Kinetic Ising Models and the Glass Transition

Daniel Sussman

May 11, 2010

Abstract

The Fredrickson-Andersen model, one of a class of Ising models that introduces constraints on the allowed dynamics of the system, was proposed in an attempt to capture some of the dynamic properties of glass formers while exhibiting trivial equilibrium behavior. After a brief introduction to some of the observed phenomena of glassy systems, the FA model and its scaling behavior is reviewed. In closing, two extensions and a few potential limitations of the FA model are discussed.

1 Introduction

Experimentally, the prescription for making a glass is both straight-forward and well known: one rapidly cools a liquid below the melting temperature so that crystallization is avoided, and then continues to lower the temperature of the supercooled liquid. The viscosity of the liquid increases dramatically as the temperature is lowered, until at some transition temperature the longest relaxation processes exceed measurable experimental timescales. At this point (conventionally taken to be 10^{12} Pa s) a 'glass transition temperature,' T_g, is operationally defined and the system behaves as a solid, albeit an amorphous one that lacks long-range order. However, T_g is not a uniquely defined temperature, but rather it depends on the rate, r, at which the liquid is cooled: the longest accessible timescales are set by $1/r$, so as the cooling rate is reduced the transition temperature is seen to decrease [1].

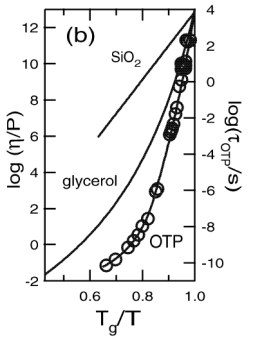

Figure 1: Log viscosity vs. inverse temperature for three liquids of varying strength/fragility (solid lines), as well as NMR data for the rotational relaxation time for the o-terphenyl sample (open circles). Figure reprinted from [2].

In addition to a transition temperature that is operationally – and not uniquely – defined, there are many other unusual properties of the glass transition which have led to considerable debate as to whether it is a true phase transition with a definable thermodynamic order parameter, or if it represents simply the properties of the fluid changing dramatically as the liquid falls out of equilibrium upon cooling [3]. A critical slowing-down of the system is certainly observed, as can be seen in Figure 1. There we can see an exponential growth in the viscosity as a function of $1/T$ for some systems (those systems

with this dependence, such as SiO_2, are called 'strong' or 'Arrhenius' glasses), and other systems that display a greater-than-exponential growth in viscosity, covering almost 15 orders of magnitude in a very narrow temperature window (these systems are referred to as 'fragile' glasses). Unfortunately, the data at the longest timescales (i.e. at temperatures closest to T_g) are not good enough to discriminate between relaxation times that exhibit a true divergence at a finite temperature (e.g. something like $\tau \sim e^{a/(T-T_0)}$) or a divergenceless but rapidly increasing function (e.g. $\tau \sim e^{b/T^2}$) [1].

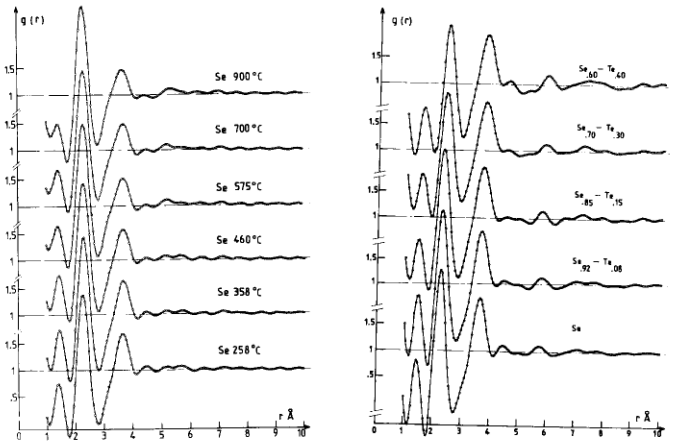

Figure 2: Neutron scattering measurement of the radial distribution function, $g(r)$, of (left) a liquid selenium system for different temperatures all above selenium's 217° C melting temperature and (right) amorphous selenium-tellurium mixtures of varying compositions, all of which exhibit glassy behavior at room temperature. Figure reprinted from [4]

In general when looking at critical phenomena we are used to associating a critical slowing down with a diverging length scale, but for glassy systems there does not seem to be a readily identifiable growing static length scale. Indeed, not only do they lack a diverging static length scale, but the entire static structure of the system shows only slight qualitative changes over the entire temperature range associated with the dramatic slowing down of the dynamics [2]. For instance, Figure 2 shows the radial distribution function (which gives the local density of the fluid a distance r away from a tagged particle located at the origin) of both liquid selenium over a broad temperature

range and a glassy selenium-tellurium mixture over a range of compositions where the viscosity increases dramatically, but there are no clear structural changes evident – only subtle changes in the glassy $g(r)$. Very recently there have been some hints that more subtle measures of the static structure might point to an associated diverging static length scale: one proposed order parameter, ψ_6, measures the tendency of the particles to hexagonally order into medium-range crystalline structures [5].

However, the current consensus is still built around models where the transition to the glassy regime is not a true thermodynamic transition with a changing structural order parameter, but is rather a purely dynamic transition. Associated with the slowing down of the dynamics, then, is a growing *dynamic* length scale. In order to identify this dynamic length scale, note that another key feature of the glassy state is the observation of a spatially heterogeneous distribution of fast- and slow-moving particles within the sample (as in [6], where a glassy colloidal suspension was observed using confocal microscopy). The dynamic length scale is often defined as either the typical size of these regions of dynamic heterogeneity or (possibly but uncertainly related) the size of a region of particles which must move cooperatively for a relaxation event to occur.

2 Kinetically constrained models: the FA facilitated Ising model

With this situation in mind – dramatically changing system dynamics with little if any changes to the static structure of the system as temperature is decreased – a class of models called kinetically constrained models (KCMs) has been developed to try to investigate the glassy phase. Their guiding philosophy is to take a model with trivial equilibrium behavior but then impose rules, i.e. kinetic constraints, on how the system is allowed to transition between different configurations [1].

One of the originally proposed KCMs is the FA model, developed by Fredrickson and Andersen [7]. In its simplest version, the Hamiltonian is given by

$$H = \sum_{i=1}^{N} S_i, \tag{1}$$

that is, an Ising model Hamiltonian with no interaction term (Fredrickson

and Andersen also studied this model for nonzero ferromagnetic J and found the qualitative predictions much the same [8]). We know that for an Ising system with no interactions and a non-zero external field there are no phase transitions above $T = 0$, so indeed this model starts out with as trivial an equilibrium behavior as could be imagined. To create more interesting dynamics, then, the FA model looks at the master equation for the evolution of the probability that the system is in the state $\vec{S}$,

$$\frac{\partial}{\partial t}p(\vec{S},t) = \sum_{\vec{S'}} w(\vec{S'} \to \vec{S})p(\vec{S'},t) - \sum_{\vec{S'}} w(\vec{S} \to \vec{S'})p(\vec{S},t). \tag{2}$$

In the absence of kinetic constraints the rates would just be related to the change in energy in flipping the necessary number of spins to go from configuration $\vec{S}$ to configuration $\vec{S'}$, but in the FA model an extra rule is applied: the rate for spin i to flip is set to zero, $w(S_i \to -S_i) = 0$, *unless* some number f of its nearest neighbors are in the spin-up state then [1]. The 'facilitation number,' f, is an integer parameter of the theory, and the dynamics turn out to depend strongly on whether $f = 1$ or $f \neq 1$.

Physically, the interpretation of the FA model is that each spin variable represents a coarse-grained region of space, with regions of higher-than-average density identified with down-spins and regions of lower-than-average density identified with up-spins. The idea is based on the plausible hypothesis that that the dynamics are controlled by the local density fluctuations, so that particles in a denser-than-average region of the fluid will have a harder time responding to local fluctuations. Thus regions of excess density will propagate very slowly unless their dynamics are facilitated by a sufficient number of nearby regions of relatively low density.

Some basic results from the FA model are most easily written in terms of the natural 'temperature' variable c, defined to be the equilibrium concentration of up spins. Since the Hamiltonian is so simple, this is just $c = (e^{2\beta} + 1)^{-1}$. Now, if we are considering the dynamics of the $f = 1$ model (so that a down-spin needs only one nearby up-spin to flip) the only interesting dynamics occur near $T = 0$, so $c \approx e^{-2\beta}$. A characteristic relaxation time, τ, can be found by first defining the single-spin self-correlation function in time,

$$\phi(t) = \frac{\langle S_i(t)S_i(0)\rangle - \langle S_i\rangle^2}{1 - \langle S_i\rangle^2}, \tag{3}$$

and then taking the zero component of its Fourier transform, $\hat{\phi}(0)$. The

model predicts that at low temperatures $\tau \sim c^{-\Delta}$ [8]. That is, the relaxation times of the $f = 1$ model correspond to a straight line as plotted in Figure 1, and thus potentially capture the features of strong glasses.

On the other hand, for $f = 2$ on a hypercubic lattice the time correlation functions predict a transition at nonzero temperature in the following sense. There is a critical temperature (concentration) above which $\phi(t)$ decays to zero at long times (as we would expect in a fluid), but below which it remains finite even as $t \to \infty$. Numerical work on a simple cubic lattice in three dimensions then shows that near this critical concentration the relaxation time is given by $\tau \approx (c - c_c)^{-1.765}$ [8]. Since the critical concentration $c_c \approx 0.0904$ is still small we can see without detailed calculation that such a power law for the relaxation time in c would look like one of the upwardly-curving lines when plotted as in Figure 1, so the $f = 2$ model has some characteristics of a fragile glass former.

In retrospect, this difference between $f = 1$ and $f > 1$ can be rationalized with a simple physical argument (see [1], [7], [8]). We can think of the low-density, spin-up sites as defects propagating through the system, and the relaxation time as related to the time for a defect to move over some characteristic length scale (where, for fixed temperature and hence equilibrium concentration c, the natural length scale is the typical distance between defects: $l \sim c^{-1/d}$ in d-dimensions). If $f = 1$ then a single, isolated defect can propagate itself with a diffusion constant proportional to a power of the concentration, so then

$$\tau \sim \frac{l^2}{D} \sim c^{-\alpha-2/d} \sim \exp\left(\frac{\alpha + 2/d}{KT}\right), \tag{4}$$

which shows a non-diverging, Arrhenius-like behavior. On the other hand, if $f > 1$ an individual defect cannot cause its own propagation over an arbitrary distance, nor in fact can any finite collection of clustered up spins. This can be seen by considering a cubic shell of down spins around a cluster of defects [8]: the defects in the interior can never flip a down-spin in this shell on their own, since on a hypercubic lattice each down-spin in the shell is nearest neighbors with only one of the interior defects. Thus, for a defect to propagate it must rely on cooperative processes involving defects propagating in from outside of such a shell. Since with decreasing temperature not only is the average distance between each defect growing but so is the *number* of defects that must be cooperatively flipping for a defect to propagate, the relaxation time cannot scale as a simple power law in c [1]. What results,

then, is a power law in the concentration that diverges at some finite $c \neq 0$, along with a diverging dynamical length scale corresponding to the size of a region that needs to act cooperatively for a defect to propagate.

For $f > 1$ there is still a relatively poor quantitative understanding of how the dynamic time- and length-scales depend on c [1]. However, for studying the 'strong glass' case of $f = 1$ various renormalization group (RG) techniques can be used to deduce the critical power-law exponents. In one dimension the easiest approach is a real-space RG scheme [9] much like we looked at in class for the Ising model: one first writes the Hamiltonian as a sum of Liouvillians which encode the rates of all of the allowed neighbor spin-flipping dynamics, coarse-grains the spins into blocks of size 2, computes the renormalized rates in the Liouvillians, and then compares with the original rates to work out how the concentration c has been renormalized by the coarse-graining procedure. What results is a relaxation time that near the $c = 0$ (low temperature) fixed point scales as $\tau \sim c^{-3}$ and a dynamic correlation length that scales as $\xi \sim c^{-1}$.

For $2 \leq d \leq 4$ (4 being the upper critical dimension for this model) a field theoretic RG scheme provides an easier approach [10]. After coarse-graining the fluid into regions of static-correlation-length size, assigning each region a time coarse-grained value of the mobility n_i ($n_i = 0$ corresponding to a down spin and $n_i = 1$ corresponding to an up-spin), and choosing kinetic constraints for the master equation to be the sum of nearest-neighbor mobilities one arrives at a field-theoretic description of the problem in the same universality class as the FA model. Renormalizing the action by considering the effects of fluctuations in an epsilon-expansion then leads to low-temperature scaling laws of $\tau \sim c^{-2.083}$ and $\xi \sim c^{-0.5625}$ in three dimensions. The scaling of τ matches very well with numerical simulations of this system, which give a scaling exponent $\tau \sim c^{-\Delta}$ with $\Delta = 2.095 \pm 0.01$ [10]. Unfortunately, in those same simulations the authors were not able to determine the scaling of ξ accurately enough to test the validity of the derived scaling exponent. Their best estimate yields a scaling exponent of 0.499, but with large enough error bars to make it difficult to establish 0.5625 as either correct or incorrect (although the mean-field value of 1/3 is certainly ruled out by their simulations) [10].

3 Extensions of the FA model

The FA model, many of its resulting properties and additional scaling behaviors having been skipped over for the sake of brevity, is an interesting and somewhat successful model that captures some of the fundamental dynamical properties of glassy systems without relying on any interesting equilibrium behavior. However, there are some natural extensions of the FA model that have been explored over the years that substantially broaden its appeal and viability. Here we restrict ourselves to briefly mentioning two such extensions.

We have already mentioned that the $f > 1$ versions of the FA model, while capturing some dynamic features of fragile glass formers, are very difficult to study analytically. The East model seeks to address fragile glassy behavior more simply than the $f > 1$ FA models by introducing directionality to the kinetic constraints. In one dimension it imposes a rule saying that a spin flip is allowed only if the nearest neighbor spin *on the left* is an up-spin (thus propagation can only occur to the East, and hence the name; in two dimensions the 'Northeast' model is defined analogously). This restriction on the allowed configurations of spins that can facilitate spin flipping has profound effects on the dynamics even in the analytically tractable case of $f = 1$. In one dimension the real-space RG technique in [9] is directly applicable. The result is a characteristic length scale that, at low temperatures, scales as $\xi \sim \exp\left(e^{1/T}/\ln 2\right)$ and a relaxation time that goes as $\tau \sim \exp\left(1/(T^2 \ln 2)\right)$. This double-exponential and super-Arrhenius behavior clearly shows dramatically slower and more cooperative dynamics than the $f = 1$ FA model, and it is plain to see that the relaxation time would be an upwardly-sloping line when plotted as in Figure 1. Thus, this is a model that mimics some dynamic features of fragile glasses.

Another extension of the FA model seeks to address a different point. For the $f = 1$ model the critical fixed point is at $T = 0$, but experimentally and in simulations the glass transition point T_g occurs at a finite, non-zero value regardless of whether the glass is strong or fragile. One model that seeks to address this starts by softening the hard kinetic constraints of the FA model: instead of a spin flip being disallowed if it is surrounded by down-spins, the rate is given by $\epsilon \propto e^{-U/T}$, where U is some activation energy assumed to be larger than the energy associated with creating an excitation [11] (so, the constraint is only modestly softened in the model studied here). Using a technique that involves introducing an extensive variable, K, that measures the total dynamical motion of a trajectory and a field, s, that couples to K

and biases it towards slow particle motion, the authors were able to show that in the presence of softened constraints the model exhibits a line of first order transitions ending in a critical point (see Figure 3). This critical point, occurring at $T \neq 0$, has the same scaling behavior as a liquid-vapor critical point [11]. Thus the model displays both a dynamical glass transition at low but finite (depending on the value of s) temperatures and has the potential to recover simple fluid behavior at high temperatures.

Figure 3: Phase diagram for the constraint-softened FA model, showing a line of first-order transitions in the T-s plane separating the active, liquid-like regime from the inactive, glassy-like dynamical regime. Figure reprinted from [11].

4 Conclusion

In the above we have seen how the FA model and some of its extensions take a model with trivial equilibrium properties and impose certain kinetic constraints on the evolution of the system – how it is allowed to transition between configurations – in an attempt to capture some of the basic dynamical properties observed in the glass transition. These models have had some success, being able to capture a range of both strong and fragile glassy behavior in the relaxation time and identify a growing dynamic length scale that this slowing down of the dynamics is associated with. Let us close, then, by also mentioning some of the weaknesses and indeterminacies of these models. They all start by coarse-graining the fluid into regions of high and low density, postulating that the surrounding density of a cell is the fundamen-

tal factor controlling the motion of particles within the coarse-grained cells. This assumption seems very reasonable and quite intuitive, but is it correct?

There is some evidence from simulations on two-dimensional disks that, while there is some coincidence between the relative free volume of a tagged particle (a particle with more relative free volume corresponding to being in a comparatively low-density region) and its ensemble-averaged mean-squared displacement, there is no strong correlation [12]. Perhaps this can be partly explained by a collection of experiments (and one theoretical analysis) which showed that for different systems the free-energetic barriers to particle motions in the glassy regime were scaling laws in (ρ^x/T), where both the scaling function and the exponent x are non-universal for different glass formers or different assumed forms of the inter-particle potential of the fluid [3], [13]. Capturing this in the FA models would then presumably involve a coarse-graining prescription into density cells that is highly system-specific. This additional free parameter would make rigorous experimental tests of the effective model difficult, leaving open the question of whether the FA model truly captures the fundamental physics of the dynamic phase transition under study.

Speaking of the coarse-graining procedure to go from the fluid to the KCM, so far we have been deliberately non-specific on how to actually perform that mapping. There seems to have been relatively little work in the direction of directly linking these models to, say, microscopic simulations of glass-forming fluids. One attempt avoids the above question of whether the density is really the controlling variable by mapping not the local density but a mean-squared measure of local particle displacement in a molecular dynamics simulation to the corresponding spin variables in a KCM [14]. This somewhat begs the question of what physically controls the slowing of the dynamics (it is a choice that says particle mobility is facilitated by particle mobility - what causes the variation in mobility is set aside), but it nevertheless produces a result less intuitive than one would expect. In their MD simulation the authors study a fragile glass former, and yet they find that it most clearly maps after coarse-graining onto a KCM that is essentially the $f = 1$ FA model, a model that we showed above was best thought of as serving as a model for *strong* glasses. Clearly, then, there is still much work to do in making concrete connections between the KCMs and the microscopic particle motions they hope to describe.

References

[1] F. Ritort and P. Sollich. Glassy dynamics of kinetically constrained models. *Adv. in Phys.*, 52(4):219–342, 2003.

[2] M.D. ediger. Spatially heterogeneous dynamics in supercooled liquids. *Annu. Rev. Phys. Chem.*, 51(99), 2000.

[3] Jeppe C. Dyre. Colloquium: The glass transition and elastic models of glass-forming liquids. *Rev. Mod. Phys*, 78(953), 2006.

[4] R. Bellissent and G. Tourand. Short range order in amorphous and liquid se(1-x)te(x) systems. *J. Non-Cryst. Solids*, 35:1221–1226, 1980.

[5] Hajime Tanaka Takeshi Kawasaki Hiroshi Shintani and Keiji Watanabe. Critical-like behaviour of glass-forming liquids. *Nature Materials*, 9(324), 2010.

[6] E.R. Weeks J.C. Crocker A.C. Levitt A. Schofield D.A. Weitz. Three-dimensional direct imaging of structural relaxation near the colloidal glass transition. *Science*, 287:627, 2000.

[7] Glenn H. Fredrickson and Hans C. Andersen. Kinetic ising model of the glass transition. *Phys. Rev. Lett.*, 53(1244), 1984.

[8] Glenn H. Fredrickson and Hans C. Andersen. Facilitated kinetic ising models and the glass transition. *J. Chem. Phys.*, 83:5822–5831, 1985.

[9] Stephen Whitelam and Juan P. Garrahan. Facilitated spin models in one dimension: A real-space renormalization group study. *Phys. Rev. E*, 70(046129), 2004.

[10] Stephen Whitelam Ludovic Berthier and Juan P. Garrahan. Renormalization group study of a kinetically constrained model for strong glasses. *Phys. Rev. E*, 71(026128), 2005.

[11] Yael S. Elmatad Robert L. Jack Juan P. Garrahan and David Chandler. Finite-temperature critical point of a glass. arXiv:cond-mat/1003.3161v1, 2010.

[12] Asaph Widmer-Cooper and Peter Harrowell. On the relationship between structure and dynamics in a supercooled liquid. *J. Phs. Condens. Matter*, 17(S4025), 2005.

[13] Ning Xu Thomas K. Haxton Andrea J. Liu Sidney R. nagel. Equivalence of glass transition and colloidal-glass transition in the hard-sphere limit. *Phys. Rev. Lett.*, 103(245701), 2009.

[14] Matthew T. Downton and Malcolm P. Kennett. Connecting microscopic simulations with kinetically constrained models of glasses. *Phys. Rev. E*, 76(031502), 2007.