phase.

Much of the recent theoretical focus[7] on the glass transition has attempted a purely dynamical explanation of freezing. This began by the efforts of several groups to develop a self-consistent mode-coupling theory.[8-10] In these theories, nonlinear terms involving the hydrodynamic viscosity act to increase the effective viscosity: the resulting feedback leads to a theoretical temperature at which the viscosity diverges. It is no longer believed that mode-coupling theories can describe the freezing transition itself,[9] although the theories may be applicable to glass-forming liquids at temperatures well above the experimental glass transition.[10] Second, there has been a flurry of simple models that exhibit a dynamical transition.[11-13] These models also provide explanations for the frequency response at fixed temperature (the "stretched-exponential" relaxation found experimentally in glasses). Mode-coupling theory will remain a valuable tool at high temperatures; the simple models will continue to have explanatory power for the ac response in supercooled liquids. It is however the view of the authors, especially considering recent experimental work[14,15] discussed in Sec. II, that the transition is a traditional second-order phase transition with a static as well as a dynamic component.

Our theoretical approach to the subject, reported in a preliminary form in an earlier publication,[16] reflects a return to older, more traditional pictures. First, several years before second-order phase transitions were understood in any detail, Adam and Gibbs[17] presented a theory of the glass transition with a diverging correlation length, driven by the vanishing of configurational entropy. The "configurational entropy" is given by the number of metastable glassy atomic networks (as opposed to the vibrational entropy of small oscillations within the network). It is usually equated to the "excess entropy": the difference between the entropy in the supercooled liquid and in the corresponding simple crystalline phase. Adam and Gibbs noted that relaxation in the supercooled liquid should necessarily involve rearranging a volume with at least $k_B \ln 2$ worth of configurational entropy, allowing for two states between which to shift. As the configurational entropy vanishes this volume diverges; they argued then that the barrier to relaxation grows with the volume and thus they explained the diverging viscosity. This picture has been supported by the rough correspondence, in a wide variety of systems, between the Kauzmann temperature T_K where the excess entropy extrapolates to zero and the temperature[18] T_0 where the viscosity extrapolates to infinity.

We are inspired by this picture, but need to refine it. Clearly, the diverging length in the Adam-Gibbs picture is indicative of a second-order phase transition. The contemporary understanding says that fluctuations are important on both sides of such a transition: the configurational entropy should already build up below the transition temperature. In particular, in our theory the specific heat will not simply have a discontinuity at the transition, but will have a cusp: the configurational entropy $\Delta S \simeq \int c/T\, dT$ at the transition will be determined in part by the ratio of the amplitudes of the cusp above and below the transition. Also, the cusp will not be correctly incorporated in typical extrapolations of the excess entropy from the liquid side. Thus in our work there is no natural relationship between T_K and T_0.

The second traditional picture[19] on which we draw was inspired by the freezing of hard-sphere liquids, and explained the glass transition as a vanishing of "free volume." Early versions of the theory had a sharp transition; later versions had a crossover back to Arrhenius behavior. This theory had semiquantitative predictive power in some systems; on the other hand, no upswelling of experimental density anomalies has occurred, and it is hard to see how the free-volume theory could be applicable in detail to most glasses. In both the entropy and the free-volume theories, the sluggish behavior of glasses was attributed to the vanishing of an equilibrium order parameter, and larger and larger regions were involved in an elementary relaxation process.

The critical phenomena approach to the glass transition was not ignored in the following years. There have been a variety of approaches attempting to explain the diverging viscosity and slow growth of correlations in terms of an underlying phase transition. To mention a few, Kléman has a theory of interacting line dislocations,[20] Safran has a theory of competing polymorphic phases,[21] Kirkpatrick, Thirumalai, and Wolynes have a replica mode-coupling theory,[22] Palmer and Stein have a first-order renormalization-group theory,[23] and Goldbart and Goldenfeld have a glassy theory of rubberization.[24] We find some of these ideas appealing on theoretical and experimental grounds, but in this paper we try to discuss scaling behavior motivated by experimental data, independent of any detailed mechanism. Souletie[25] has recently proposed an alternative scaling analysis, based on traditional power-law critical-slowing-down rather than thermally activated transitions. We discuss in Sec. II our experimental reasons for believing in thermal activation, although clearly the dust remains unsettled.

In Sec. II, we summarize both old and new experimental work on the glass transition, and interpret it within our theoretical framework. We discuss in detail the recent work on $FeEr_2H_{3.4}$ by Fecht, Fu, and Johnson,[14] which managed to show a cusp in the specific heat by raising the temperature of a complex crystalline phase until it became amorphous. We interpret their experiment as having approached our proposed second-order transition from below. We argue (with hindsight) that heating from the solid phase can allow the transition to be approached much more effectively than cooling from the liquid side. We discuss the diverging viscosity in the supercooled liquid, the range of behaviors found in various systems (from strong to fragile), and recent work by Dixon *et al.*[15] showing that the diverging relaxation times do not cross over back to an Arrhenius law. Our theory is that the supercooled liquid is approaching a second-order transition into a solid phase, perhaps a crystalline or quasicrystalline phase. This new critical point is unusual mostly in that the dynamics is apparently not diffusive (time scales diverging with power laws near T_0) but rather is activated (with exponentially diverging time scales because of diverging barrier heights).

In Sec. III we *outline* a renormalization-group (RG) framework for understanding the glass transition. Within the framework of second-order phase transitions we have attempted to form the simplest theory which is compatible with the observed behavior. We begin by reviewing the ordinary RG description of the *ordered* phase. Flipping the magnetization in a low-temperature ferromagnet, for example, demands crossing an energy barrier which diverges in the thermodynamic limit: the zero-temperature RG fixed point describing the ferromagnetic phase has singular dynamics. We propose that the glass transition can be understood as a finite-temperature transition dominated by a zero-temperature RG critical point. Just as in the ordered phase of a ferromagnet, thermal fluctuations are less and less important as the lengths get longer, and barrier heights diverge as the correlation length grows.

II. SCALING NEAR THE GLASS TRANSITION

A large variety of liquids will form glasses when cooled quickly enough to avoid crystallization.[26] Covalent glasses (windows), polymer glasses (Plexiglass), metallic glasses quenched on rotating copper drums, and organic molecular glasses (hard candy) all share the same behavior on cooling from the melt: The viscosity diverges rapidly, the material falls out of equilibrium and freezes into a molecular configuration typical of the supercooled liquid.[27]

Our work on this problem in the past few years[16] has been based upon the assumption that there is a common explanation for these translations, and that the glass transition reflects an underlying second-order phase transition from the liquid to some rigid phase. Last April, Fig. 1 appeared in the literature: Fecht, Fu, and Johnson[14] had measured a cusp in the specific heat on heating from a crystal to an amorphous, glassy state. The classic signature of second-order phase transitions are cusps (power-law or logarithmic singularities) in the specific heat, susceptibility, or other thermodynamic functions. The experimentalists convincingly associated the cusp with the destruction of the crystalline Bragg peaks.

Our interpretation of this experiment is, of course, not the only one. Fecht, Fu, and Johnson interpret it as a transition between a crystal and an ideal glass state. We interpret the high temperature phase as a sluggish liquid. A stronger objection is that the whole connection with the glass transition may be missing. The system could become amorphous through a simple instability of the complex crystalline configuration, rather than a competition between entropy and energy. The peak could be a perversely smeared first-order transition. The rapid increasing partial pressure of hydrogen could be dynamically disordering the system (the constant-concentration sample shown in Fig. 1 apparently blew up somewhere near where the data ends). Finally, one must note that it is suspicious that a similar specific heat cusp has not been seen in other materials.

More experimental work is needed, but this data clearly provides tentative support for our assumption of a second-order transition, at least for Fe_2ErH_x. Why is it such a surprise? Consider Fig. 2, a tabulation of specific heats measured on *cooling* through the glass transition.[28] On the one hand, one can see that the specific heat drops substantially as each material falls out of equilibrium. As the molecular configurations freeze in, the contribution to the specific heat from their rearrangements disappears, and the specific heat falls to roughly that of a crystal. On the other hand, there is no indication of a cusp or singularity in the specific heats in Fig. 2.[29] Until Fecht, Fu, and Johnson there has been little convincing indication of static critical fluctuations in any glass transition: no diverging length scales and no power laws.

We suggest in this paper that the critical point underlying the glass transition is a second-order melting transition of a rigid phase, crystal or quasicrystal. Figure 3 shows our proposed phase diagram, where the vertical axis represents increasing temperature T and the horizontal axis represents the increase of a second control parameter F. The parameter F might represent a tunable frustration in a theoretical model; it represents hydrogen concentration in Fe_2ErH_x.

There is an argument due to Landau[30] that transitions from liquids to crystals should be first order. The argument starts by generating a Taylor expansion for the coarse-grained free energy of the system, and continues by showing that a third-order term in the amplitude of the crystalline order is allowed by symmetry. This leads immediately to a temperature range in which local minima in the free energy exist with both liquid and crystalline order: a first-order transition. However, Landau's argument ignores the possible importance of fluctuations. Thermal fluctuations will be important on short length scales; the effective free energy at long length scales can be renormalized in singular ways by the short length fluctuations. Indeed, the Landau criterion is known to break down in several models.

In particular, crystalline melting in two dimensions is thought, like Fig. 3, to have both a first-order and a continuous region. The continuous melting transition

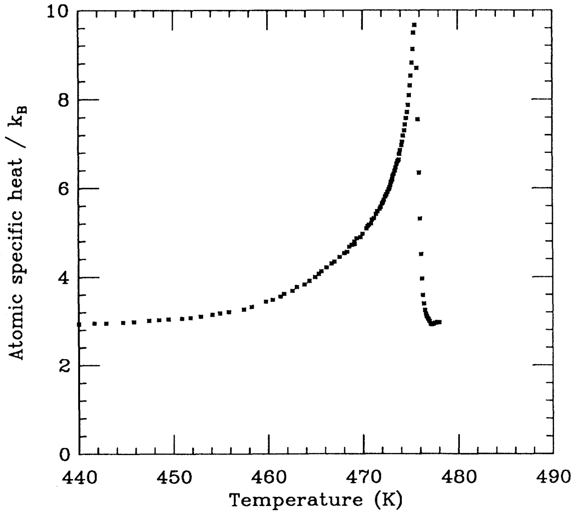

FIG. 1. The specific heat of $Fe_2ErH_{3.4}$ measured on heating, during the transition from a crystal to a glass, from Fecht, Fu, and Johnson (Ref. 14). The Laves phase Fe_2Er crystal was doped with hydrogen and then heated at a scanning rate of 20 K/min. On cooling, the transition is "kinetically sluggish" and smeared. The peak can be shifted down 5 K by preannealing.

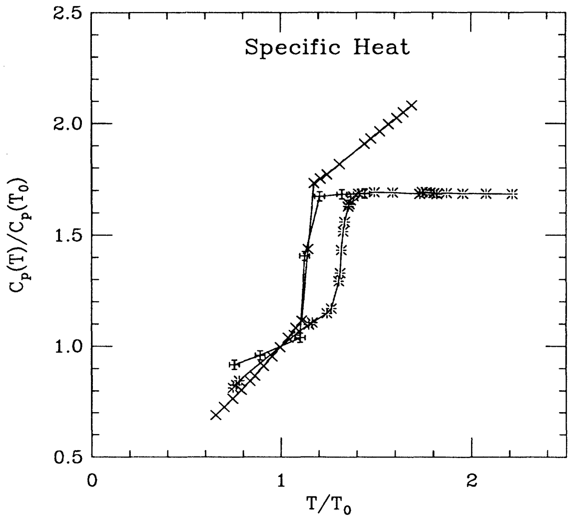

FIG. 2. The specific heat, measured on cooling, shows little indication of an impending second-order phase transition. Here is compiled the specific heats for a few glass-forming materials, measured on cooling. The horizontal axis is in units of T_0, the temperature at which the viscosity diverges in the Vogel-Fulcher fit. The vertical axis gives the specific heat scaled by its value at T_0. ✳ : B_2O_3. + : $0.6KNO_3-0.4Ca(NO_3)_2$. ×: *o*-Terphenyl. The breaks in the curves occur when the materials fall out of equilibrium; SiO_2 (not shown) falls out of equilibrium around $T/T_0=5.4$ (Ref. 28).

proceeds in two stages, with an intermediate hexatic phase.[31] The control parameter corresponding to F for two-dimensional (2D) melting is the core energy of the defects mediating the transition.[32] The transitions are in the Kosterlitz-Thouless universality class, and have rather unusual critical properties. Two dimensions teaches us that continuous melting is possible; however, it also reminds us that the simplest scenario is not always the correct one. Nonetheless, in this paper, we confine ourselves to the simplest picture.

While the static behavior of a glass may not show critical fluctuations when cooled through the glass transition, the dynamic behavior is striking. The most obvious property about liquids as they cool into glasses is the dramatic rise in their viscosities. Figure 4 shows the viscosity of a variety of glass-forming liquids.[28] Notice first the 17 order-of-magnitude vertical scale: the viscosity is growing exponentially as we reduce the temperature. This diverging viscosity is characteristic of glass-forming liquids. Seen another way, it is because the relaxation in these liquids becomes so sluggish that they fall out of equilibrium and form glasses.

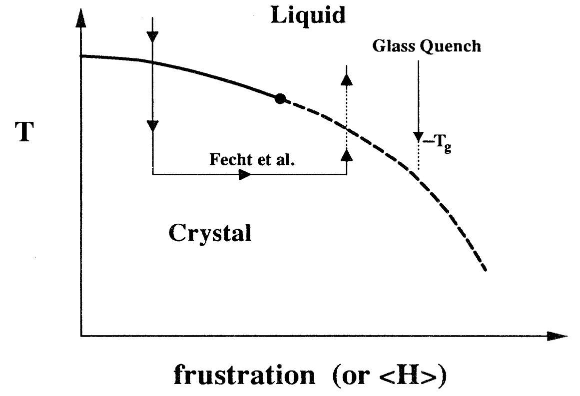

FIG. 3. Proposed phase diagram for glass-forming materials. The vertical axis is temperature; the horizontal axis represents some parameter which varies the frustration in the material (hydrogen concentration for Fecht, Fu, and Johnson, Ref. 14). The solid boundary between the crystal and liquid phases represents an ordinary first-order transition line. The dashed boundary represents a hypothetical second-order crystal-liquid transition line. The dynamics in these materials should be exponentially slow as the transition is approached. Approaching the transition from above (glass quench) inevitably leads to the system falling out of equilibrium at rather short correlation lengths, thus forming a glass rather than a crystal or a quasicrystal. We believe that Fecht, Fu, and Johnson managed to approach the transition from below; the dynamics is also sluggish, but the liquid phase must eventually be formed. Note that the "crystalline" low-temperature phase depicted here probably is unrelated to the simple equilibrium crystal phase formed at high temperatures if the system is not supercooled. We imagine the transition is to a complex crystalline or quasicrystalline phase, and that the simple crystal is dynamically inaccessible and unimportant to the glassy behavior.

The natural explanation for exponential dependence on temperature is activated transport. Figure 4 is an Arrhenius plot, for which thermally activated relaxation $\eta \propto e^{E/kT}$ leads to a straight line. Silicon dioxide does, indeed, form a straight line; however, the other materials clearly form a continuous family of glass-forming liquids with increasing curvature. The most straightforward interpretation of this curvature is that the barrier $E(T)$ is growing as the temperature decreases.[35] This interpretation is supported by the behavior of the viscosity after the liquid falls out of equilibrium (most easily measured by increasing the cooling rate). The viscosity of a rapidly cooled liquid falls below its equilibrium form and straightens on the Arrhenius plot, consistent with a barrier height which freezes in when the liquid falls out of equilibrium. In addition, it is thought that this low-temperature slope on the Arrhenius plot for the glass grows steeper with decreasing cooling rate, indicating that the barriers of the equilibrium fluid are growing with decreasing temperature.[36]

Given that this picture is correct, an obvious question to ask is how large the barriers are where the system falls out of equilibrium near T_g. It is an easy exercise to show that the energy barrier at a temperature T is given by

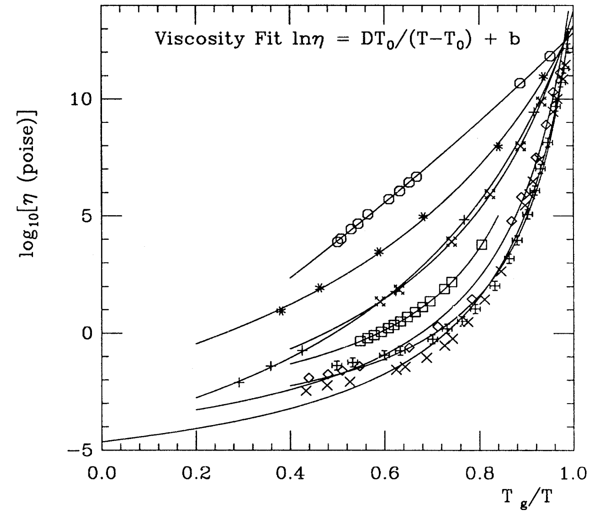

FIG. 4. Viscosity η, in poise, for liquids above the glass transition (Ref. 28). The vertical axis is $\log_{10}(\eta)$; the glass transition T_g on the right is defined as the temperature at which the viscosity equals 10^{13} poise (at which point it takes 2.5 h for an artifically strained liquid to relax to 10% of the strain) (Ref. 33). The solid lines are fits to the Vogel-Fulcher law in the form $\ln(\eta) = DT_0/(T-T_0)+b$. ○ : SiO_2, $T_g/T_0=5.4$. * : $Na_2O-2SiO_2$, $T_g/T_0=1.63$. +: Propanol, $T_g/T_0=1.44$. ⊠ : $CaAl_2Si_2O_8$, $T_g/T_0=1.32$. ☐: $69ZnCl_2 \cdot 31PyHCl$, $T_g/T_0=1.08$. ◇: Propylene carbonate, $T_g/T_0=1.14$. ⊞ : $0.6KNO_3-0.4Ca(NO_3)_2$, $T_g/T_0=1.10$. ×: *o*-terphenyl, $T_g/T_0=1.14$. The materials like *o*-terphenyl with large curvatures on this plot are characterized in the literature as "fragile," the materials like vitreous silica SiO_2 with nearly Arrhenous behavior are called "strong." (Ref. 34).

$$E(T)=k_B T\{\ln[\eta(T)]-\ln[\eta(T=\infty)]\} .$$

If we examine the ratio of the energy barriers at T_g to those at $T=\infty$, we discover that even for the materials like *o*-terphenyl which show the most curvature in Fig. 4, the barriers have increased by the rather modest factor of about 5 or 6. Thus, the barriers, though increasing, have not gotten very large.

Viscosities of glass-forming liquids are usually fit phenomenologically to the Vogel-Fulcher[37] form,[38] which corresponds[39] to

$$E_{\rm vf}(T)=DT_0\left|\frac{T-T_0}{T}\right|^{-1} . \tag{1}$$

Here D is a dimensionless parameter which characterizes the curvature of the Arrhenius plot; D in Fig. 4 varies from 164 (for SiO_2) to 4.3 [for $0.6KNO_3-0.4Ca(NO_3)_2$]. If we identify T_0 with an underlying critical point, we discover that we never get very close to it: reduced temperatures $(T_g-T_0)/T_g$ vary from 0.8 to 0.07. Good experiments on traditional second-order phase transitions must span several decades of reduced temperature (e.g., $10^{-1}-10^{-4}$). Thus it is not surprising that compelling evidence for compelling evidence for critical fluctuations and diverging length scales have (until Fecht, Fu, and Johnson[14]) never been seen in glasses: the atoms get frozen into position far from the critical point while the correlation length is still short.

Properties with power-law singularities are typical of second-order phase transitions. In ordinary dynamical critical phenomena, the time scale diverges with a critical exponent z:

$$\tau\simeq\tau_0\left|\frac{T-T_0}{T}\right|^{-z} . \tag{2}$$

The critical exponent is universal, but the prefactor τ_0 depends on the material. The Vogel-Fulcher law form for the barrier heights (1) has the same properties: the prefactor D depends upon the material, while the exponent is assumed to be universally -1. The time-scale divergence for ordinary critical points is weak enough that experimentalists with patience can keep their systems in equilibrium until quite large correlations have developed; the divergence at the glass transition makes patience irrelevant.

Have phase transitions with diverging barrier heights been studied in the past? Not until recently. There are two reasons for this: one theoretical and one practical. Theoretically, "ordinary" renormalization-group fixed points do not allow the energies to be singular. It is the singular part of the free energy which is assumed to reach a fixed point as the system is coarse grained: other quantities will diverge, but the free energy contained in a correlated region will reach a scaling limit of order $k_B T$. This results in the hyperscaling exponent relation, which will be discussed in more detail in the next section. Hyperscaling is indeed a typical feature of most known transitions, but it is violated, for example, by the Ising model in spatial dimensions greater than four. Systems which violate hyperscaling are awkward to discuss theoretically; one must introduce singular scaling functions and "dangerous irrelevant variables."[40] (It is also possible that our transition might obey hyperscaling for equilibrium energy fluctuations, but that the barriers to relaxation might diverge.[41])

The practical reason these transitions have not been studied is that phase transitions with diverging barrier heights are almost impossible to observe. Diverging barriers have cropped up in the study of randomly disordered systems, in particular in the random-field Ising model.[42,43] The random-field Ising model had such slow relaxation that a rigorous proof[44] was necessary to convince some investigators that the ground state in three dimensions was ferromagnetic. The anthropic principle in cosmology states that universes whose fundamental constants are incompatible with intelligent life never get studied. The same principle appears to apply to critical phenomena. Phase transitions with diverging barrier heights have exponentially slow relaxation; in any experiment on human time scales they fall out of equilibrium far above their critical points into glassy states. Thus, most recognized phase transitions have nonsingular barriers to relaxation.

There is no particular reason to believe that the critical exponent for the divergence of barrier heights in glasses is -1 [assumed in the Vogel-Fulcher law (1)]. In the renormalization-group analysis of the next section, we will show that this exponent should have a universal value: $E(T)\simeq|(T-T_0)/T|^{-\theta\nu}$, independent of material. In Fig. 5 we replot the viscosity data on a scale which

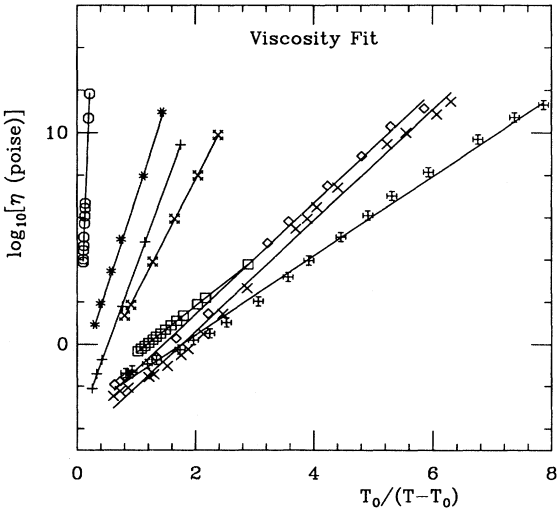

FIG. 5. The viscosity data of Fig. 4 replotted here with a different x axis, to test the assumption that the barrier height scales with reduced temperature with the exponent $-\theta\nu=-1$. The straight lines are fits by the Vogel-Fulcher form $\ln(\eta)=DT_0/(T-T_0)+b$. One can notice in the lowest two curves (× and ⊕) that the data systematically oscillates around the best fit.

makes the dependence (1) into a straight line. There seems a hint of a systematic bias in the bottom two curves (which get closest to the critical point); the deviations suggest higher critical exponents and even lower transition temperatures. The fits, however, appear good, and one should hesitate to draw any strong conclusions using data so far from the critical point.

One imagines that the underlying critical point might be at zero temperature. In Fig. 6 we attempt to fit the data allowing a variable critical exponent but forcing the transition temperature to zero. The necessary critical exponents range from one to eight. While it is not impossible that we have many universality classes, $T_0=0$ seems an unpromising direction for exploration.

If the relaxation near the glass transition is so sluggish, how do we explain the observed cusp in the specific heat of Fecht, Fu, and Johnson shown in Fig. 1? Surely they should have fallen out of equilibrium as well. Most second-order phase transitions show critical fluctuations that are rather symmetric around T_c. Why is heating better than cooling in the approach to the glass transition?

Fecht, Fu, and Johnson are indeed far out of equilibrium at their measured T_c. Their measured cusp is not an equilibrium measurement of the specific heat. It is not reversible; on cooling, the transition is "kinetically sluggish and smeared over the entire temperature range."[14] Of course if this had not happened it wouldn't have been a glass. More important, on annealing just below T_c (measured), cooling to room temperature, and reheating, the cusp reappears at a new temperature shifted downward by 5 K. Equilibrium phase transitions are by definition not history dependent. However, out of equilibrium does not mean unimportant: their measurement clearly indicates strong fluctuation precursors in the crystalline phase. Such precursors are not observed in ordinary first-order melting, even if the crystal is superheated.

Why is heating from the crystal better than cooling from the melt? The key difference is that the system must eventually melt on heating, but need not ever crystallize on cooling. More formally, the high temperature phase has no broken symmetry: all liquidlike fluctuations in the crystalline phase can join smoothly into the final liquid phase. The crystalline phase has both broken translational symmetry and broken rotational symmetry. Various crystalline fluctuations in the liquid will need to reorient to join into a single crystal (Fig. 7).

The picture we are presenting, of crystalline fluctuations freezing into a glass, demands an immediate defense on three fronts. First, microcrystalline models for glasses

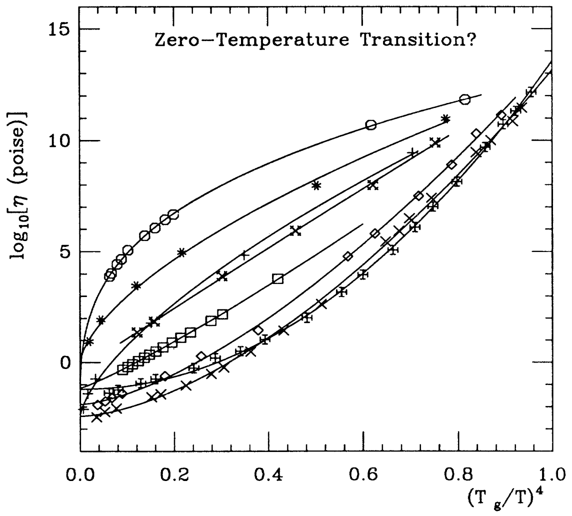

FIG. 6. The viscosity data of Fig. 4 replotted here with a different x axis, to test whether a critical point underlying the glass transition might occur at $T_0=0$. Given the limited range of temperatures and the distance from the critical point, the viscosity data for each material can be fit by a power law $\ln\eta \propto A+C/T^B$. $B=4$ would be a straight line on this plot. The exponents range from one to eight, as shown by the upward and downward curvatures on this plot. It would seem that a nonzero critical temperature is indicated.

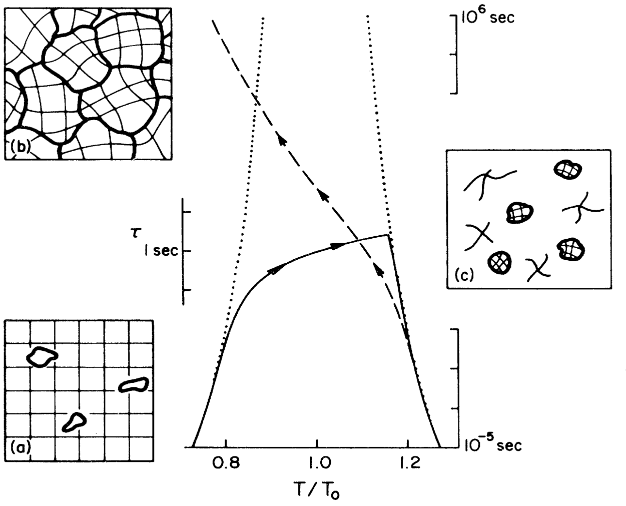

FIG. 7. Relaxation times around the glass transition, as given by the primitive fictive temperature model described in the text. The dotted curve shows the equilibrium relaxation times for the fictive temperature model. The equilibrium relaxation in the rigid phase involves only small fluctuating regions inside a system with long-range order, as illustrated by the first inset (a). The solid curve gives the relaxation times on heating: there is a lag, but eventually the system must melt into the uniform liquid phase with only small regions of local order [inset (c)]. The dashed curve shows the relaxation times on cooling. As shown by inset (b), our picture of the glass is one of small domains with various broken symmetries. The barriers to relaxation are those needed to reorient these domains to match one another. They are given not by the equilibrium properties at the current temperature, but rather by the barrier heights at the temperature T_F at which the system fell out of equilibrium. The net result is that heating from the crystal takes us from equilibrium state (a) to equilibrium state (c), but cooling from the melt takes us from (c) to the nonequilibrium glassy state (b).

were abandoned years ago on structural grounds.[45] At least for network glasses, any microcrystals would have to be rather small and strained to be compatible with the structural probes. Indeed, the simple network glasses are typically "strong" (Fig. 4), falling out of equilibrium particularly far from the transition where their correlation lengths ought to be on atomic length scales. We are not proposing microcrystals as a practical structural description; indeed, we would not dignify our tiny correlated regions with the term. Our emphasis is not on structure, but on finding the underlying explanation for the transition.

Second, although second-order phase transitions suffer critical slowing down near T_c, they often speed up again in the low-temperature broken symmetry phase. The various broken symmetry regions coarsen into larger and larger clusters. This coarsening process can be fairly sluggish, but is certainly not compatible with the extremely sluggish relaxation in glasses.[46] In the traditional system, there are no barriers which diverge with the coarsening length scale in the low-temperature phase: the power-law growth of the length scale with time is controlled by the diffusive motion of interfaces. It is thought in spin glasses[47] that the dynamics in the low-temperature phase has barriers which diverge with the length scale. We have results[48] indicating that similar diverging barriers also occur during domain coarsening in the low-temperature phase of the Ising model with weak antiferromagnetic second-neighbor interactions. We believe that the low-temperature phases of many models—including glasses—will show such sluggish coarsening. (We discuss the singular dynamics of the low-temperature phase more fully in the next section.) Thus the dynamics can stay slow even at temperatures well below the transition temperature.

Third, first-order transitions have broken orientational symmetries, but large single crystals can be grown. Why is the low-temperature phase in glasses so much more elusive? At a first-order transition, large single crystals are typically grown by placing a small seed crystal inside a supercooled melt. This method depends completely on the nucleation and growth patterns typical of first-order transitions: fluctuations in the melt are rare, so by having only one crystalline nucleus later reorientations are avoided. Indeed, if one quenches through a first-order transition, one does get microcrystalline patterns which do not coarsen substantially after they are formed.[49]

Let us return now to the experiment. How can we test our ideas of diverging barrier heights and broken symmetries against the data in Fig. 1? Unfortunately, we do not have a statistical mechanical model for the glass transition yet. We would be delighted to have a model with many degrees of freedom exhibiting a phase transition with diverging barrier heights, to compare with the experiment. For now, we can only see if the crude picture is applicable, placing the ingredients in by hand.

We are inspired by the partial success of the fictive temperature theories of glassy behavior.[50] In these theories, the properties of the glass are described as the equilibrium properties of the liquid at a temperature T_F, roughly where the melt fell out of equilibrium. The complicated behavior under annealing and under various external conditions during the quench are presumed to be described as shifts in this single parameter. While this is surely not correct, it does capture some of the behavior rather well.

In our approach, T_F will describe the critical properties both on heating and on cooling: $T_F < T_0 < T$ will describe a superheated crystalline system,[51] while $T < T_0 < T_F$ will describe a glass. T_F will lag behind the real temperature T, and will drift toward T with a rate constant which is thermally activated over a barrier $E(T, T_F)$:

$$\dot{T}_F = \gamma_0 e^{-E(T,T_F)/k_B T}(T - T_F) \ . \tag{3}$$

In equilibrium, the barrier height to relaxation $E_{\text{eq}}(T)$ will diverge at a critical point T_0. We assume a Vogel-Fulcher form (1):

$$E_{\text{eq}}(T) \simeq D T_0 \left| \frac{T - T_0}{T} \right|^{-1}$$

on both sides of the transition.[52] The actual barrier height to relaxation depends on the current nonequilibrium structure (represented by T_F) as well as the equilibrium structure for the current temperature T.[53] Here is where the asymmetry between the two phases comes in. In the low-temperature glass where $T < T_F$, relaxation can only occur if regions of size given by T_F can reorient: the barrier is

$$E(T, T_F) = E_{\text{eq}}(T_F), \quad T < T_F \ .$$

In the superheated crystal, local regions can melt whenever they are bigger either than the equilibrium or the fictive correlation length, so

$$E(T, T_F) = \min(E_{\text{eq}}(T), E_{\text{eq}}(T_F)), \quad T > T_F \ .$$

Thus when the temperature happens to be near T_0, but the fictive temperature has been left at a lower temperature, the local melted regions are still small, and the barrier is given by $E_{\text{eq}}(T_F)$. When the fictive temperature is near T_0 but the real temperature is much higher, the large correlated regions need not cooperate to melt, as smaller domains can melt independently, and the barrier is given by $E_{\text{eq}}(T)$.

Finally, we need to introduce the equilibrium specific heat by hand. It will have a component $c_{\text{vibrational}}$ which is unrelated to the glass transition, and a singular piece with the form

$$c_{\text{eq}}(T) = \begin{cases} A \left[\dfrac{T - T_0}{T_0} \right]^{-\alpha} + B, & T > T_0 \ , \\[2ex] A' \left| \dfrac{T - T_0}{T_0} \right|^{-\alpha} + B', & T < T_0 \ . \end{cases}$$

This form is standard in critical phenomena; the exponent α and the amplitude ratio A'/A are universal (independent of which material is undergoing the phase transition).[54] We follow Fecht, Fu, and Johnson in using a logarithm, which is formally given as the limit $\alpha \to 0$. [Thus for $T > T_0$, we write $c_{\text{eq}}(T) = -A \ln|(T-T_0)/T_0| + B$.] In the spirit of the fictive temperature approximation, the singular part of the specific heat will enter and leave the sample not as the temperature changes, but as the fictive temperature changes. The measured specific heat is the rate of energy flow per unit temperature, which thus is given by

$$c_{\text{measured}}(T) = c_{\text{eq}}(T_F)(\dot{T}_F/\dot{T}) + c_{\text{vibrational}} .$$

This will obviously force a cusp when $T_F = T_0$ on heating; in real systems, the buildup of large-scale sluggish fluctuations will be cut off as the system melts locally, and the cusp will be rounded.

What do we learn from this exercise (Fig. 8)? First, it illustrates the asymmetry between heating and cooling: one never reaches the transition when cooling, while on heating one does melt, albeit at an elevated temperature. Second, the measured singular contribution to the specific heat on cooling (multiplied by 10 in Fig. 8) is small. The system falls out of equilibrium long before the transition: there is a drop in the specific heat on cooling, but no visible cusp. The exercise thus reconciles us to the differences between Figs. 1 and 2. Measured on heating, we expect a cusp as the crystal melts; measured on cooling, we expect a drop without a cusp.

In the next section we sketch a proposed renormalization-group description of the critical point underlying the glass transition.

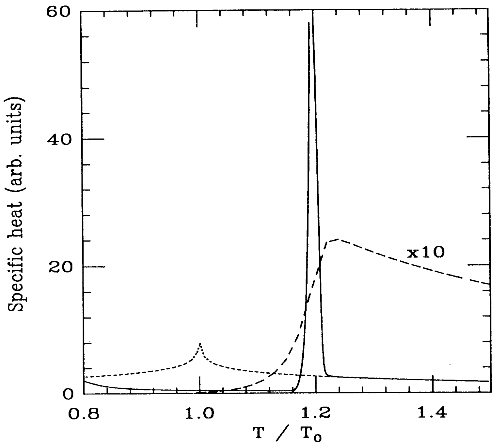

FIG. 8. "Specific heat," for the one-parameter fictive temperature model described in the text. The dotted curve is the equilibrium specific heat [Eq. (3)]. The dashed curve is the predicted specific heat on cooling; the system becomes trapped at a fictive temperature $T_F = 1.17T_0$ and no cusp is observed. The solid curve is that predicted on heating at a dimensionless rate of $\gamma/\gamma_0 = 10^{-13}$; the cusp is larger and narrower than the equilibrium one and is shifted upward in temperature to T_c (measured) $= 1.19T_0$. The parameters were chosen arbitrarily as $D = 5$, $\omega_0 = 10^{13}$, $\alpha = 0$ (log), and $A = A' = B = B' = 1$. Only the singular (configurational) part of the specific heat is plotted: there will be a vibrational background which remains in equilibrium and does not depend on $\dot{T}_F/\dot{T}$.

III. TOWARD A THEORY OF THE GLASS TRANSITION

Suppose that we accept that the nonequilibrium formation of glasses reflects an underlying equilibrium second-order phase transition. We now should search for a tractable model that describes the universal features of the glass transition. What properties should this model have? Two properties are self-evident.

(1) No disorder. Much progress has been made in the study of systems with externally imposed disorder. Localization in doped semiconductors is a good example: the dopant atoms are implanted at random, and the conductivity depends on the competition between hopping and a fixed impurity potential. Glasses have no disorder in their Hamiltonians: the disorder is frozen in as the system falls out of equilibrium. Many disordered systems have "glass transitions" as some parameter is varied: spin glasses and random-field models freeze as the temperature is lowered, charge-density waves stop sliding as the external field is lowered, disordered electrons stop conducting as the Fermi energy is lowered through the mobility edge, and networks fall apart as the fraction of bonds is lowered through the percolation threshold. These thresholds, although superficially sharing many features with the glass transition, are all driven by an external disordering field. We must find a different mechanism for real glasses.

(2) Small correlation lengths. Glasses fall out of equilibrium quickly. While there have been occasional reports of glass experiments showing intermediate-range correlations, the distinctive property of glasses is that their structures look much like the supercooled liquid.[55] Thus if the equilibrium theory involves diverging correlation lengths, it must also provide a qualitative explanation of why the correlation length in glasses never grows to observable size when cooled on laboratory time scales. A useful theory of glasses will also need to deal with the fall from equilibrium and the history-dependent properties.[5,6]

Two necessary features of the eventual model were extracted from experimental evidence, as presented in the last section.

(3) Growing barriers to relaxation. The relaxation times in glasses (as measured by ultrasonic attenuation, dielectric loss, viscosity, and specific heat) change by over 14 orders of magnitude within a factor of 2 in temperature (Fig. 4). As noted in the last section, this is naturally attributed to thermal activation, except that the barriers to relaxation are growing as the temperature is lowered. In ordinary critical phenomena, just as there is only one diverging length scale, there is only one energy scale—the temperature. There is something different about the critical point in glasses that allows an energy scale to diverge at the critical temperature.

(4) Phase transition at a nonzero temperature. As shown in Fig. 6, the experimental data is not consistent with a divergence with a critical temperature of $T_0 = 0$.

Finally, there is a feature which has been central to theoretical approaches to metallic glasses[56,57] and other glassy materials[58,59] in the past decade and a half.

(5) Frustration. Frustrated systems have local low-

energy structures which cannot be fit together to fill space. The classic example is fivefold symmetry.[60] Figure 9(a) shows a hypothetical two-dimensional liquid where fivefold rings are energetically favored. At the temperature shown, the dark rings are to be considered energetically quite stable. The bulk of the material remains disordered because the existing fivefold rings interfere with the formation of new ones. The frustration is embodied in the fact that no arrangement of atoms allows all bonds to be part of fivefold rings.

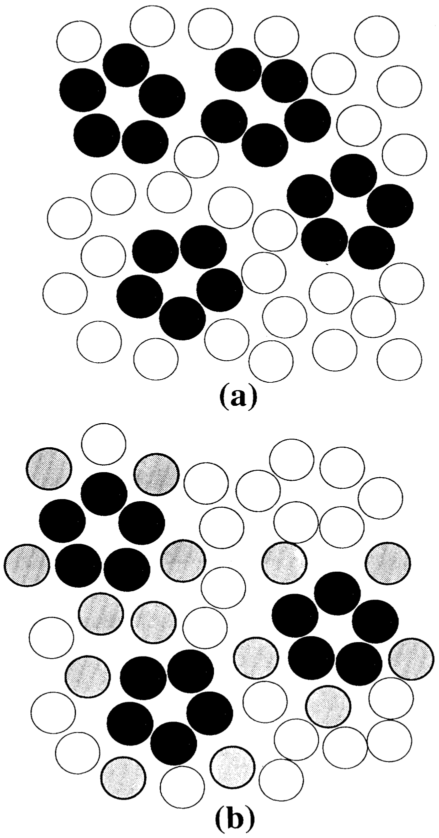

FIG. 9. (a) Sketch of the traditional picture of frustration in glass formation. In this two-dimensional representation, the glass is trying to form fivefold symmetric structure. Atoms in low-energy local configurations are drawn more darkly. Because the low-energy local structure cannot be repeated over all space, strains build up, inhibiting the growth of the local structures. This does not prevent these tightly ordered regions from gaining energy by grouping into larger clusters. The frustration means, however, that there will be less energy gained by increasing the size of an ordered region. This means the outermost atoms are held more loosely, and thus that the interactions between the ordered regions become smaller. The system can continue to order by forming larger associations of more and more weakly interacting regions. (b) Our picture of the same local region as in (a), after the correlation length has doubled. Notice the central upper fivefold cluster in (a) had to be disrupted in order to allow the other three regions to associate more closely. Since this cluster was initially tightly ordered, we imagine that destroying it necessarily involves an energy cost. That is, while there is a net gain in energy in going from (a) to (b), there is a necessary intermediate configuration in which the tightly ordered cluster energy is lost and the longer-range ordering energy has not yet been regained. Furthermore, as the correlation length increases, the size of the ordered regions which must be destroyed becomes larger and so the barrier heights increase.

There are a number of models which have several of the above properties. The Frenkel-Kontorova model in one dimension[61] and the XY model in two dimensions,[62] when incommensurately frustrated, have short correlation lengths when cooled at a finite rate; however, they have their critical points at $T_0=0$. (For the Frenkel-Kontorova model, the correlation ξ grows with decreasing cooling rate γ only as $\xi \simeq \ln[\ln(1/\gamma)]$. This incredibly slow growth is a result of the fact that the energies of the equilibrium defects present at a given correlation length get very small as the correlation length increases, while the energy barriers to relaxation remain roughly fixed.[61] Such a separation of energy scales between equilibrium energy differences and energy barriers is a crucial ingredient in our picture of glasses.) The three-dimensional random-field Ising model has frustration, a small correlation length, diverging barriers to relaxation, and a nonzero phase transition to an ordered ferromagnetic state; however, it has externally imposed disorder.

One must note that frustrated spin models without randomness have been extensively studied[63] and, apart from our recent work to be discussed below, none have shown glassy dynamics or diverging barriers to relaxation. We believe this is because these models, although frustrated at the microscopic level, lose this frustration upon coarse graining: After the local degrees of freedom work out their uneasy compromise, the blocks assemble happily into regular structures. Frustrated one-dimensional continuum models[64] have shown glassy behavior in their low-energy excitations, but no extremely long time scales have been reported. To understand glasses we propose to look for models closer in spirit to the inflation models of quasicrystals, where the frustration is maintained (albeit renormalized) when the system is inflated.

We have recently[48] found a very simple frustrated spin model—the three-dimensional Ising model on a cubic lattice with added weak antiferromagnetic next-nearest-neighbor bonds—which does exhibit glassy dynamics due to energy barriers that diverge with length scale. This system still differs from our picture of a glass in that the slow dynamics do not occur as one approaches a critical point and the diverging length scale is not the equilibrium correlation length. Rather, they occur only when the system is far out of equilibrium, during the coarsening process, and the diverging length scale is the characteristic size of the domains in this coarsening system. Specifically, we find that the size of the ordered domains increases only logarithmically in time during the coarsening process following a quench from high to low temperatures, provided the final temperature is below a "corner-rounding" temperature which is proportional to the amount of frustration (i.e., the strength of the next-nearest-neighbor bonds).

There are well established models for metallic glasses[56,65] which could have all of the above five properties. The physical origin of the frustration is the natural tendency for metallic liquids to form icosahedral local clusters. These icosahedral clusters cannot pack to fill space (quasicrystals have at least two different local clusters). The frustration can be neatly parametrized by a *curvature:* the atoms would pack into a regular Euclidean solid on the surface of a hypersphere in four dimensions of the appropriate curvature. Substantial progress has been made in describing the local order in metallic glasses using these ideas.[66] Nonetheless, their glass transitions, remain intractible (see, however, Ref. 67). Related ideas[58] have been proposed for tetrahedrally bonded amorphous semiconductors, again with the curvature as the controlling frustration. What connection one can draw with the Laves phase Fe_2ErH_x,[14] apart from complexity, is yet to be seen.

Frustration can provide, at least on a qualitative level, an explanation for the diverging barriers to relaxation. Figure 9(b) shows the same system as Fig. 9(a), at a lower temperature where the correlated regions have grown to roughly double their original volume. Notice that the ordering is necessarily inhomogeneous, with tightly knit low-energy clusters interacting weakly with one another. The growth of three of the dark regions in Fig. 9(a) demanded that the fourth, in the upper center, be dismantled. The net energy gain presumably occurs after an initial cost for breaking up the low-energy cluster. More formally, since the energy density is inhomogeneous, the domain walls between regions of different broken symmetries will be pinned in the low-energy "defective" regions. As the correlated regions become larger and better ordered, the barriers to dismantling them (or to sweeping domain walls across them) will diverge.

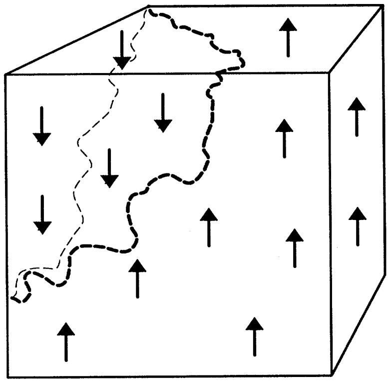

FIG. 10. Singular dynamics at the ordinary zero-temperature fixed point. This figure shows a finite-sized $L \times L \times L$ Ising model, attempting to make the transition from a mostly spin-up state to a mostly spin-down state. In the process, a domain wall of area at least $L \times L$ must form, costing free energy $\mathcal{F}(L) = \sigma(T)L^2$. Thus the dynamics of finite-sized Ising models involves crossing barrier heights which diverge with the length. In an infinite system, the well-known fact that the different broken symmetry states are mutually inaccessible is due precisely to this diverging barrier. When weak next-nearest-neighbor antiferromagnetic bonds are added to the Ising model, a similar diverging barrier exists even for flipping a finite cluster of up spins, of linear dimension L, embedded in a sea of down spins. Simulations show that this results in glassy coarsening when such a system is quenched (Ref. 48).

Barrier heights which diverge with diverging lengths are not new. Indeed, they form the basis of the field of phase transitions. Broken symmetries only occur in the thermodynamic limit: any finite-sized sample will eventually explore all possible states. Different broken symmetry phases become mutually inaccessible as the system size gets large. In Fig. 10 we see a finite-sized chunk of an Ising model, say with free boundary conditions. Below the ferromagnetic phase transition temperature T_c, the system will have two states of rather low free energy, consisting of mostly spin up, and mostly down. Because the system is finite, it will spend roughly half of its time in each of these two states. However, the transitions between these states will be rare. In particular, to go from up to down the system must pass through a state with nearly zero magnetization, which is most economically realized by having a domain wall halfway through the system. Below T_c, this domain wall has a surface-free energy per unit area $\sigma(T) > 0$. The barrier between the up and down states will diverge as $\sigma(T)L^2$ as $L \rightarrow \infty$. Transitions between these two states will occur with an activated time scale $\tau(T) \simeq \exp[\sigma(T)L^2/kT]$. Thus the transition rate goes to zero in a singular way as the length scale of the finite cluster goes to infinity. The singular dynamics we need to explain glasses is already present in every low-temperature broken-symmetry phase: we just need to find it at a critical point.

This example can be fleshed out into a renormalization-group picture.[68] Consider the renormalization-group flow diagram for the Ising model, shown schematically in Fig. 11. The space is meant to represent an infinite-dimensional Hamiltonian space of Ising-like models with various nth-neighbor interactions. The renormalization group is a transformation $\mathcal{R}$ of Hamiltonian space into itself, illustrated in Fig. 12. It replaces a Hamiltonian H acting on L^d sites with an effective Hamiltonian $\mathcal{R}(H)$ acting on $(L/2)^d$ coarse-grained "block" spins, each representing a 2^d block of old spins. Tracing over the internal degrees of freedom within each 2^d region introduces more complicated effective couplings between spins. The arrows in Fig. 11 represent the action of coarse graining, connecting H to $\mathcal{R}(H)$.

In Fig. 11 the vertical axis represents the temperature. (Equivalently, the Hamiltonians can be assumed all to be at a fixed temperature, and the vertical axis represents decreasing bond strength.) Hamiltonians in the upper region of the diagram are above their critical temperature, and are in the paramagnetic phase. On a local level, spins tend to be aligned, but this correlation quickly dies away with distance. The coarse-grained Hamiltonian $\mathcal{R}(H)$ has correlations that die away twice as quickly with distance, and is effectively at a higher temperature: the Hamiltonians in the upper region flow toward the infinite temperature, disordered, paramagnetic fixed point.

The horizontal curve in Fig. 11 represents the critical surface. A given Ising model will pass through its T_c when it crosses this surface. Points on the critical surface must be mapped onto one another by the renormalization-group transformation: if H is at T_c, then $\mathcal{R}(H)$ must be too. The fact that all Ising models have the same long-wavelength behavior near T_c stems from the existence of a critical fixed point, toward which the entire critical surface is attracted.[69] A Hamiltonian just above its critical temperature will be renormalized near to the critical fixed point before turning upward. There will be a range of coarse-grained length scales in which the system will have correlations which look much like those of the critical point. The scaling properties of the Ising transition can be deduced from the behavior of $\mathcal{R}$ near the critical fixed point. For example, the universal critical exponents are given by the eigenvalues of the linearization of $\mathcal{R}$ at that point.

The bottom region in Fig. 11 flows toward zero temperature. This is the region of most interest to us. An Ising model in equilibrium below T_c will have an average magnetization M, with local fluctuations whose range will decrease with decreasing temperature. Coarse graining this mottled pattern of up and down spins quickly converges to a uniform shade of grey. Thus thermal fluctuations are not important at long length scales in the low-temperature phase. The ferromagnetic phase, at all temperatures below T_c, is described by a zero-temperature fixed point, with no thermal fluctuations.

More specifically, as shown in Fig. 12, the effective coupling strength at low temperatures of two block spins in $\mathcal{R}(H)$ is four times larger than that for H. If we rescale the energies to keep the bond strengths fixed, this implies that the effective temperature decreases by a factor of 4. At the ferromagnetic zero-temperature fixed point, if we linearize $\mathcal{R}$, the eigenvalue corresponding to the temperature direction is $\lambda_T = \frac{1}{4}$. Thus near the zero-temperature fixed point, the characteristic time for flipping a $(2L)\times L\times L$ block, $\exp[\mathcal{F}(L,T)/T]$, must be equal (Fig. 12) to the time for flipping the coarse-grained $L\times(L/2)\times(L/2)$ system. The Hamiltonian for the coarse-grained system is the same as that for the original system (because we are near the fixed point), except that the effective temperature is down by a factor of 4. Thus the free-energy barrier $\mathcal{F}$ satisfies $\mathcal{F}(L/T)/T = \mathcal{F}(L/2,T/4)/(T/4)$. Repeating this argument, we find the barrier to flipping the domain approaches $L^{-\ln\lambda_T/\ln 2}\mathcal{F}(1,0)\propto L^2$. $\mathcal{F}(1,0)$ is the nearest-neighbor bond strength; thus the surface tension $\sigma(T)$ is given by the renormalized bond strength at the fixed point. The "universal" fact that the interfacial energies between up and down-spin regions scales with the area of contact L^2 thus can be deduced from the eigenvalue $\frac{1}{4}$ in the temperature direction at the fixed point.

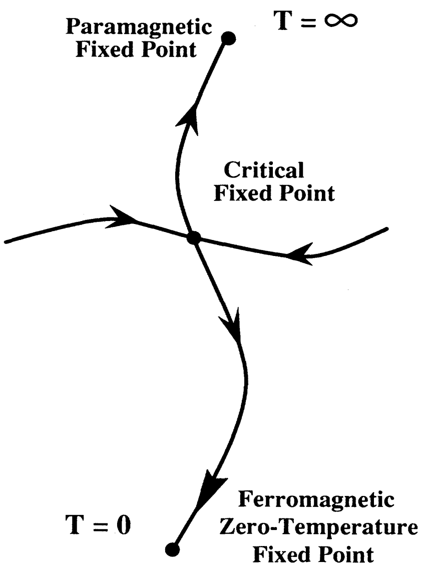

FIG. 11. The ordinary zero-temperature fixed point. This is the renormalization-group flow for a traditional critical point (e.g., for the Ising model in spatial dimensions greater than one). As we coarse grain to larger and larger length scales, systems initially below the critical temperature (the horizontal curve) scale toward the zero-temperature ordered fixed point (Ref. 69). This fixed point describes a uniformly ordered system without thermal fluctuations. The entire ordered phase is thus characterized by thermal fluctuations which only occur on short length scales. The ordered phase at finite temperature is described by the zero-temperature fixed point.

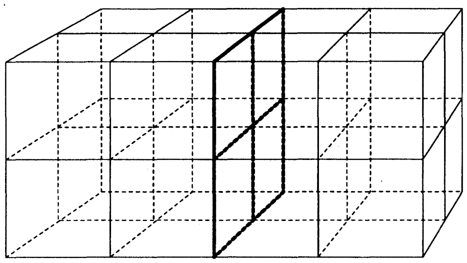

FIG. 12. Block-spin renormalization group. We can get a simple picture of the renormalization-group flows near the ordinary low-temperature fixed point by using Kadanoff's block-spin renormalization group. We want an effective coarse-grained Hamiltonian describing the energy of a domain wall in the ordered phase. Imagine clumping together groups of 2^d spins together and describing them as a single spin. If we are near the critical point, these clumps will have large fluctuations in their magnetizations, and the effective coupling between them will grow according to the renormalization-group flows near the critical fixed point shown in Fig. 11, with the effective temperature slowly decreasing. If we are at a low temperature, or have coarse grained to a low effective temperature, then the spins in our clump will mostly all be aligned with one another. The effective coupling between the clumps of spins will be 2^{d-1} times the coupling between the original spins, because that is the number of original bonds connecting the two clumps. This immediately predicts that the domain wall energy across a finite system of length L will scale as L^{d-1}. As discussed in the text, this can be interpreted either as a diverging coupling energy or, alternatively, as a decreasing effective temperature.

Returning to the singular dynamics in the ferromagnetic phase, we now have two equivalent descriptions. The first is activation over a diverging barrier: $\tau = \exp[E(L)/T]$, with $E(L)$ diverging as the length scale grows. The second is a description in terms of a length-dependent effective temperature: $\tau = \exp[E/T(L)]$, with the coarse-grained temperature going to zero as the length scale increases. Thus we see that energy barriers which diverge with length can happen in a renormalization group with a zero-temperature fixed point.[70]

What we need is a *phase transition,* not a low-temperature phase, with diverging barriers. The simplest scenario for a finite-temperature phase transition governed by a zero-temperature fixed point is drawn in Fig. 13. A glassy system cooled from the fluid phase, were it able to remain in equilibrium, would develop long-range solid order at a temperature T_0. After coarse graining the system, the effective temperature decreases and the effective frustration level increases. At longer and longer length scales, the glass near T_0 looks more frustrated but has less thermal fluctuation. Although temperature is the control parameter, it is not controlling the transition directly. Rather, the important effect of changing the experimental temperature is to change the effective frustration at long length scales.

The glass transition occurs when the long-wavelength frustration reaches a critical value. Consider the zero-temperature axis on Fig. 13. Frustration less than the critical value will decrease as the length scale of observation grows: the local regions, after struggling with one another on short distances, will finally find a regular pattern that they can compromise on, and form an ordered solid. Frustration greater than this value increases with length scale: the free energy gained by grouping larger clusters together becomes less important, and the system stays disordered.

Below T_0, the glass-former flows into the ordered fixed point, and becomes a solid, perhaps a crystal. At T_0, it

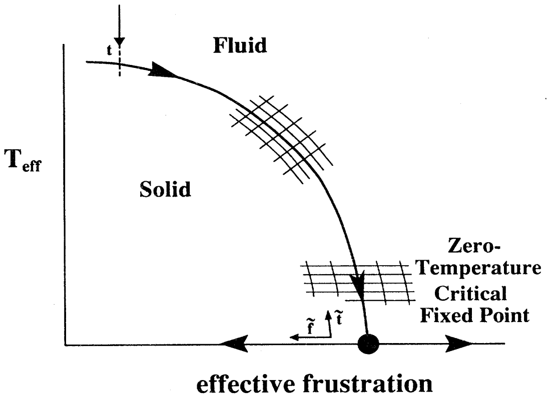

FIG. 13. Proposed renormalization-group flows for the glass transition. We propose that the critical point underlying the glass transition is a *zero temperature critical fixed point.* The vertical axis denotes the temperature; the horizontal axis denotes frustration (compare with Fig. 3). A hypothetical system in equilibrium at the phase transition would flow, as we coarse grain the system, toward lower effective temperatures and higher frustration. At long length scales the effective temperature goes to zero, and the relevant parameter driving the transition is the frustration. Do not be confused by the language: the critical point happens at finite temperature (Fig. 6), it is the RG fixed point governing the critical properties that lies at zero temperature. (This is analogous to the way the finite-temperature ferromagnet is described by the zero-temperature ordered fixed point.) We believe that at long length scales near the critical point, the energy scales become large compared to the temperature. The thermal fluctuations can keep the phase fluid only because of the delicate balancing of competing energies produced by the frustration (Fig. 9). A renormalization group designed to find the fixed-point Hamiltonian describing the barriers to relaxation must therefore have an effective temperature which decreases as we coarse grain.

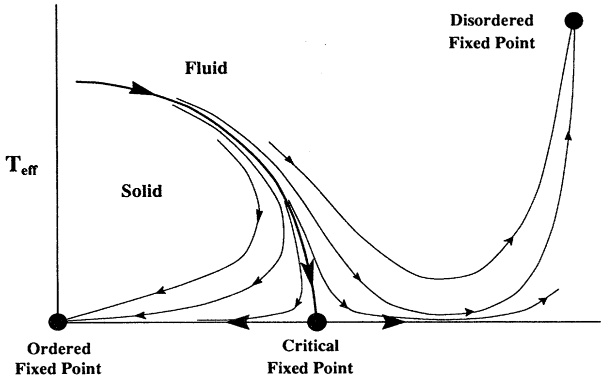

FIG. 14. The complete flow diagram for the glass transition. Here we sketch the flow trajectories for the equilibrium behavior of glass-forming materials above and below their transition temperatures T_0. Systems near their phase transition temperatures $T \sim T_0$ have critical fluctuations on length scales up to their correlation lengths $\xi(T)$: this is reflected in the initial renormalization-group flow of these systems toward the critical fixed point. Insofar as the effective temperature in this part of the trajectory approaches zero, these thermally activated critical fluctuations will be exponentially sluggish. As the coarse-graining length becomes larger than $\xi(T)$, the trajectories bend away from the zero-temperature critical fixed point. If the temperature is below T_0, the equilibrium trajectory flows toward the ordinary zero-temperature fixed point describing the solid phase. If one can prepare the glassy material in equilibrium in the rigid phase, the effective temperature would decrease with coarse graining, and the thermal fluctuations would die away. Normally, when cooled from the melt, the ordered domains in the glass cannot equilibrate; the rate of domain growth continues to decrease as the effective temperature decreases. The result is a glass, where the configurational relaxation grinds to a halt and the system falls out of equilibrium in a liquidlike configuration. If the temperature is above T_0, the trajectory turns to higher effective frustration. The effective temperature continues to decrease for a while, but can, in principle, turn around again and flow toward a high-temperature fluid fixed point.

flows into the critical fixed point, and becomes frustrated on all length scales. Above T_0, naturally, it must flow toward the disordered, infinite temperature fixed point. Figure 14 shows a plausible sketch of the relevant renormalization-group trajectories. Although temperature is shrinking under renormalization near the critical fixed point, it can grow under renormalization for larger values of the frustration. Thus a system just above T_0 will have extremely little in the way of thermal fluctuations in a range of length scales; however, on the largest length scales it will look thermally melted (albeit sluggish).[71]

The renormalization-group analysis of this zero-temperature critical fixed point is precisely the same as that for the random-field Ising model.[72,42,73] The difference is the mechanism: we replace the external random field with a uniform frustration. We will repeat this analysis in our own words.

First, let us set up some notation. We continue to use the variable $t=(T-T_0)/T_0$ to represent the experimental reduced temperature. The fixed point is at the effective frustration and temperature $(F^*,T^*=0)$. We use $\tilde{t}=T$ to represent the distance in the temperature direction to the zero-temperature fixed point, and $\tilde{f}=(F-F^*)/F^*$ to represent the dimensionless distance in the frustration variable to the fixed point. The important eigenvalues of the renormalization-group transformation, linearized about the zero-temperature fixed point, are λ_T and λ_F.

Second, let us analyze the behavior near the critical fixed point, at $(F^*,T^*=0)$. λ_F represents the fact that deviations from the critical frustration level grow under the renormalization-group transformation. If we imagine each transformation as a doubling of the lattice constant (as depicted in Fig. 14), then a zero-temperature Hamiltonian H with reduced frustration $\tilde{f}$ will decimate to $\mathcal{R}(H)$ with frustration $\lambda_F\tilde{f}$, with $\lambda_F>1$. As we approach the critical surface, the correlation length ξ will diverge. Since ξ is divided by two under a coarse-graining step, it must double each time we decrease $F-F^*$ by a factor of λ_F. This immediately implies $\xi\simeq|F-F^*|^{-\ln 2/\ln\lambda_F}$. We define $\nu=\ln 2/\ln\lambda_F$, so $\xi\simeq|F-F^*|^{-\nu}\simeq|\tilde{f}|^{-\nu}$.

The other important eigenvalue of the renormalization-group transformation near the critical fixed point, $\lambda_T<1$, describes the decrease in the effective temperature with each coarse-graining step. Let the free-energy barrier to relaxation be $\mathcal{F}$; the relaxation time τ at $(\tilde{f},\tilde{t})$ will be thermally activated over the barrier, so $\tau\simeq\exp[\mathcal{F}(\tilde{f},\tilde{t})/\tilde{t}]$. This time is preserved under coarse graining. Thus, just as for the Ising model, near the critical fixed point we will have

$$\begin{aligned}\mathcal{F}(\tilde{f},\tilde{t})/\tilde{t}&=\mathcal{F}(\lambda_F\tilde{f},\lambda_T\tilde{t})/(\lambda_T\tilde{t})\\&=\lambda_T^{\ln\tilde{f}/\ln\lambda_F}\mathcal{F}(1,0)/\tilde{t}\\&=\tilde{f}^{\,\ln\lambda_T/\ln\lambda_F}\mathcal{F}(1,0)/\tilde{t}\;.\end{aligned}$$

The free energy barrier $\mathcal{F}(1,0)$ is a barrier height at zero temperature at a fixed frustration level far from criticality; we imagine it to be a characteristic energy scale for an atomic rearrangement. Defining the exponent $\theta=-\ln\lambda_T/\ln 2$, we see that $\mathcal{F}\simeq|F-F^*|^{-\theta\nu}\simeq\xi^{\theta}$.

Third, let us ask what happens to an experiment run far from the fixed point (as shown in Fig. 13). What does the scaling near the fixed point, in $\tilde{f}$ and $\tilde{t}$, imply about the behavior as $t\to 0$? Near $t=0$, the experimental Hamiltonian will flow toward the fixed point under coarse graining. As shown by the grids in Fig. 13, changing the experimental reduced temperature t not only changes the component $\tilde{t}$ of the coarse-grained system, it also changes the component $\tilde{f}$ along the frustration eigendirection. The renormalization-group transformation $\mathcal{R}$ rotates the frustration and temperature axes as the Hamiltonian flows toward the fixed point; the action of t is to change the effective coarse-grained frustration $\tilde{f}$. Thus, as t goes to zero, the correlation length will diverge as

$$\xi\simeq|t|^{-\nu}$$

and the barriers to relaxation will diverge as

$$E/T\simeq|t|^{-\theta\nu}\simeq\xi^{\theta}\;.$$

Thus a zero-temperature critical fixed point allows us to have a diverging barrier height[74] within a renormalization-group description.

IV. CONCLUSIONS

The viscosities and time scales for relaxation in glass-forming liquids rise exponentially as they are cooled. Based on analysis of the experimental evidence, we argue that this is due to a free barrier which grows with decreasing temperature. We attribute this diverging energy scale to an underlying, finite temperature second-order phase transition into an ordered, rigid phase, probably a crystal or a quasicrystal.

We are looking for a model of this underlying transition. It must have no intrinsic disorder, must get stuck with small correlation lengths at realistic cooling rates, must have energy barriers which grow with power laws near a nonzero transition temperature, and must have frustration. We expect it to be described by a renormalization group with a zero-temperature critical fixed point.

ACKNOWLEDGMENTS

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[1] G. W. Morey, *The Properties of Glass* (Reinhold, New York, 1938).

[2] Papers by G. E. Weber (1835), F. Kohlrausch (1863–1876), and L. Boltzmann (1875), discussed in Morey (Ref. 1), p. 316.

[3] C. A. Angell and J. Wong, *Glass, Structure by Spectroscopy* (Marcel Dekker, New York, 1976).

[4] "The equilibrium properties of the supercooled liquid" may sound like a contradiction in terms. Throughout this paper, we will unashamedly use the term "equilibrium" to refer to the supercooled liquid. By this, we mean the metastable equilibrium excluding the phase-space region occupied by the crystal that would have formed at the melting temperature had it been allowed to do so. (We also must exclude phase space regions with crystalline nuclei larger than the critical radius.) Since this crystalline phase plays no role in our theory (Ref. 26) we trust that this usage will not cause confusion.

[5] S. A. Langer and J. P. Sethna, Phys. Rev. Lett. **61**, 570 (1988); S. A. Langer, A. T. Dorsey, and J. P. Sethna, Phys. Rev. B **40**, 345 (1989); S. A. Langer, J. P. Sethna, and E. R. Grannan, *ibid.* **41**, 2261 (1990).

[6] M. Huang and J. P. Sethna, Phys. Rev. B **43**, 3245 (1991).

[7] A recent review of these dynamical theories is given in G. H. Fredrickson, Ann. Rev. Phys. Chem. **39**, 149 (1988).

[8] E. Leutheusser, Phys. Rev. A **29**, 2765 (1984).

[9] The original paper presented a sophisticated diagrammatic version of the mode-coupling theory, with a critical point [S. P. Das, G. F. Mazenko, S. Ramaswamy, and J. J. Toner, Phys. Rev. Lett. **54**, 118 (1985)]. Mazenko and Das later noticed that the original approach has problems on the microscopic cutoff [S. P. Das and G. F. Mazenko, Phys. Rev. A **34**, 2265 (1986)]. Toner also noticed that their freezing solution, while self-consistent, cannot be realized in finite systems (which cannot freeze) and thus cannot occur in the thermodynamic limit either.

[10] U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17**, 5915, 1984; W. Götze, in *Liquids, Freezing and Glass Transitions* (Les Houches, session LI), edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991). Their theories suggest that there is a second critical point, where the behavior of the fluid crosses over from a simple liquid to one with glassy properties. This occurs when the viscosity $\eta \simeq 10^1 - 10^3$ poise, at a temperature well above the phase transition. While this second transition has gained some experimental support [see, e.g., N. J. Tao, G. Li, and H. Z. Cummins, Phys. Rev. Lett. **66**, 1334 (1991) and Refs. 5–11 therein], we are not concerned with it here.

[11] G. H. Fredrickson and H. C. Anderson, Phys. Rev. Lett. **53**, 1244 (1984).

[12] G. H. Fredrickson and S. A. Brawer, J. Chem. Phys. **84**, 3351 (1986).

[13] T. A. Weber, G. H. Fredrickson, and F. H. Stillinger, Phys. Rev. B **34**, 7641 (1986); J. G. Harris and F. H. Stillinger, *ibid.* **41**, 519 (1990).

[14] H. J. Fecht, Z. Fu, and W. L. Johnson, Phys. Rev. Lett. **64**, 1753 (1990).

[15] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, Phys. Rev. Lett. **65**, 1108 (1990)

[16] J. P. Sethna, Europhys. Lett. **6**, 529 (1988).

[17] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[18] We use T_0 to denote the critical temperature for the phase transition underlying the glass transition. T_c is traditionally reserved for the transition from the liquid to the simple crystalline phase, and is not of interest to us in this paper. T_g is basically the temperature at which the supercooled liquid falls out of equilibrium; more precisely, it is defined as the temperature at which the equilibrium viscosity reaches 10^{13} poise.

[19] M. H. Cohen and G. S. Grest, Phys. Rev. B **20**, 1077 (1979); G. S. Grest and M. H. Cohen, *ibid.* **21**, 4113 (1980).

[20] M. Kléman, in *Continuum Models of Discrete Systems 4,* edited by O. Brulin and R. K. T. Hsieh (North-Holland, Amsterdam, 1981), p. 287.

[21] The original theory is presented in S. A. Safran, Phys. Rev. Lett. **46**, 1581 (1981). The theory relied upon the extremely weak potential energies of interaction between domain walls. Later work [S. A. Safran, P. S. Sahni, and G. S. Grest, Phys. Rev. B **28**, 2693 (1983); P. S. Sahni, G. S. Grest, and S. A. Safran, Phys. Rev. Lett. **50**, 60 (1983); P. S. Sahni, D. J. Srolovitz, G. S. Grest, M. P. Anderson, and S. A. Safran, Phys. Rev. B **28**, 2705 (1983)] realized that shape fluctuations of the domain walls produce effective interactions. Recent numerical work shows the dynamics are not glassy even for many ground states [G. S. Grest, M. P. Anderson, and D. J. Srolovitz, Phys. Rev. B **38**, 4752 (1988)].

[22] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A **40**, 1045 (1989).

[23] D. L. Stein and R. G. Palmer, Phys. Rev. B **38**, 12 035 (1988).

[24] P. Goldbart and N. Goldenfeld, Phys. Rev. Lett. **58**, 2676 (1987); Macromolecules **22**, 948 (1989); Phys. Rev. A **39**, 1402 (1989); **39**, 1412 (1989).

[25] J. Souletie, J. Phys. (Paris) **51**, 883 (1990).

[26] Can we ignore the simple crystalline phase? The existing experimental evidence is that the glass transition is unrelated to the underlying equilibrium simple crystal. The time scale for nucleating the simple crystalline form appears to remain longer than the intrinsic relaxation time in the liquid, even as the glass transition is approached [C. A. Angell and J. Donnella, J. Chem. Phys. **67**, 4560 (1977)]. From a theorist's perspective, there are two sides to the issue. On the one hand, it would seem in principle that if the simple crystalline phase is lower in free energy at T_0, the nucleation rate must be finite. On the other hand, it should be possible to tinker with the interactions in some subtle way to keep the simple crystal higher in energy at T_0 without substantially changing the energy of the important glassy configurations. In this paper we wil ignore the simple crystal (e.g., quartz), and concentrate on the transition from the supercooled liquid to an equilibrium solid phase, which could be a complex crystal or a quasicrystal.

[27] Glasses also share the same behavior at temperatures near absolute zero [R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971)].

[28] The viscosity and specific-heat data have been assembled from a few collections. Viscosity data are from C. A. Angell, J. Phys. Chem. Solids **49**, 863 (1988). Specific heat data for *o*-terphenyl, B_2O_3, and $0.6KNO_3-0.4Ca(NO_3)_2$ are from, respectively, S. S. Chang and A. B. Bestul, J. Chem. Phys. **56**, 503 (1972); N. E. Schmidt, Russ. J. Inorg. Chem. **11**, 241 (1966); J. Wong and C. A. Angell, *Glass Structure by Spectroscopy* (Marcel Dekker, New York, 1976), p. 39.

[29] If one measures the specific heat of a glass on heating, there is often a cusplike singularity as it melts. This singularity is understood as a nonequilibrium effect: atomic arrangements which occurred slowly while the glass was at low temperatures all melt near the glass transition point (Ref. 5). It is typically much more rounded than that shown in Fig. 1.

[30] L. D. Landau, *Collected Works of L. D. Landau,* edited by D.

ter Haar (Gordon and Breach–Pergamon, New York, 1965), p. 193.

[31] J. M. Kosterlitz and D. J. Thouless, in *Progress in Low Temperature Physics,* Vol. VII-B, edited by D. F. Brewer (North-Holland, Amsterdam, 1978), p. 373; B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979); A. P. Young, *ibid.* **19**, 1855 (1979).

[32] K. J. Strandburg, Rev. Mod. Phys. **60**, 161 (1988).

[33] W. Vogel, *Chemistry of Glass* (American Ceramics Society, Columbus, Ohio, 1985).

[34] C. A. Angell, in *Relaxations in Complex Systems,* edited by K. L. Ngai and G. B. Wright (U.S. G.P.O., Springfield, VA, 1985), p. 3; C. A. Angell, A. Dworkin, P. Figuière, A. Fuchs, and H. Szwarc, J. Chim. Phys. **82**, 773 (1985), S. W. Martin and C. A. Angell, J. Phys. Chem. **90**, 6736 (1986).

[35] More properly, the free energy barrier $\Delta F(T)=\Delta E-T\Delta S$ diverges. The Adam-Gibbs theory (Ref. 17) and the free-volume theory (Ref. 19) both describe the glass transition as entropy driven. The free-volume description has an entropy cost of the elementary motion which grows with decreasing temperature: $\Delta S(T)\rightarrow\infty$ as $T\rightarrow T_0$; they do not include an energetic cost for rearranging ordered regions.

[36] This is a dogma, but we have been unable to find a direct experimental confirmation. On p. 154 in Scherer (Ref. 76) there is a theoretical plot of the viscosity under various cooling rates. The model is a modified fictive temperature analysis (Ref. 75) and the parameters were chosen to fit a variety of features in a network soda-lime-silicate glass. None of the experimental measurements appear to involve different cooling rates. The theoretical prediction has a crossover from Vogel-Fulcher to Arrhenius behavior, with an increasing low-temperature activation energy on slower cooling. It predicts, however, that a factor of 10^8 in cooling rate might be necessary for a substantial change in slope. An experiment on a more fragile material might produce a larger effect in a smaller range of cooling rates.

[37] There has been considerable discussion in the literature about how well the viscosity can be fit by the Vogel-Fulcher law [C. A. Angell and D. L. Smith, J. Phys. Chem. **86**, 3845 (1982); C. A. Angell, J. Phys. Chem. Solids **49**, 863 (1988)]. This is prompted by the observation (which is apparent for *o*-terphenyl in Fig. 1) that for some materials, one cannot obtain a good fit over the whole range of the viscosity data. When one tries to fit over part of the range, one finds that the data at higher viscosities imply a significantly lower T_0 than that at lower viscosities. In fact, it has been reported that for viscosities above about 10^5 P there is essentially a return to Arrhenius behavior [P. B. Macedo and A. Napolitano, J. Chem. Phys. **49**, 1887 (1968); J. H. Ambrus, C. T. Moynihan, and P. B. Macedo, J. Electrochem. Soc. **119**, 192 (1972); G. S. Grest and M. H. Cohen, Adv. Chem. Phys. **48**, 455 (1981); M. Cukierman, J. W. Lane, and D. R. Uhlmann, J. Chem. Phys. **59**, 3639 (1973), W. T. Laughlin and D. R. Uhlmann, J. Phys. Chem. **76**, 2317 (1972)]. Recent careful work by Nagel's group on *o*-terphenyl and several other materials demonstrates that, if one measures relaxation times from quantities (such as the frequency-dependent specific heat or the dielectric loss) which are well coupled to most or all of the degrees of freedom, one does not find the return to Arrhenius behavior seen in viscosity measurements (although there is evidence for a crossover in the value of T_0, i.e., the Vogel-Fulcher Law does not fit the data over the entire frequency range of the data) [P. K. Dixon and S. R. Nagel, Phys. Rev. Lett. **61**, 341 (1988)]. On the one hand, there remains hope that subtleties in the viscosity measurements could allow the data to be reconciled. On the other hand, as Angell has pointed out, the viscosity may not be the right variable to measure: as the glass transition is approached, the viscosity could decouple from the important degrees of freedom, and thus would no longer serve as a good measure of the relevant relaxation times.

[38] P. W. Anderson, in *Ill Condensed Matter, Proceedings of the 1978 Les Houches Summer School, Session 31,* edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, Amsterdam, 1979).

[39] For this discussion we are using a nonstandard form for the reduced temperature. Usually, one expresses diverging quantities in terms of $t=(T-T_0)/T_0$; we are using the equivalent form $\tilde{t}=(T-T_0)/T$ in discussing the diverging energy barriers because it reproduces the Vogel-Fulcher law without analytic corrections. For example, the diverging energy represented in Eq. (1) can be rewritten in terms of t

$$\begin{aligned}E_{\mathrm{vf}}&=DT_0\tilde{t}^{\,-\theta\nu}\\&=DT_0t^{-\theta\nu}(1+t)^{\theta\nu}\\&=DT_0t^{-\theta\nu}[1+\theta\nu t+\theta\nu(\theta\nu-1)t^2/2+\cdots]\,,\end{aligned}$$

where the series represents a (nonuniversal) analytic dependence of the barrier height on temperature.

[40] M. E. Fisher, in *Critical Phenomena,* edited by F. J. W. Hahne, Lecture Notes in Physics 186 (Springer-Verlag, Berlin, 1983). See particularly Appendix D.

[41] Michael Fischer pointed out to us that, strictly speaking, energy barriers are not equilibrium quantities, and they could diverge without violating hyperscaling (M. Fisher, private communication). Actually, we can imagine four possible scenarios. (1) There is no transition: the glass transition occurs smoothly as the energy scale needed to break bonds becomes prohibitive. Practically speaking, this is probably the best description for vitreous silica. (2) The transition is purely a dynamical one: the atoms jam into one another until they cannot rearrange. This view, described in the Introduction, is being challenged at the moment by the experiment of Fecht, Fu, and Johnson. (3) There is a second-order phase transition, with nonsingular equilibrium energy fluctuations but diverging free energy barriers to relaxation. (4) There is an underlying second-order phase transition, with diverging barrier heights reflecting a violation of hyperscaling. We are torn between scenarios (3) and(4).

[42] D. S. Fisher, Phys. Rev. Lett. **56**, 416 (1986).

[43] G. Grinstein and J. F. Fernandez, Phys. Rev. B **29**, 6389 (1984).

[44] J. Z. Imbrie, Phys. Rev. Lett. **53**, 1747 (1984); Commun. Math. Phys. **98**, 145 (1985).

[45] The microcrystalline point of view was developed in Russia by A. Lebedev (Trans. State Optical Inst. **2**, 1921). The competing view was given by W. H. Zachariasen [J. Am. Chem. Soc. **54**, 3824 (1932)] at the University of Chicago who proposed the continuous random network model for oxide glasses. An unfriendly debate ensued between Zachariasen and Hägg [Gunnar Hägg, J. Chem. Phys. **3**, 42 (1935); W. Zachariasen, *ibid.* **3**, 162 (1935); Gunnar Hägg, *ibid.* **3**, 363 (1935)]; Hägg felt that Zachariasen's rules could not possibly describe more complicated glasses or even simple glasses whose crystal structure consisted of ribbons or sheets. Hägg published a few papers arguing for small-scale crystal-like order in

glasses, but his ideas were quickly refuted by Zachariasen. Hägg quit publishing in the field of glasses. Thanks to S. Shumway for this summary (S. Shumway, private communication).

[46] Some glasses with special properties (such as Vycor) are made by spinodal decomposition. In these materials, two chemical components separate in the melt; during the separation process the system is quenched into a glass. The spinodal decomposition thus is a separate transition, probably unrelated to the glass transition.

[47] D. S. Fisher and D. A. Huse, Phys. Rev. Lett. **56**, 1601 (1986); D. A. Huse and D. S. Fisher, Phys. Rev. B **35**, 6841 (1987).

[48] J. D. Shore and J. P. Sethna, Phys. Rev. B **43**, 3782 (1991).

[49] The grain size of the resulting microcrystals depends on the nucleation rates at the quench temperature, along with the growth kinetics. Because so few regions in nucleated first-order transitions find their way across the nucleation barrier, the length scales of the resulting microcrystals can be large. In contrast, fluctuations into the crystalline phase at a second-order transition are typical, not rare. The length scale is the correlation length, which grows painfully slowly as one cools the melt. Thus the domains in glasses are naturally much smaller.

[50] A. Q. Tool, J. Res. **34**, 119 (1945), discussed in Scherer, Chap. 9.

[51] One should be warned that "superheating" in our picture of the glass transitions is by nature quite different from superheating in a first-order transition. One is not waiting for a critical nucleus to form, and the growth of the new phase is not rapid once it starts. Rather, the system is already melting itself as fast as it can: it's just slow.

[52] Note that the empirically observed Vogel-Fulcher law gives us this divergence for $T > T_c$. However, critical phenomena tells us that the exponent for the divergence must be the same on both sides of the transition. For simplicity we assume here that the coefficient DT_0 is also the same, although it need not be.

[53] There are many forms of $E(T, T_F)$ extant in the literature, as discussed by Scherer (Ref. 76). We choose to invent a form not because it fits the data well (it does not), but because it follows naturally from our picture of the transition.

[54] Kauzmann, in estimating the critical temperature from the residual entropy, implicitly assumed $A'=B'=A=0$. This assumption can make his extrapolated temperature T_K either higher or lower than the true transition temperature T_0.

[55] The differences between the short-range order in the liquid and in the glass have been important tests for structural models of glasses. By emphasizing the striking but obvious similarities between glasses and liquids we do not mean to ignore the important work that has gone into studying the short-range differences.

[56] M. Kléman and J. F. Sadoc, J. Phys. (Paris) Lett. **40**, L569 (1979); M. Kléman, J. Phys. (Paris) **43**, 1389 (1982); D. R. Nelson, Phys. Rev. Lett. **50**, 982 (1983); D. R. Nelson, Phys. Rev. B **28**, 5515 (1983); D. R. Nelson and M. Widom, Nucl. Phys. **B240**, 113 (1984).

[57] J. P. Sethna, Phys. Rev. Lett. **51**, 2198 (1983); Phys. Rev. B **31**, 6278 (1985).

[58] J. F. Sadoc and R. Mosseri, Philos. Mag. B **45**, 467 (1982); M. H. Brodsky and D. P. DiVincenzo, J. Non-Cryst. Solids **59&60**, 101 (1983); Physica **117B&118B**, 971, 1983; D. P. DiVincenzo, R. Mosseri, M. H. Brodsky, and J. F. Sadoc, Phys. Rev. B **29**, 5934 (1984).

[59] D. C. Wright and N. D. Mermin, Rev. Mod. Phys. **61**, 385 (1989).

[60] The discovery of quasicrystals has usurped the use of fivefold symmetry as an illustrative tool. The chemistry behind the local order in quasicrystals seems more complicated than the packing arguments traditionally used to describe the metallic glasses. We remain convinced that icosahedral local order and frustration are keys to understanding metallic glasses. Indeed, we are encouraged by the existence of an ordered, complex solid phase which embodies icosahedral local order: it can act as the low-temperature phase for our critical point.

[61] S. L. Shumway and J. P. Sethna (unpublished).

[62] T. C. Halsey, Phys. Rev. Lett. **55**, 1018 (1985); Phys. Rev. B **31**, 5728 (1985).

[63] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986); see Sec. VI E.

[64] P. Reichert and R. Schilling, Phys. Rev. B **32**, 5731 (1985); W. Kob and R. Schilling, Phys. Rev. A **42**, 2191 (1990); W. Kob and R. Schilling, J. Phys. A **23**, 4673 (1990).

[65] For details, see Ref. 57.

[66] S. Sachdev and D. R. Nelson, Phys. Rev. Lett. **53**, 1947 (1984).

[67] R. G. Calflisch, H. Levine, and J. R. Banavar, Phys. Rev. Lett. **57**, 2679 (1986).

[68] Apologies to those familiar with renormalization-group methods. Much of this section is a standard exposition, provided to make the paper accessible to a wider audience.

[69] Roughly speaking, universal properties of this fixed point are described by hydrodynamics and elementary excitations [D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin/Cummings, Reading, Mass., 1975)] and dynamically (if the order parameter is conserved) by spinodal decomposition. Spinodal decomposition is discussed in terms of a zero-temperature renormalization-group fixed point by A. J. Bray, Phys. Rev. Lett. **62**, 493 (1989); Phys. Rev. B **41**, 6724 (1990).

[70] Is this a renormalization group describing only the barriers (Ref. 41), or does it describe equilibrium fluctuations as well? It is hard to say here, because equilibrium fluctuations in the Ising model are frozen out at low temperatures. On the other hand, analogous arguments can be made for systems with continuous symmetries: the Goldstone modes for these systems (the long-wavelength low-energy hydrodynamic elementary excitations) should be correctly described by the Hamiltonian at the zero-temperature fixed point.

[71] If we take Fig. 14 seriously we must wonder what a coarse-grained version of a zero-temperature Hamiltonian with frustration just above critical would look like. (That is, to where does the unstable manifold of the critical fixed point flow?) If they flow to another fixed point (say, near the lower right-hand corner of Fig. 14) then it would control the crossover behavior for systems just above T_0. On the other hand, the two-dimensional picture shown in Fig. 14 may be a misleading picture of the infinite-dimensional Hamiltonian space: perhaps the unstable manifold flows directly into the disordered fixed point.

[72] A. J. Bray and M. A. Moore, J. Phys. C **18**, L927 (1985).

[73] G. Grinstein, Phys. Rev. Lett. **37**, 944 (1976).

[74] Is hyperscaling (Refs. 41 and 70) violated? If we apply our renormalization-group transformation to the free energy density F, it is multiplied by the change-in-volume factor, and also by the rescaling factor in energy: $F(\tilde{f},\tilde{t})=(2^{-d}/\lambda_T)F(\lambda_F\tilde{f},\lambda_T\tilde{t})\simeq|\tilde{f}|^{-\theta\nu+d\nu}$. This would immediately imply that $2-\alpha=(d-\theta)\nu$, where the specific heat is singular at the transition with exponent $c\simeq|t|^{-\alpha}$. Thus hyperscaling appears to be violated. There is a hidden as-

sumption, however, in this analysis: that the energy asymmetry between the initial state and the final state in an activated motion scales in the same way as the barrier height scales. Precisely the same assumption is made in the random-field Ising model analysis. The discussion of frustration (Fig. 9) would suggest that for the case of glasses, this assumption might be wrong. The other natural assumption would be that equilibrium energy fluctuations would continue to be on the microscopic scale $k_B T_0$, and that the diverging energy scales are all associated with barriers which are important to the dynamics but not to static properties. In this case, the static properties would continue to obey hyperscaling.

[75] O. S. Narayanaswamy, J. Am. Cer. Soc. **54**, 491 (1971), discussed in Scherer (Ref. 76), Chap. 9.

[76] G. W. Scherer, *Relaxation in Glasses and Composites* (Wiley, New York, 1986).