

Speculations on the Glass Transition.

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Abstract. - I speculate about the ingredients needed for a theory of the liquid \rightarrow glass transition. Experimental phenomenology suggests that there is an underlying equilibrium thermodynamic transition. Because of a breakdown of hyperscaling, the free-energy barriers to relaxation diverge at the critical point leading to a Vogel-Fulcher-like divergence of the characteristic relaxation times. The glass is thus a material trapped just above its critical point.

Why⁽¹⁾ are glasses solid? From a chemist's point of view, the answer is simple: glasses are bonded together into a rigid network. From a physicist's point of view, rigidity is much more subtle. If a glass is solid, then it must be separated by a phase transition from the liquid state; the transition occurs when the viscosity first becomes infinite.

The experimental answer is that glasses are not solid. As one cools from the liquid state [2] the viscosity does rise sharply in a narrow temperature range, but below this «glass transition» the viscosity continues to rise, with an apparent Arrhenius law (fig. 1). However, at low temperature Arrhenius behavior is due to the failure of the material to stay in equilibrium. As one cools more slowly, the viscosity rises to higher values before crossing over, and rises with a steeper slope afterward⁽²⁾ (fig. 1). Thus it is reasonable to postulate an underlying equilibrium phase transition into a truly solid state, which drives the material from liquid to glassy behavior. Perversely, it is because the viscosity grows so quickly that it is hard to study whether and how it diverges⁽³⁾. However, a wide variety of liquids, when

⁽¹⁾ This paper is intended to review well-known phenomena related to the glass transition, in order to advocate a general approach to the problem. I make no claims that this is a theory: no new insights into the nature of the order parameter are presented here. At places the text will be inescapably vague. (The alternative of making up a detailed model was explored in the free-volume theories [1], which at least show that such models are possible.) To avoid an endless series of caveats, I will write as if my position were established as the correct one: references to critical phenomena will be made as if an underlying second-order phase transition were known to exist.

⁽²⁾ This is why many people say that glass freezing is a «dynamical transition». However apt this phrase may be, it does not imply that equilibrium thermodynamics is not driving the transition—only that the final nonequilibrium state depends on the cooling history.

⁽³⁾ The characteristic relaxation time in the system scales linearly with the viscosity, with viscosities of 10^{13} poise roughly corresponding to relaxation times of 100 s (ref. [3]). There are a couple of experimental systems in which it is claimed that the viscosity crosses over back to an Arrhenius law

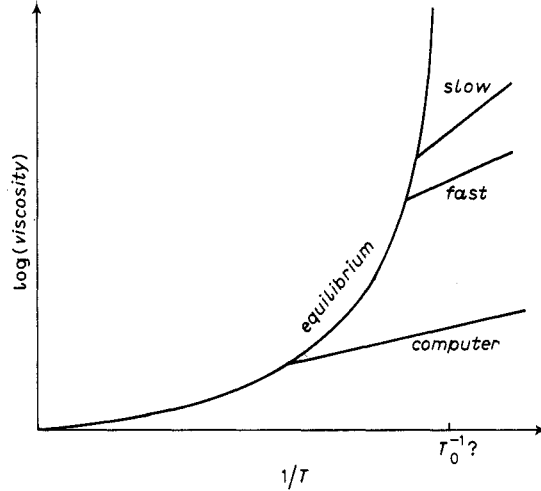


Fig. 1. – Schematic Arrhenius plot of viscosity of various cooling rates for a liquid being cooled into a glass. At a given cooling rate, one stays in equilibrium until the microscopic relaxation time gets too long compared to the quench rate. Numerical simulations cool at a ferocious rate, and cannot get close to the critical point. A slower cooling rate makes the liquid remain in equilibrium longer, leading to a higher viscosity and larger activation energy at low temperatures.

cooled through a relatively narrow temperature range under conditions which preclude crystallization, become very sticky. It is likely that there is a common explanation.

In ordinary critical phenomena, the characteristic time scale diverges at the critical point (critical slowing-down). The characteristic relaxation time τ scales with reduced temperature with critical exponent z :

$$\tau \sim \tau_0 \left(\frac{T - T_0}{T} \right)^{-z} . \quad (1)$$

The critical exponent is universal, but the prefactor τ_0 is material dependent. In principle, any experiment must fall out of equilibrium when passing through the transition. In practice, the power-law divergence of the time scale is weak enough so as to be only a hindrance in studying the critical phenomena. Also, the system typically will continue to order below the transition temperature: ordered domains will grow at a reasonable rate in the low-temperature phase. The time scales in glasses rapidly cripple experimental attempts to study the critical phenomena, and become even longer below the transition region.

In glasses, the characteristic time scale appears to diverge as the exponential of a power law. Figure 2a) shows the equilibrium viscosities of a variety of materials [3]. The elementary relaxation process is probably thermally activated over a barrier; curvature in fig. 2a) represents the temperature dependence of the barrier height. If we assume that the free energy barrier to relaxation scales with a critical exponent -1 ,

$$E \sim DT_0 \left(\frac{T - T_0}{T} \right)^{-1} , \quad (2)$$

even in equilibrium. In one of these cases (σ -terphenyl), recent measurements by Nagel's group (presented at the Relaxation Kinetics workshop at ITP) seem to continue to curve upward. It is also conceivable that viscosity does not directly measure the order parameter.

then the viscosity will diverge with the Vogel-Fulcher law

$$\eta = \eta_0 \exp [DT_0/(T - T_0)] . \tag{3}$$

Here again D should be material dependent; one imagines that more frustrated systems might have larger barriers for a given transition temperature, and be more frustrated. In any case, a relatively small range of D spans the data from the «strong» glasses like SiO_2 which show no critical phenomena to the «fragile» glasses which show clear non-Arrhenius behavior in the experimentally accessible range (fig. 2*b*). The point is not that the Vogel-Fulcher law is the best way to fit the data, nor that the data indicate that the viscosity diverges at T_0 (or even that the barriers diverge at a nonzero temperature). Rather, there are three points I want to emphasize. 1) Diverging barrier heights form a natural starting point for studying the glass transition. 2) The spectrum of observed behavior does not indicate that there are different kinds of glass transitions, only that the barrier heights have a material-dependent prefactor. 3) Large barriers hinder the approach to the critical point. Fragility, not patience, will allow one to get close to the glass transition.

Spawned in part by an attempt to understand the properties of glasses, the study of disordered systems—spin glasses, percolation, charge density waves, random field models, and so on—has become a rich and productive science. Before attention completely shifts to neural networks (which may admittedly be more important in the long run), we should look for ideas about «real» glasses. In particular, the random-field Ising model is known to have an equilibrium phase transition into a ferromagnetic state [4]. Experimental work on this

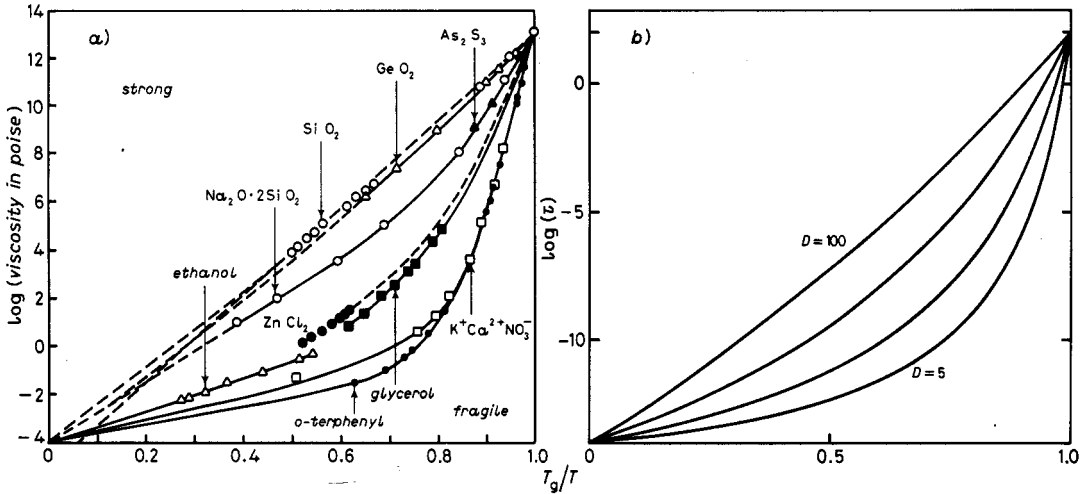


Fig. 2. - *a*) Arrhenius plots of the viscosities of various glass-forming liquids, from ref. [3]. The observed behavior seems to span the range from Arrhenius dependence (the straight line SiO_2 dependence) to what has been called a crossover between two Arrhenius dependences (*o*-terphenyl; see however footnote ⁽²⁾). The way the data is collapsed does not illuminate the underlying physics, but illustrates well the relationship to the laboratory world: the temperature is scaled until the viscosity at the right is 10^{13} poise (a large viscosity to measure conveniently, corresponding roughly to a relaxation time of 100 seconds). This plot has been used to argue that the glass transition is not universal; to emphasize this, the terms «strong» and «fragile» glass-forming liquids were coined. *b*) The viscosity data of fig. 2*a*) is simply explained in terms of a single scaling law, with one nonuniversal parameter. $\tau = 10^{-14} \exp [DT_0/(T - T_0)]$. (Naturally, it has always been known that the Vogel-Fulcher law provides a reasonable fit to each set of data.) At $D = 5$, $(T_g - T_0)/T_g = 0.12$. Clearly, to get closer to the critical point, one must find systems with lower values of D (more «fragile»).

system has been beset by controversy, which was resolved by the realization that the relaxation times were growing very long at the critical point. Just as in glasses, the experimental systems fall out of equilibrium because the barrier heights to relaxation diverge at the critical point.

The random field Ising model is a set of spins ferromagnetically coupled with bond strength J , each with a fixed external force of strength h pushing the spin to point either up or down at random. In three dimensions, the phase diagram is thought to look schematically like fig. 3 [5]. If the random field is strong compared to the bonds, the spins will point mostly in the field directions and the phase will be paramagnetic; if the temperature is large compared to the bonds, the ferromagnet melts. These two transitions, at zero temperature and zero random field, have different critical properties. The critical properties along the rest of the phase boundary in the (h, T) -plane are not intermediate between these two extremes; rather, disorder is a relevant variable, and at long length scales the critical properties are dominated by the disordered fixed point at zero temperature. Thus the renormalization group flows (also shown in fig. 3) all point upward. As one approaches the disordered fixed point from above, the spins form a patchwork with a longest characteristic size ξ , which are arranged to make best use of the random field while breaking as few bonds as possible.

Fisher [6] has developed a scaling theory for the dynamics of the random-field Ising model. The free energy barrier to relaxation is the energy needed to flip over one of the domains of size ξ^d . In ordinary critical phenomena, the energy E associated with a critical volume stays roughly T as one approaches the critical point (that being the only energy scale

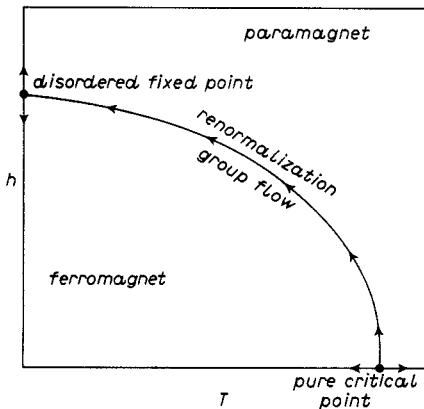


Fig. 3.

Fig. 3. - The random-field Ising model. This diagram can be viewed as the phase diagram or as an illustration of the renormalization group flows. At the pure critical point, the system is in the universality class of the Ising ferromagnet, but as soon as disorder is introduced, the critical exponents and behavior become those of the $T=0$ transition as a function of the random field h . Because temperature is an irrelevant variable in this system, the free energy barriers are set by the disorder, and become very large as one approaches the phase boundary (ref. [7]).

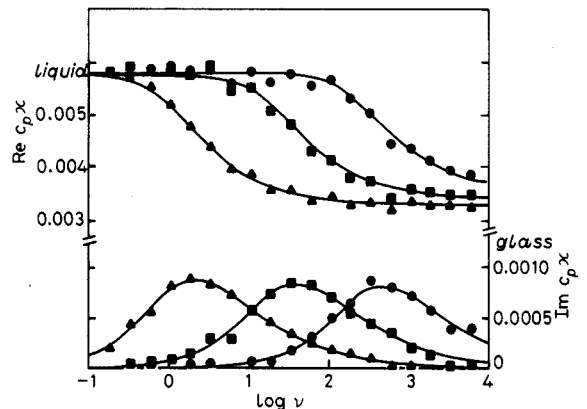


Fig. 4.

Fig. 4. - Real and imaginary parts of the product of the specific heat and thermal conductivity, measured in glycerol as a function of frequency (from ref. [8]). As the temperature is lowered, the peak frequency becomes slower: circles are $T=219.0$ K, squares are 211.4 K, and triangles are 203.9 K. Notice the crossover from glassy behavior at short times to liquid behavior at long times and the relatively narrow distribution of relaxation times. (Exponential relaxation would have a full width at half maximum of 1.1 decades.)

in the problem); this equality leads to the hyperscaling relation. In the random-field model, the energies near the critical point are dominated by the disorder, and the hyperscaling relation is violated. The correlation length will diverge as one approaches the phase boundary

$$\xi \sim \left(\frac{T - T_c}{T} \right)^{-\nu} \tag{4}$$

Because temperature is an irrelevant variable, the divergence of the barrier height will depend on temperature only through the correlation length:

$$E = \xi^\theta = \left(\frac{T - T_c}{T} \right)^{-\nu\theta} \tag{5}$$

Thus the time scales in the random-field Ising model diverge as

$$\tau \sim \exp \left[\frac{E}{T} \right] = \exp \left[\frac{T - T_c}{T} \right]^{-\nu\theta} / T. \tag{6}$$

It is a natural assumption that the diverging time scales in glasses are also due to a breakdown of hyperscaling at the underlying critical point; for glasses, presumably $\nu\theta \approx 1$ explains the success of the Vogel-Fulcher law.

Figure 4 shows the real and imaginary parts of the product $c_p \chi$ as a function of frequency measured in equilibrium [9] just above the glass transition. (Measurements of a number of other quantities would appear similar.) First, notice that the magnitude of the product crosses over from the bulk liquid value of low frequencies to its value in the glass at high frequencies. There is no experimental evidence for a diverging length scale in the glass transition⁽⁴⁾, but there is a clear crossover in the dynamics with a diverging time scale. In ordinary critical phenomena just above the critical point there is a crossover from liquid behavior at small wave vectors $k \ll \xi^{-1}$ to critical behavior at large wave vectors $\xi^{-1} \ll k \ll a^{-1}$ (lengths small compared to the correlation length but large compared to the lattice). Just as in ordinary critical phenomena, here the crossover in frequency should be described by a scaling function⁽⁵⁾. Glasses represent an equilibrium phase transition which is trapped just above its critical point by a diverging relaxation time⁽⁶⁾.

Second, notice that the range of frequencies at a given temperature is remarkably narrow. The characteristic relaxation time has changed by fourteen orders of magnitude

⁽⁴⁾ The correlation length, of course, may never get large. Time scales for relaxation of even rather small clusters of atoms can be very long.

⁽⁵⁾ This «nonexponential relaxation» has been discussed at length recently. While many models have been constructed which show similar relaxation, I believe that it cannot be understood properly except in the context of the underlying phase transition.

⁽⁶⁾ One must ask what the low-temperature phase would be. It has long been speculated that metallic glasses have icosahedral local order (see, e.g., [7]). Numerical evidence suggests that this order increases as one cools more slowly (H. C. ANDERSEN, to be published); Andersen reports, in fact, that the five-fold order is invisible at the glass transition temperature, and is only apparent upon quenching the system to low temperatures. Despite the complete lack of chemical similarity between bulk quasi-crystals and metallic glasses, the apparent importance of five-fold axes in the latter makes it natural to assume that the low-temperature state of metallic glasses is quasi-crystalline. (Why some materials naturally form bulk quasi-crystals may be a question of growth kinetics.) Another model, with an underlying «phase transition» at zero temperature, is given by the kinetic Ising models [8].

from the microscopic time scale (fig. 1), but the range of relaxation times still spans only a couple of decades. This is in sharp contrast to the random-field Ising model, where the disorder provides a distribution of barrier heights leading to a very broad distribution of relaxation times [6]. Glasses, of course, have no disorder in their Hamiltonian—the randomness is formed in the transition. The remarkable homogeneity of glasses is a question that must be addressed whatever notions one has about the origins of the glass transition. Perhaps it lends support to theories with a single fundamental hopping process.

Let me list my conjectures. I) There is an underlying thermodynamic glass transition that is obscured by rapidly growing barrier to relaxation. II) The scaling theory for glasses will involve a breakdown of hyperscaling, which leads to the rapidly diverging free energy barriers. III) Glasses are distinct from random spin systems because they are not disordered—the randomness freezes in at the glass transition. Thus their relaxation is nearly exponential.

Fragility, not patience, will get one close to the glass transition; we should look there for critical phenomena and scaling.

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