The glass transition as a spin glass problem

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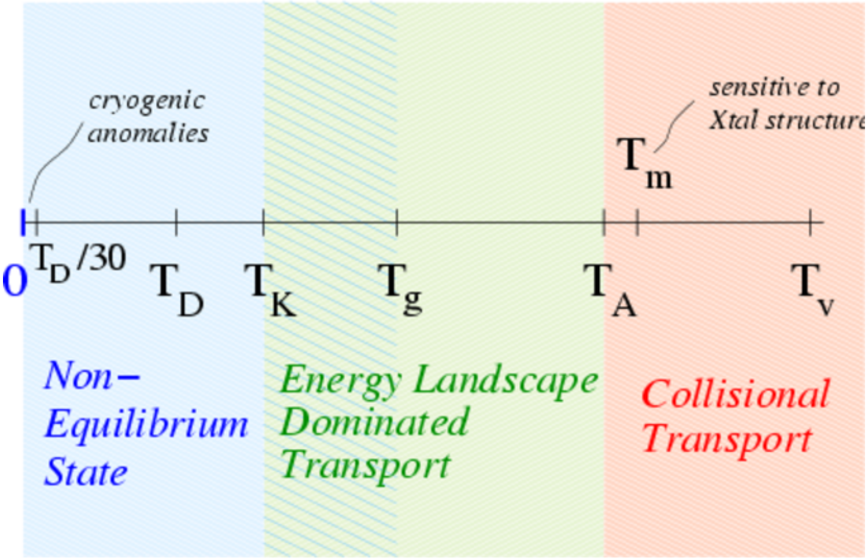
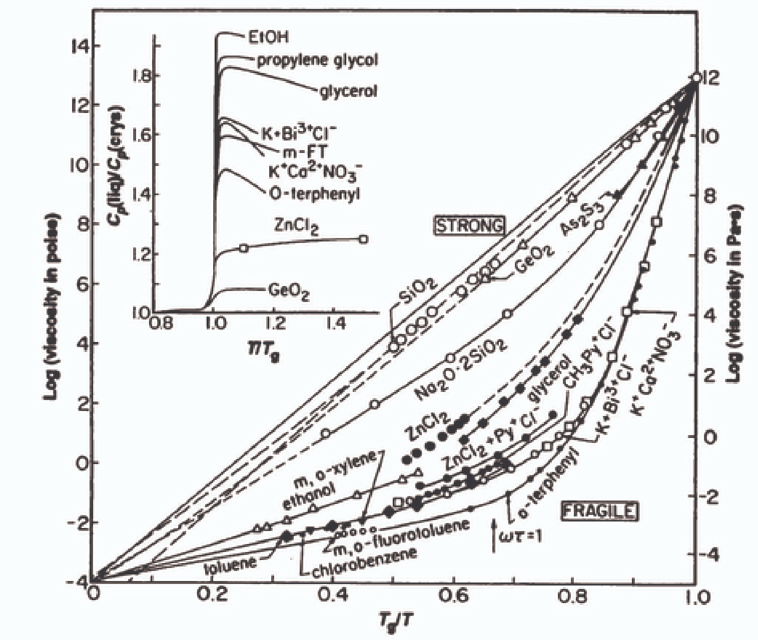
Regimes of Liquid/Glass Physics





EtOH
propylene glycol
glycerol
K+Bi3+Cl-
m-FT
K+Ca2+NO3-
O-terphenyl
ZnCl2
GeO2
T/Tg
STRONG
FRAGILE
SiO2
GeO2
As2S3
Na2O·2SiO2
ZnCl2
ZnCl2+Py+Cl-
glycerol
CH3Py+Cl-
K+Bi3+Cl-
K+Ca2+NO3-
o-terphenyl
m, o-xylene
ethanol
m,o-fluorotoluene
chlorobenzene
toluene
ωτ=1
Log (viscosity in poise)
Log (viscosity in Pa s)
Tg/T

Plan of Talk

- Glass phenomenology
- Formalism — to show that the supercooled liquid (with no disorder) near its glass transition is in the universality class of the Ising spin glass in a field (with quenched disorder)
- Droplet scaling ideas: predicts behavior on long lengthscales and timescales
- Long lengthscales are probably not being reached in experiments.
- Glasses are in a pre-asymptotic regime — numerical work on Ising spin glass in a field indicates that it mimics conventional glass phenomenology when lengthscales are modest.

Some Glass Phenomenology

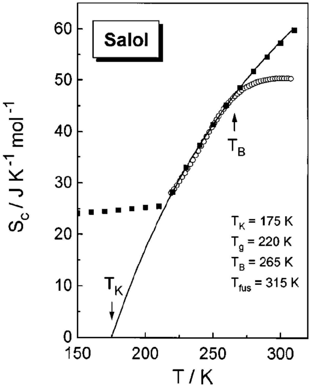
- Vogel-Fulcher law

$$\eta \sim \exp[DT_0/(T - T_0)].$$

  In truth just ‘curve-fitting’.
- Relaxation time(s) $\tau \sim \eta$.
- Kauzmann Paradox: Configurational entropy per molecule apparently goes to zero at T_K

$$s_c(T) \sim k_B(1 - T_K/T) \sim \Delta C_p(1 - T_K/T) \sim (1 - T_K/T)/D.$$

- The ratio T_K/T_0 lies between 0.9-1.1 for many glass formers for which T_K ranges from 50 K to 1000 K.
- Simulations (and experiment) support existence of a growing lengthscale $L^*(T)$; increasingly large regions have to move simultaneously for the liquid to flow.
- But at T_g, $L^*(T)$ is only a few particle diameters.



- "Equilibrium" near T_K or T_0 cannot be obtained due to freezing into an amorphous solid on experimental time scales.
- Consequence: experimental lengthscales cannot be made large and evidence for universality and well-defined power laws will (always?) remain weak.

The thermodynamic transition

- The apparent divergence of η at T_0
- The apparent vanishing of $s_c(T)$ at T_K
- The closeness of T_0 and T_K for many glasses
- A growing lengthscale $L^*(T)$

All the above suggest a transition as $T \to T_0$.

- We will argue the transition is in the universality class of the Ising spin glass in a field $h(T)$ as $h(T) \to 0$.
  (For all $T < T_c$, there is a line of critical points at $h = 0$ when $d < 6$).
- Lengthscales get large when $h(T)$ gets small: $h(T)^2 \sim (T - T_0)$.
- The spin glass transition temperature in zero field $T_c \approx T_A$.

Glass theories

- Locally geometrically frustrated systems; $\Rightarrow$ an avoided transition. Explain simply the existence of supercooling.
- Kinetically contrained dynamical models.
- RFOT theory of Wolynes and co-workers.
  A theory at the level of molecules (a "plus"), whose underlying physics related to that of the "p-spin" model in the infinite dimensional limit e.g. use of the "mosaic" picture.
- Mapping to an Ising spin glass in a field. (Not a theory at the level of molecules, (a "minus").
  The p-spin model maps to this when treated as a three dimensional system.
  It allows prediction of the universal exponents ψ, θ, d_s etc.

$$\tau \sim \exp\left[B_0 L(T)^{\psi}/k_B T\right], \qquad L(T) \sim \left[\frac{1}{T - T_0}\right]^{\frac{1}{d-2\theta}}$$

d_s is the fractal dimension of the dynamically active regions in α–relaxation processes.

Effective Potential Formalism

(cf Franz and Parisi, Dzero et al.)

- Define the overlap
$$p_c(\mathbf{r}) = \delta\rho_1(\mathbf{r})\delta\rho_2(\mathbf{r})$$
between two configurations of density variations $\delta\rho = \rho - \langle\rho\rangle$ in two copies of the liquid.
- Compute the constrained partition function by averaging over the density configurations in the first copy:
$$Z[p_c(\mathbf{r}), \delta\rho_2(\mathbf{r})] = \langle\delta(p_c(\mathbf{r}) - \delta\rho_1(\mathbf{r})\delta\rho_2(\mathbf{r}))\rangle_{\rho_1}.$$
- The effective potential is given by averaging the free energy with respect to the density configurations in the second copy
$$\Omega[p_c(\mathbf{r})] = -T\langle\ln Z[p_c, \delta\rho_2]\rangle_{\rho_2}.$$
- Use the replica trick to average the logarithm
$$\ln Z = \lim_{n\to 0}(Z^n - 1)/n.$$

Use an integral representation of the delta function.

$$\Omega[p_c(\mathbf{r})] = -T\int\prod_\alpha \frac{\mathcal{D}\lambda_\alpha}{2\pi}\,\exp\left[i\sum_\alpha\int d\mathbf{r}\lambda_\alpha(\mathbf{r})p_c(\mathbf{r})\right]$$

$$\times\left\langle\left\langle\exp\left[-i\sum_\alpha\int d\mathbf{r}\delta\rho_1^\alpha(\mathbf{r})\delta\rho_2(\mathbf{r})\lambda_\alpha(\mathbf{r})\right]\right\rangle_{\rho_2}\right\rangle_{\rho_1^\alpha}.$$

Define $q_{\alpha\beta}(\mathbf{r}) = \lambda_\alpha(\mathbf{r})\lambda_\beta(\mathbf{r})$ for $\alpha\neq\beta$. Trace out the λ_α, ρ_1^α and ρ_2 fields using cumulant averaging (and further integral representations).

$$\Omega[p_c] \sim \int\prod_{\alpha<\beta}\mathcal{D}q_{\alpha\beta}\exp[-H[q]].$$

$p_c(\mathbf{r})$ is determined from the condition $\delta\Omega/\delta p_c = 0$.
$H[q_{\alpha\beta}]$ is an even function of $p_c(\mathbf{r})$ so $p_c(\mathbf{r}) = 0$ is always a solution and this describes the liquid phase. But at the "transition", $T = T_0$, $\delta\Omega/\delta p_c = 0$ gives

$$\lim_{t\to\infty} < \delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r},t=0) >= q_{EA} = p_c.$$

To cubic order when $p_c(\mathbf{r}) = 0$

$$H[q] = \int d\mathbf{r} \left\{ \frac{c}{2} \sum_{\alpha<\beta} (\nabla q_{\alpha\beta}(\mathbf{r}))^2 + \frac{\tau}{2} \sum_{\alpha<\beta} q^2_{\alpha\beta}(\mathbf{r}) - \frac{w_1}{6} \mathrm{Tr}\, q^3(\mathbf{r}) - \frac{w_2}{3} \sum_{\alpha<\beta} q^3_{\alpha\beta}(\mathbf{r}) \right\}.$$

- The coefficients c, τ, w_1 and w_2 will be functions of the temperature T and density of the liquid, with smooth dependence on them.
- If one knows the correlation functions of the liquid, then in principle one could determine these parameters.
- The transition is usually driven by τ changing sign as a function of temperature. Here the growing lengthscale will arise from w_2 going to zero: $w_2 \sim (T - T_0)$ in the 'low-temperature' regime $\tau < 0$.
- The w_2 term breaks time-reversal invariance.
- The physical significance of $q_{\alpha\beta} = \lambda_\alpha \lambda_\beta$ is not simple!

Properties of the Functional

- The same replica functional arises in studies of the p-spin model (and also Potts models).
- If $w_2/w_1 > 1$ there are two transitions at mean-field level, a dynamic transition at T_A and a first-order thermodynamic glass transition at T_K (below which $p_c(\mathbf{r})$ becomes non-zero).

$$0 \text{ ——— } T_K \text{ ——— } T_A \text{ ———} \longrightarrow$$

- Glass phase ($T < T_K$) has one-step replica symmetry breaking (1RSB) order.
- Above T_A, dynamics parallels that in mode-coupling theory.

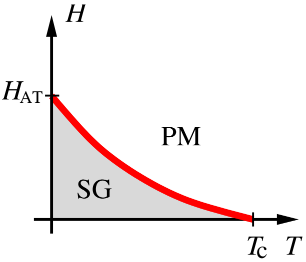
Beyond the mean-field approximation

- Outside mean-field theory no true dynamical transition T_A exists as true metastable states do not exist in finite dimensions.
- Outside mean-field theory the 1RSB phase below T_K does not exist. It is destroyed by thermal excitation of large droplets: the free energy cost of a droplet of linear extent L falls as $\exp(-L/\xi)$.
- Numerical studies of the 10-state Potts models in three dimensions: no sign of MCT like effects or a glass transition or growing lengthscales. (All visible at mean-field level).
- When $w_2/w_1 < 1$ a continuous transition to a glass state with full RSB exists at mean-field level.
  Moore and Drossel (2003), Moore and Yeo (2006) showed that this transition was in the same universality class as that of an Ising spin glass in a field.

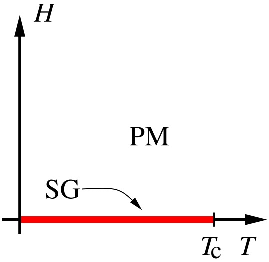
$$\mathcal{H} = -\sum_{<ij>} J_{ij} S_i S_j - h \sum_i S_i, \qquad w_2 \sim h(T)^2$$

Ising spin glass in a field

- de Almeida-Thouless (AT) line at which there is a continuous 'replica symmetry breaking transition'. Exists at mean-field level and possibly for all $d > 6$?
- No AT transition for $d < 6$ (Moore 2005) where the loop expansion around the mean-field theory fails.
- For $d < 6$, a transition arises only if $h(T) \to 0$. The whole line $T < T_c$ is critical i.e. the correlation length is infinite.



$d > 6$



$d < 6$

Droplet scaling

- The lengthscale $L(T)$ is the size of a compact region, (containing $\sim L^d$ spins) in which the spins flip to lower their magnetic energy.
- Domain wall energy $\sim L^\theta$, $\theta \approx 0.2$ when $d = 3$.
- Magnetic field energy gained $\sim h(T)L^{d/2}$
- Equating these two energies – the Imry-Ma argument

$$L(T) \sim \left[\frac{1}{h^(T)^2}\right]^{\frac{1}{d-2\theta}} \sim \left[\frac{1}{T - T_0}\right]^{\frac{1}{d-2\theta}} \sim \left[\frac{1}{T - T_0}\right]^{0.4}$$

- Contrast with the mosaic picture: $\gamma(T)L(T)^{d-1} \sim s_c(T)L^d$.
- Barrier against flipping $B(T) \sim B_0 L(T)^\psi$, ψ not yet determined.
- From Arrhenius

$$\tau \sim \tau_0 \exp\left[\frac{B(T)}{k_B T}\right] \sim \tau_0 \exp\left[\frac{D T_0}{T - T_0}\right]^{0.4\psi}$$

The broken symmetry of the glass transition

- The transition arises from taking the field $h(T)$ to zero as $T \to T_0$. At $h = 0$, the Ising spin glass Hamiltonian has time-reversal invariance (up-down symmetry).
- At the level of molecules the transition is driven by w_2 going to zero at T_0. There must be an extra symmetry in the system at this temperature.
- What is it? Particle-hole symmetry?
- Notice that $< q_{\alpha\beta} >=< \lambda_\alpha \lambda_\beta >$ is non-zero at all T.

Relation to RFOT theory and MCT theories

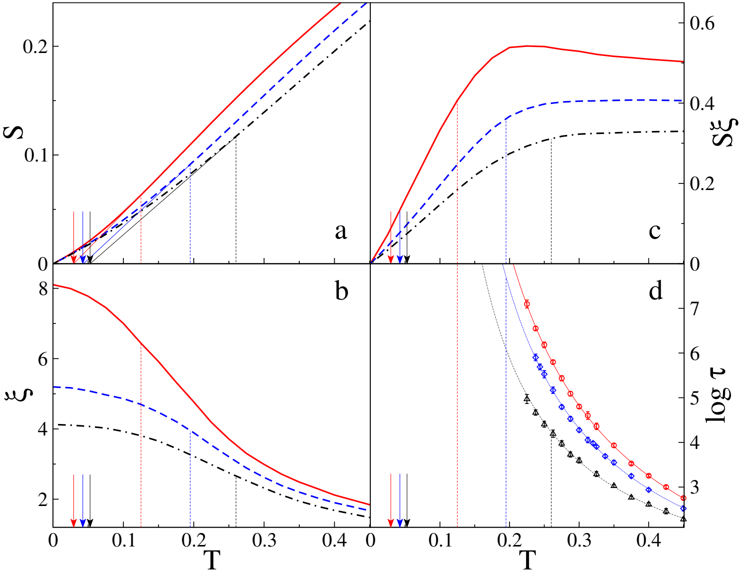
- The p-spin version of the RFOT and the Ising spin glass in a field have the same starting functional.
- The mapping to the Ising spin glass in a field applies when the loop corrections destroy the mean-field character of the transition.
- The RFOT and mosaic pictures will be OK in a regime not too close to T_0 where loop corrections might be small.
- The existence of such a regime would seem to require the existence of "long-range" interactions.
- This does not imply that the intermolecular interactions have to be long-ranged, but just that the parameters c, τ, w_1, w_2 in the functional are such as to make loop corrections small and $w_2/w_1 > 1$ when $T \approx T_A$.
- 'Success' of MCT and RFOT theories suggest that this might be the case! Then only as $T \to T_0$ would the crossover to Ising spin glass behaviour in a field emerge.

Numerical Studies of Ising Spin Glass in a Field

3d spin glasses in a field are being studied by Peter Young.
One-dimensional Ising spin glass – useful illustration of some points:

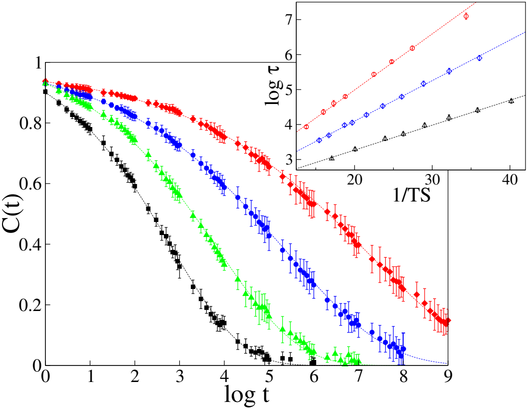
$$\mathcal{H} = -\sum_i J_i S_i S_{i+1} - h \sum_i S_i.$$

In $d = 1$ there is no spin glass phase. $h(T)$ was kept temperature independent, (so entropies are too low to be "realistic").
Glass-like features emerge because of a growing lengthscale as T is reduced.
Size of domains saturates at a lengthscale: ξ at $T = 0$: $J\xi^{\theta} \sim h\xi^{d/2}$
For $d = 1$, $\theta = -1$, so $\xi \sim h^{-2/3}$
$\xi(T)$ and S can be exactly calculated by RG decimation.



S
0.2
0.1
0
a
c
0.6
0.4
0.2
0
Sξ
8
6
4
2
ξ
b
d
7
6
5
4
3
log τ
0
0.1
0.2
0.3
0.4
T

Relaxation time τ: $\langle S_i(t_W) S_i(t + t_W) \rangle_c \sim \exp(-(t/\tau)^\beta)$



- Vogel-Fulcher fit $\tau = \tau_0 \exp[A/(T - T_0)]$ with T_0 similar to T_K works!
- Streched exponential exponent β arises because there is a range of relaxation times.

Conclusions

- A functional can be derived from liquid state theory which maps the glass transition problem onto the Ising spin glass problem in a field.
- Droplet arguments predict that lengthscales should increase as the temperature decreases, but at T_g lengthscales may not be large enough for asymptotic droplet scaling formulae to be appropriate.
- Conventional fits, (Vogel-Fulcher, Kauzmann, Adams-Gibbs) may 'work' in this pre-asymptotic region as well as (possibly) RFOT ideas.