The glass transition, first part

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THESIS

We assume the same old physical picture of Kaufmann, Adams, Gibbs, Dimarzio, Goldstein.

- We can define a configurational entropy $\Sigma(T)$, which goes to zero at the phase transition point.
- Inherent structure dominance.

We add new ingredients.

- We construct a microscopic realization of the previous ideas in the mean field models.
- We assume that *minimal* corrections are present in finite dimensions to mean field predictions.
- The replica method gives tools to do the appropriate computations, both in mean the mean field approach and in short range models.

OUTCOME:

- The properties of glasses can be computed in the framework of replicated liquid theory.
- We have a many valleys picture with detailed predictions on the landscape.

THE MANY VALLEYS PICTURE

Each valley is labeled by a and has a free energy $f_a(\beta)$.

For simplicity let us assume that valley do maintain their identity when changing the temperature.

(in reality they split into smaller valleys when we decrease the temperature).

Under this assumption there is a one to one correspondence among

VALLEYS

and

INHERENT STRUCTURES, i.e. minima of $H(C)$.

THE FREE ENERGY LANDSCAPE.

Let us define a free energy of the density $\rho(x)$:

$$F[\rho]$$

We state which are (in mean field) the properties of the free energy (computable in microscopic models):

- $T > T_c$: One relevant minimum with $\rho(x) = const.$ Many solutions of equation

$$\frac{\delta F}{\delta \rho} = 0, \tag{1}$$

  which are not minima (there are some negative eigenvalues).

- $T > T_c$: the negative eigenvalues become zero. There is an exponentially large number of minima, connected by flat regions.

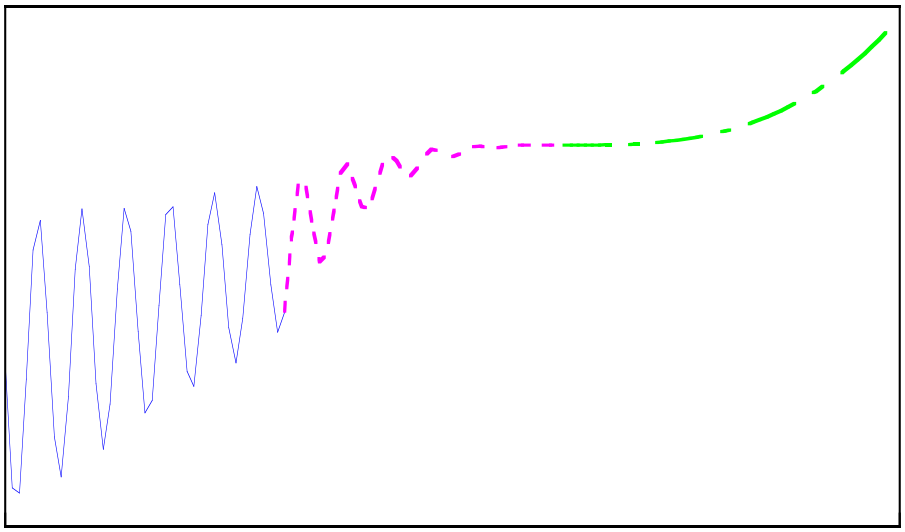
- $T_c > T > T_K$: The number of relevant minima is proportional to $\exp(N\Sigma^*(\beta))$.

  $\Sigma^*(\beta)$ is the configurational entropy or complexity.

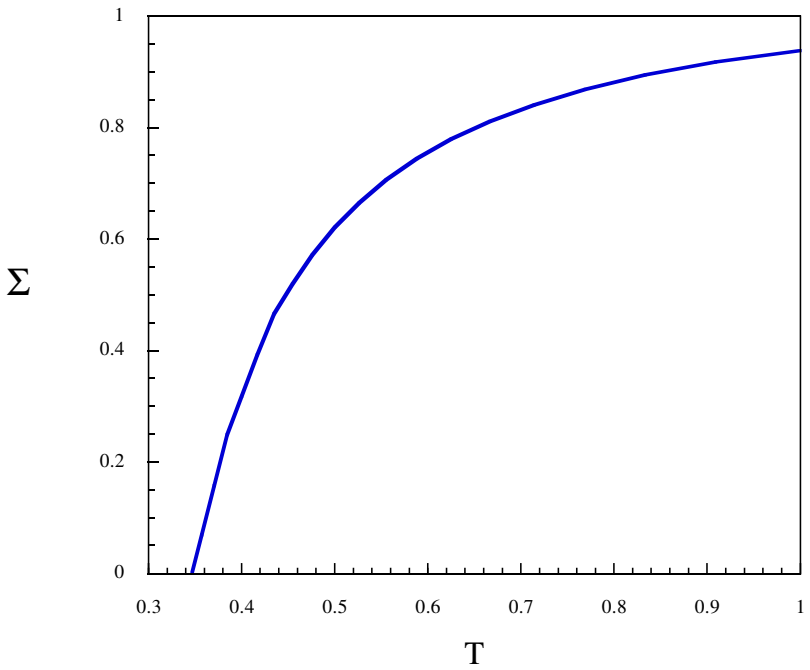
  The minima are separated by barriers that

  - diverge with the number of particles N (mean field)
  - are finite (beyond mean field theory).

- $T_K > T$: The number of relevant minima is finite. The minima are separated by barriers that diverge with N.



All the previous discussions in one artistic ;-) graph.



The equilibrium complexity (these are analytic estimates for LJ binary mixtures).

For $T_c > T > T_K$

there is a dual description: *liquid* and *solid* (with an exponentially large number of different solid structures).

Duality tell us that all the information needed to study the glass can be extracted from the liquid phase.

$$Z(\beta) = \sum_a \exp(-\beta N f_a(\beta)) = \int d\mathcal{N}(f,\beta) \exp(-\beta N f),$$

$f_a(\beta)$ is the free energy density of the valley labeled by a at the temperature β^{-1} ,

$\mathcal{N}(f,\beta)$ is the number of valleys with free energy density (per particle) less than f.

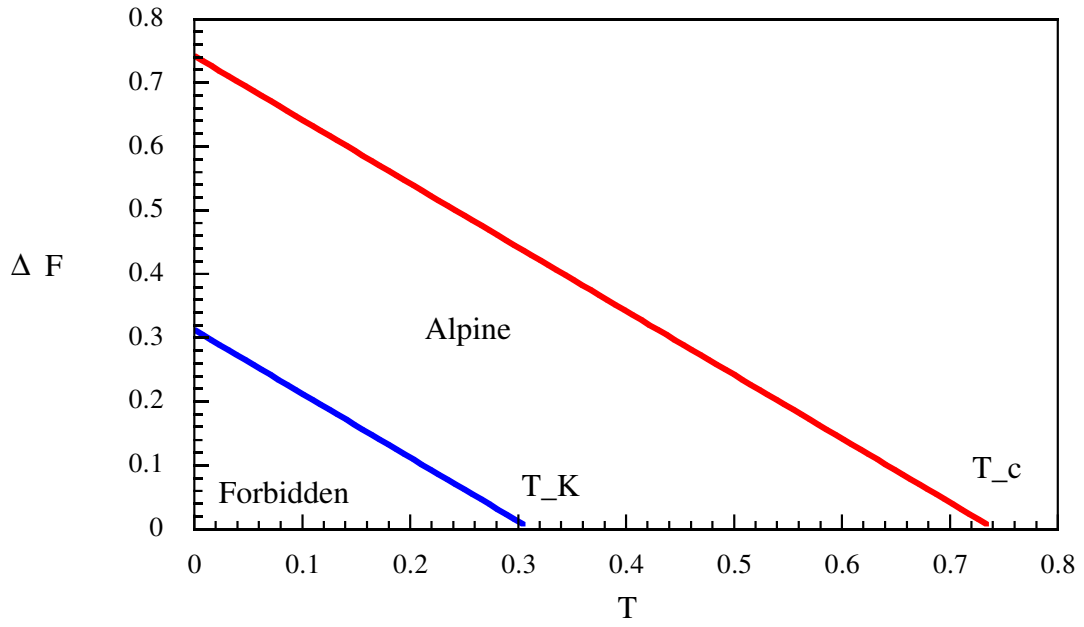
$$\mathcal{N}(f,\beta) = \exp(N\Sigma(f,\beta)),$$

where the configurational entropy, or complexity, $\Sigma(f,\beta)$ is positive in this region and vanishes at $f = f_0(\beta)$.

The quantity $f_0(\beta)$ is the minimum value of the free energy: $\mathcal{N}(f,\beta)$ is zero for $f < f_0(\beta))$.

Free energy excess $\Delta F =$

true free energy - would be liquid free energy.



Alpine region (Mountains and valleys) and the forbidden region.

The barriers go to infinity at T_c and there is dynamical transition. (Mode coupling theory.)

In reality T_c indicates the crossover from entropic regime to energy activated regime.

The thermodynamic transition is at $T = T_K$.

We **need** to know $\Sigma(f,\beta)$.

A SIMPLE STRATEGY

We define

$$Z(\gamma;\beta) \equiv \exp(-N\gamma\Phi(\gamma;\beta)) = \sum_a \exp(-\gamma N f_a(\beta))$$

$$\gamma\Phi(\gamma;\beta) = \gamma f - \Sigma(\beta,f), \quad f = \frac{\partial(\gamma(\Phi(\gamma;\beta)))}{\partial\gamma}. \qquad (2)$$

The complexity can be simply obtained from $\Phi(\gamma;\beta)$ in the same way as the entropy can be obtained from the usual free energy.

We will eventually use duality:

$$Z(\gamma;\beta) =$$
$$\int dC \exp\left(-\gamma H(C) - N\gamma f(\beta,C) + N\gamma f(\gamma,C)\right) =$$
$$\int dC \exp\left(-\gamma H(C) - N\gamma \hat{f}(\beta,C) + N\gamma \hat{f}(\gamma,C)\right),$$

where $\hat{f}(\beta,C) = f(\beta,C) - f(\infty,C)$

and $f(\beta,C)$ is is constant in each valley and it is equal to the free energy density of the valley to which the configuration C belongs.

THE QUENCHED APPROXIMATION:

$$\exp(-A\hat{f}(\beta, C)) = \exp(-A\hat{f}_\gamma(\beta)),$$

where $\hat{f}_\gamma(\beta)$ is the expectation value of $\hat{f}(\beta, C)$ taken with the probability distribution proportional to $\exp(-\gamma H(C))$.

(This quenched approximation would be certainly bad if we were using the free energy $\hat{f}(\beta, C)$ at the place of $f(\beta, C)$).

$$\Phi(\gamma; \beta) = F_{liquid}(\gamma) + \hat{f}_\gamma(\beta) - \hat{f}_\gamma(\gamma),$$

$$\Sigma(\gamma; \beta) = S_{liquid}(\gamma) - S_\gamma(\gamma) + \hat{f}'_\gamma(\gamma) - \hat{f}'_\gamma(\beta),$$

$$\hat{f}'_\gamma(\beta) = \partial \hat{f}_\gamma(\beta)/\partial\gamma.$$

Everything is computable using liquid theory.

Different approximations for $\hat{f}_\gamma(\beta)$,

harmonic, (Einstein, Debay ...).

In many cases we use REPLICAS or CLONES.

We consider systems with m replicas:

C_α with $\alpha = 1, m$.

- Physics is more clear.
- Computations are straightforward.

A crucial concept is the overlap $q(C, C')$:

- $q(C, C')$ is near to 1 for similar configurations
- $q(C, C')$ is near to zero for unrelated configurations.

Example of a possible definition:

$$q(x, y) = 1/N \sum_{i,k=1,N} w(x_i - y_k),$$

$$w(x) = 1 \quad \text{for} \quad x \text{ small}, \; w(x) = 0 \quad \text{for} \quad x \text{ large}.$$

We can define a distance among two configurations

- $d = 1 - q$.
- $d^2 \propto N^{-1} \sum_i (x_i - y_{k(i)})^2$,
  where $y_{k(i)}$ is the position of nearest particle of the second configuration to the i^{th} particle of the first configuration (x_i).

QUENCHED POTENTIAL

$$\exp(-N\beta F(y,\epsilon)) = \int dx \exp(-H(x) + \epsilon N q(x,y)).$$

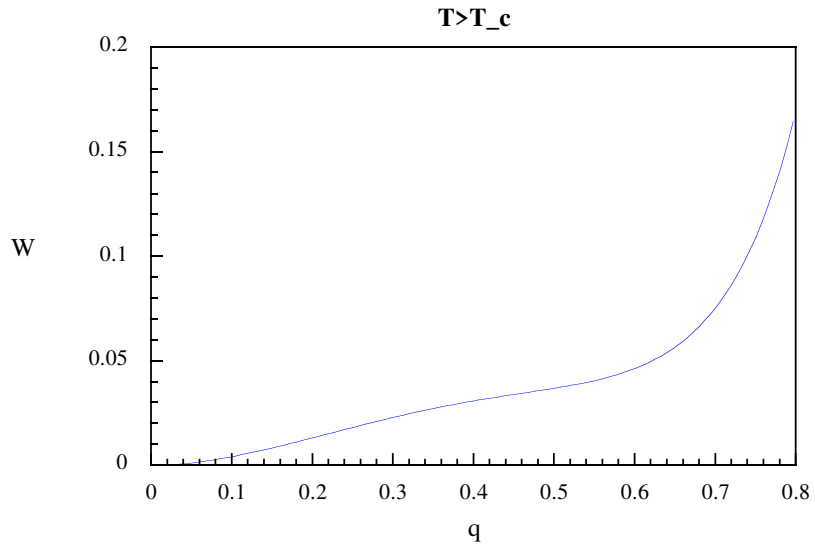
$$F(\epsilon) = \langle \beta F(y,\epsilon) \rangle,$$

where $\langle f(y) \rangle$ denotes the average value of f over equilibrium configurations y at temperature β^{-1}.

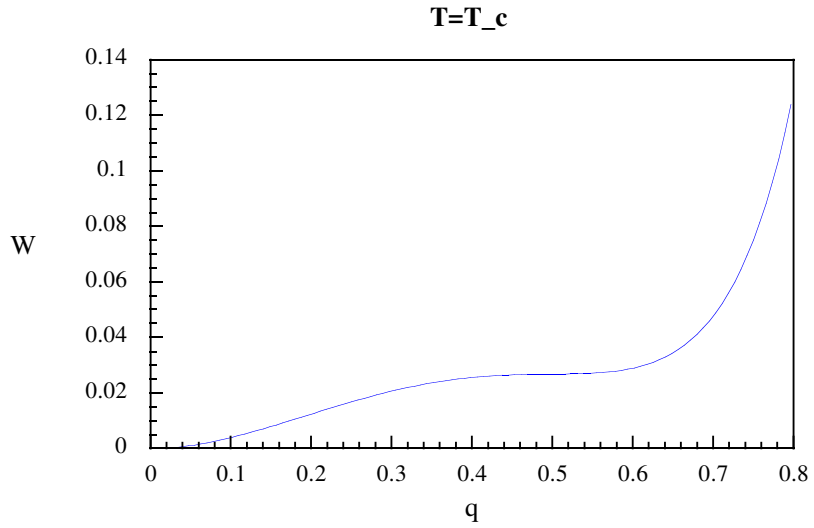
We introduce the Legendre transform $W(q)$ of the free energy

$$q = \frac{\partial F}{\partial \epsilon} \ . \tag{3}$$

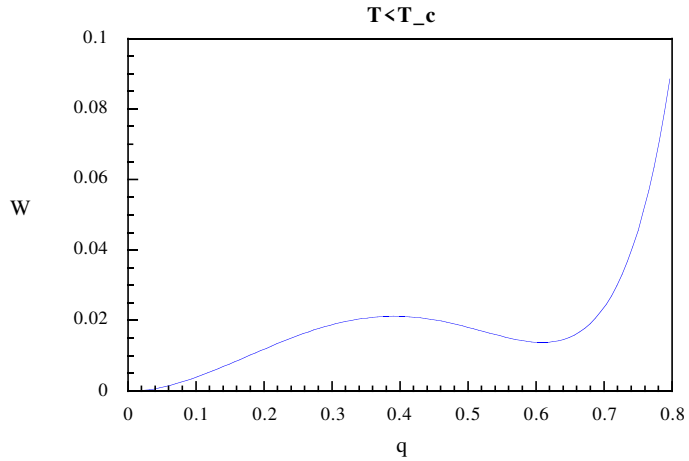
Different shapes of $W(q)$ as function of the temperature.



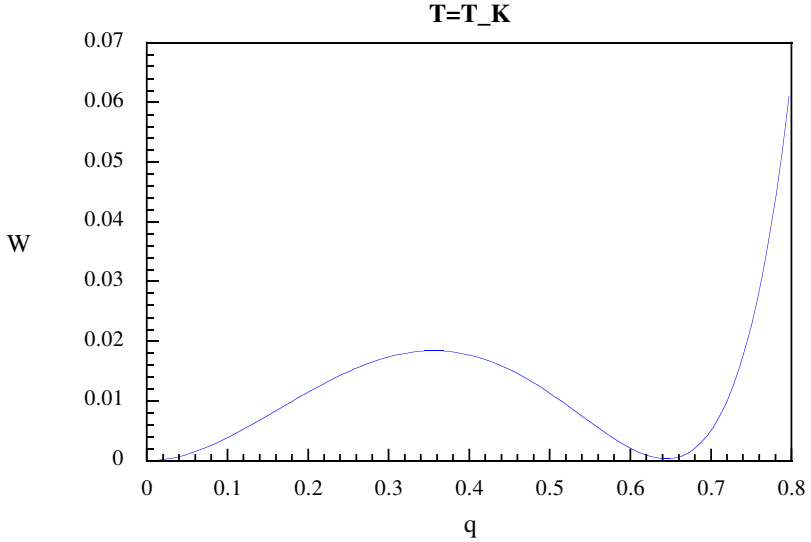
$W(q)$ for $T > T_c$.



$W(q)$ for $T = T_c$.



$W(q)$ for $T < T_c$.



$W(q)$ for $T = T_K$.

Take care of the Maxwell construction!

T_c is in the metastable region.

ANNEALED POTENTIAL with m clones

$$\exp(-Nm\beta F(\epsilon, m)) =$$
$$\int dx \exp(-\sum_\alpha H(x_\alpha) + \epsilon N \sum_{\alpha,\gamma} q(x_\alpha, y_\gamma)).$$

This can be defined also for non integer m

- By analytic continuation from integer m.
- By the compact formula
  $\exp(-Nm\beta F(\epsilon, m)) = \int d\mu[\phi] Z[\phi]^m$,
  where $\phi(x)$ has a Gaussian distribution and
  $\int d\mu[\phi] = 1, \quad \int d\mu[\phi]\phi(x)\phi(y) = \epsilon w(x-y)$
  $Z[\phi] = \int dx \exp\left(-H(x) - \sum_\alpha \phi(x_\alpha)\right)$

The annealed free energy can be written in terms of the the free energy of the valleys:

$$\exp(-Nm\beta F(\epsilon, m)) = \sum_{a_1} \dots \sum_{a_m}$$

$$\exp(-\beta N \sum_{\alpha=1,m} f_{a_\alpha}(\beta) + N\epsilon \sum_{\alpha,\gamma=1,m} q(a_\alpha, a_\gamma))$$

By Legendre transform we get a free energy $F(m, q)$ which has a shape similar to $W(q)$:

$$mF(m, q) = A + (m-1)W(q) + O((m-1)^2).$$

For $\epsilon = 0$ the contribution at q at the non trivial minimum is when all the m replicas stay in the same valley.

$$\exp(-Nm\beta F(0, m)) = \sum_a \exp(-m\beta N f_a(\beta))$$

It follows that

$$\beta F(0, m)) = \gamma\Phi(\gamma; \beta)), \tag{4}$$

where $\gamma = m\beta$.

Free energy of the valleys Φ is thus equal free energy $F(0, m)$ of m clones with high overlap.

The true free energy can be obtained by *maximizing* $F(0, m)$ with respect to m.

(This is the old replica recipe)

It is crucial to compute $F(0, m)$.

It is not too difficult because in some sense we are in the liquid phase.

This can be done in two different ways:

- We can use liquid theory for molecules.
- For soft potentials we can construct a small cage expansion.

  We set

  $x_\alpha(i) = x(i) + \delta x_\alpha(i)$,

  where

  $\sum_\alpha \delta x_\alpha(i) = 0$.

  There are only quadratic and higher terms in δx.

  (i.e. no linear term).

Before seeing how to perform the computations in details it would be useful to look better to the phase diagram in the β ϵ m space.

We now segue into the second part of the talk.

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