The Physics of the Glass Transition

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A short summary.

1. Glasses: phenomenological considerations
2. The glass transition: theoretical interpretation
3. Complexity
4. A divergent dynamical correlation length
5. Open problems

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Glasses $\Longrightarrow$ Liquids that do not crystallize

(to be precise: they also do not quasi-crystallize).

Two possibilities:

- The liquid does not crystallize because it is cooled very fast: the crystallisation time may become very large at low temperature.

  Example: hard spheres at high pressure (high pressure $\Leftrightarrow$ low temperature).

- The liquid does not crystallize even at equilibrium.

  Example: a binary mixture of hard spheres with different radius

  50% type A, 50% type B, $R = r_B/r_A$,

  if $.77 < R < .89$ (the bounds may be not precise).

  The amorphous packing is more dense than a periodic one, distorted by defects.

OTHER HAMILTONIANS

$$a = 1, M;\ N(a) = Nc(a);\ \sum_a c(a) = 1.$$

e.g. $M = 2$, $c(1) = .8$, $c(2) = .2$

$$H = \sum_{a,b=1,M} \sum_{i=1,N(a)} \sum_{k=1,N(b)} V_{a,b}(x_a(i) - x_b(k))$$

$M(M+1)/2$ functions $V_{a,b}(x)$ describe the model.

EXAMPLES

Soft spheres (non-realistic, but simple)

$$M = 2,\ c(1) = .5,\ c(2) = .5,\ V_{a,b}(x) = R_{a,b}x^{-12}$$

Lennard-Jones (realistic)

$$M = 2,\ c(1) = .8,\ c(2) = .2,$$
$$V_{a,b}(x) = R_{a,b}x^{-12} - A_{a,b}x^{-6}$$

OTHERS

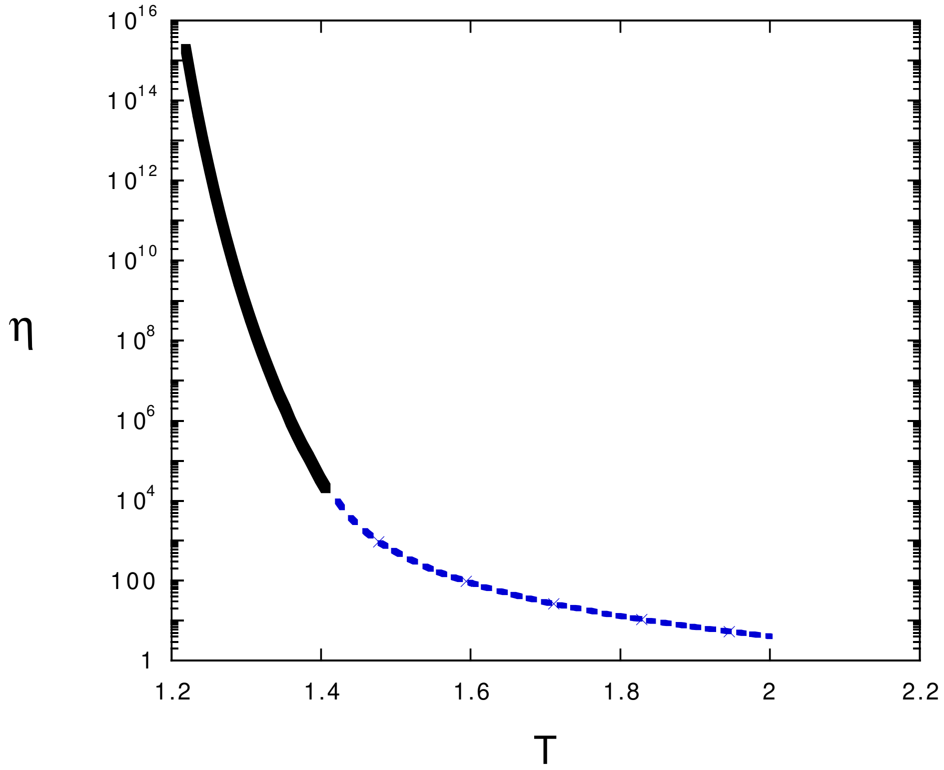
Short polymers, asymmetric molecules (e.g. OTP) ...

VISCOSITY: System in a box of large volume V.

$T_{\mu,\nu}(t)$ is the total stress tensor.

$$\langle T_{\mu,\nu}(t) T_{\rho,\sigma}(0)\rangle = V S_{\mu,\nu,\rho,\sigma}(t)$$

$$\eta \propto \int dt S(t) \approx \tau^{-\alpha},\ \alpha = 1?$$



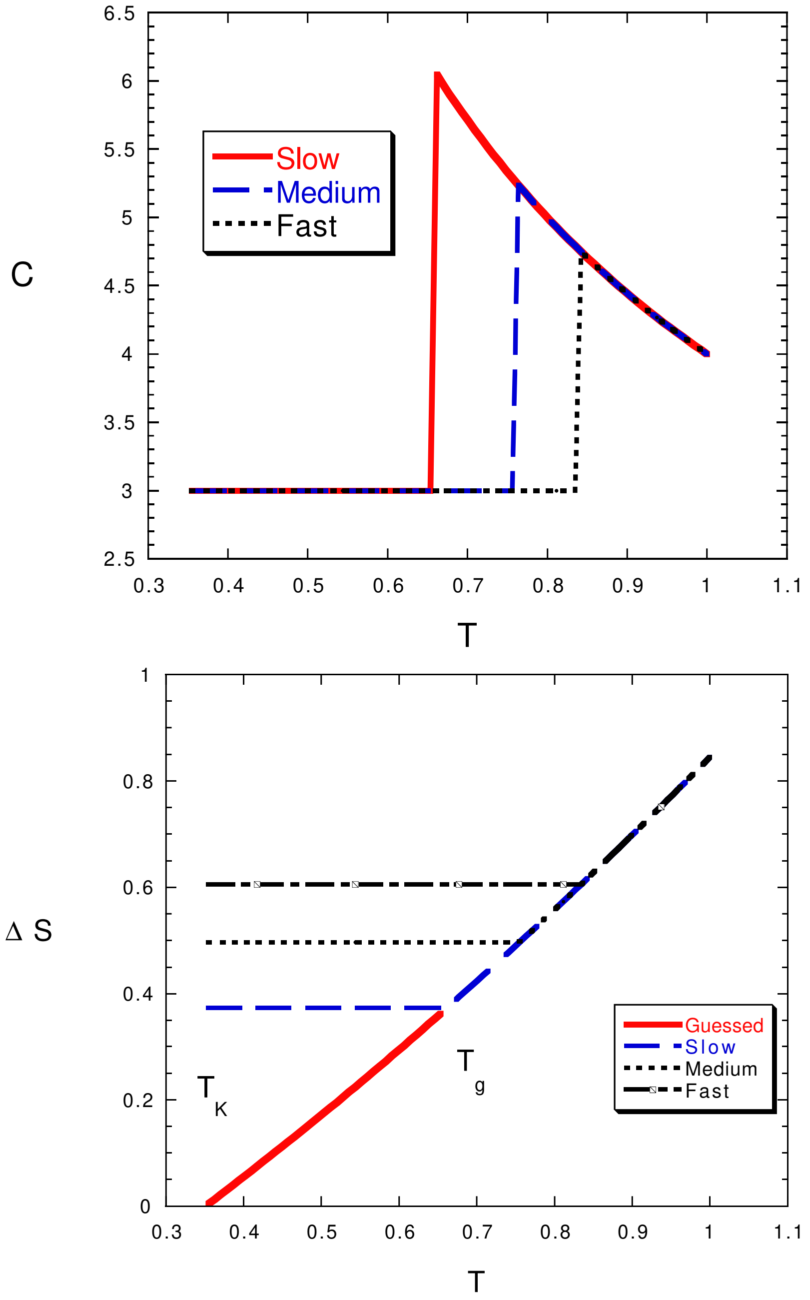
$\eta \propto \exp(A(T - T_K)^{-1})$ Vogel Fulcher law (1921)
($T_K = 1$ full line)

$\eta \propto (T - T_c)^{-\gamma}$ mode coupling theory (1983)
($T_K = 1.375$ dotted line)

No transition at T_c

FRAGILE glasses $T_K \neq 0$; STRONG glasses $T_K \approx 0$.

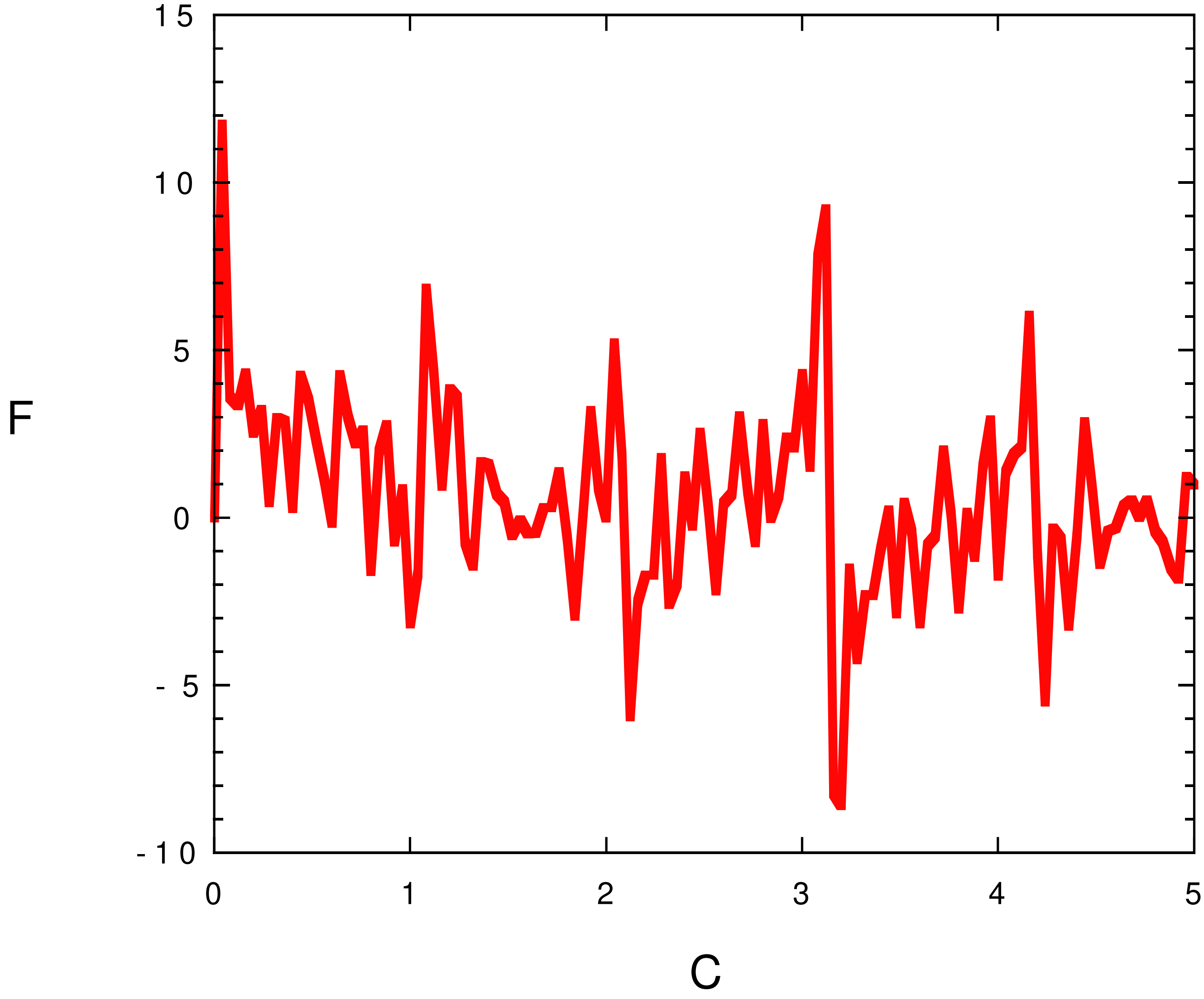
Specific heat depends on cooling rate.



$$\Delta S(T_B) \text{ versus } T_B$$

$$\Delta S = S(liquid) - S(crystal)$$

Glass $\Longrightarrow$ frozen liquid



Many valley or states

$Z = \sum_a \exp(-\beta N f_a)$ is dominated by $f = f^*(\beta)$

Number of minima at the free energy $f^*(\beta)$:
$\exp(N\Sigma(\beta))$

$\Sigma(\beta) \approx \Delta S$: Configurational entropy or Complexity

OLD THESIS

- The configurational entropy $\Sigma(T)$, goes to zero at the phase transition point.
- The partition function is dominated by configurations neat to minima also in the fluid phase (Inherent structure dominance or duality).

We recently 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).

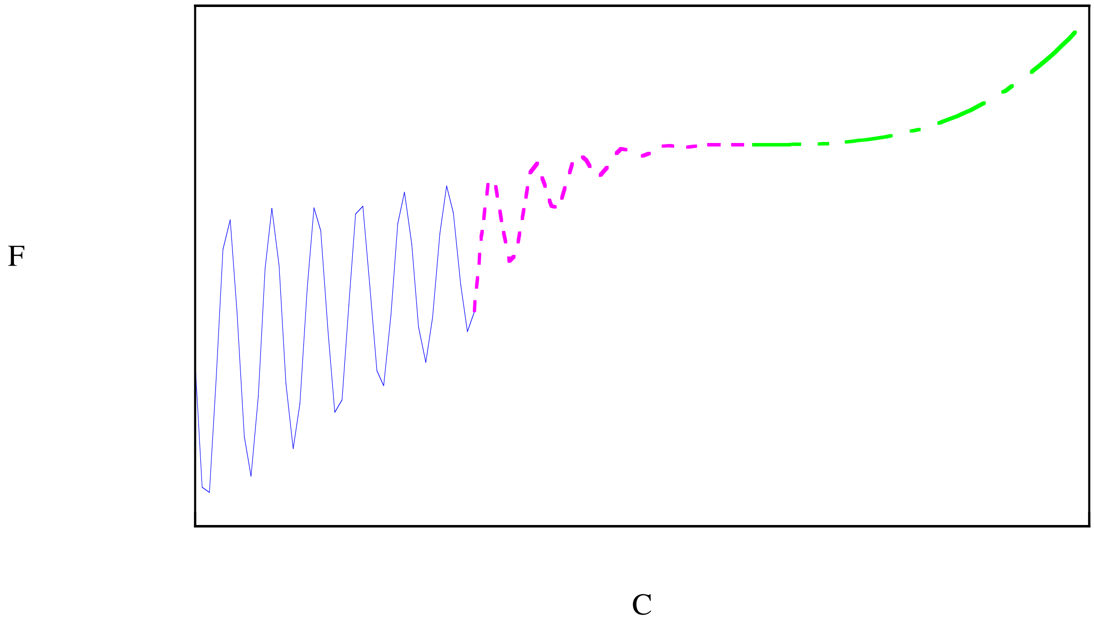
- $T = T_c$: the negative eigenvalues become zero.
  There is an exponentially large number of minima, connected by flat regions.

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

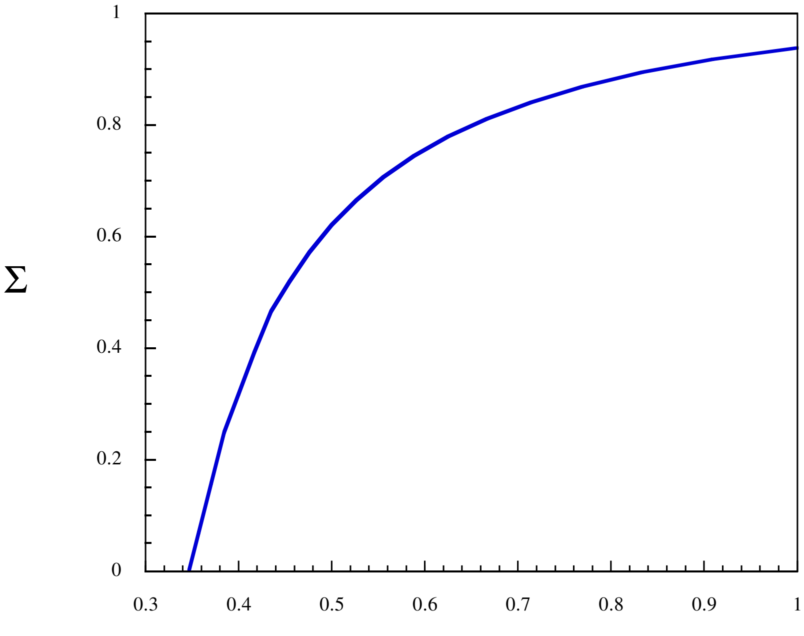
  $\Sigma^*(\beta)$ is the configurational entropy or complexity.

  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.

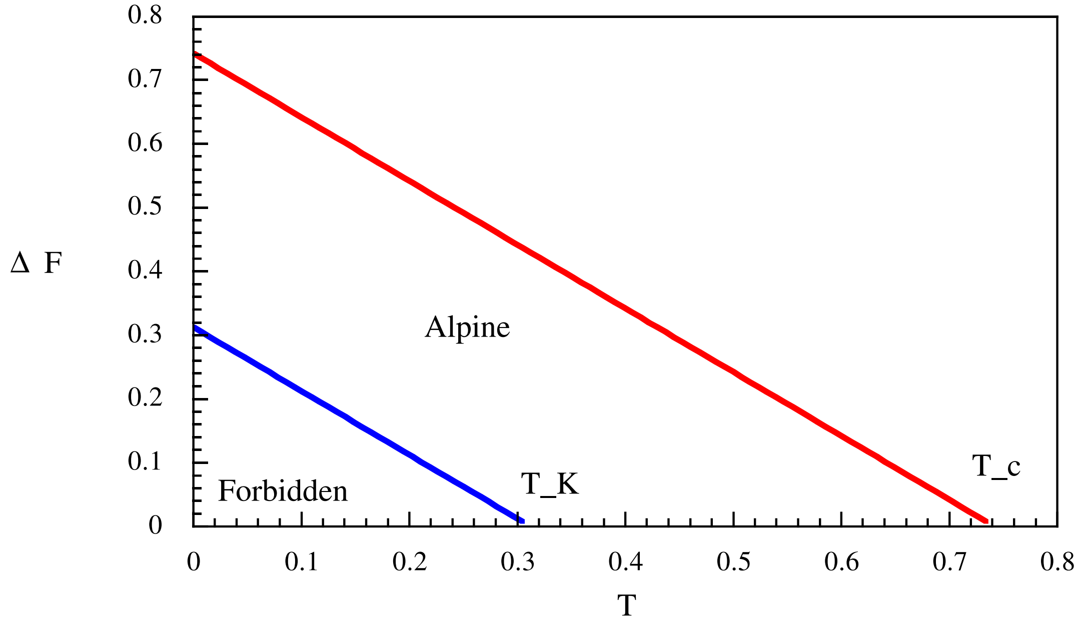
$$\mathcal{N}(f,\beta) = \exp(N\Sigma(f,\beta)),$$

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 ΔF =

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.

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

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

$$\left(\beta F(\beta) = \beta E - S(E), \quad E = \frac{\partial(\beta(F(\beta)))}{\partial\beta}.\right)$$

The complexity is obtained from $\Phi(\gamma;\beta)$ in the same way as the entropy is obtained from the usual free energy:

$$\Sigma(\beta,f) = \frac{\partial\Phi(\gamma;\beta)}{\partial\gamma} \; ; \; \left(S(E) = \frac{\partial F(\beta)}{\partial\beta}\right)$$

- In the new formalism γ plays the same role of β in the usual formalism.
- In the new formalism β only labels the free energy landscape which is sampled.
- When $\beta \to \infty$ we sample the energy landscape:
  $Z(\gamma;\beta=\infty) = \sum_a \exp(-\gamma N e_a)$
  where e_a are the energy density of the minima of the Hamiltonian.
- The equilibrium complexity is given by
  $\Sigma^*(\beta) = \Sigma(\beta;\beta)$

It is convenient to write

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

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

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

We will eventually use duality and liquid theory to evaluate the properties of $\hat{f}(\beta,C)$:

A simple approximation

THE QUENCHED APPROXIMATION:

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

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

The quenched approximation would be exact if all the valleys at a given temperature (also with different free energy) would have the same entropy.

(Energy fluctuates, not entropy)

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

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

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

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

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

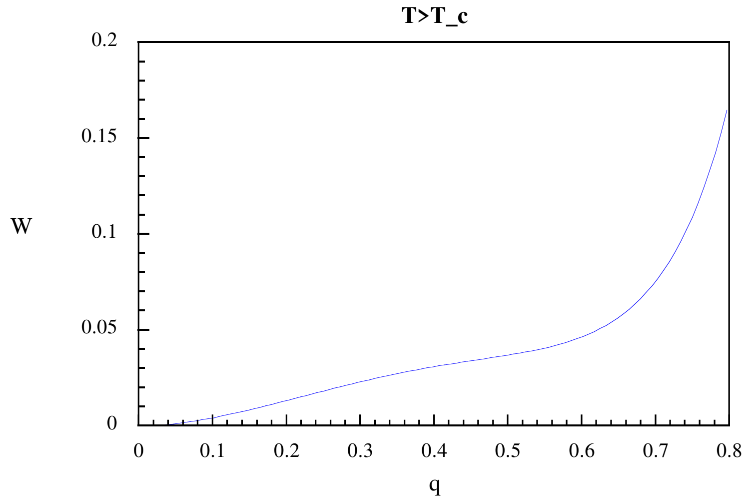
$$F(\epsilon) = \langle \beta F(y,\epsilon) \rangle,$$

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

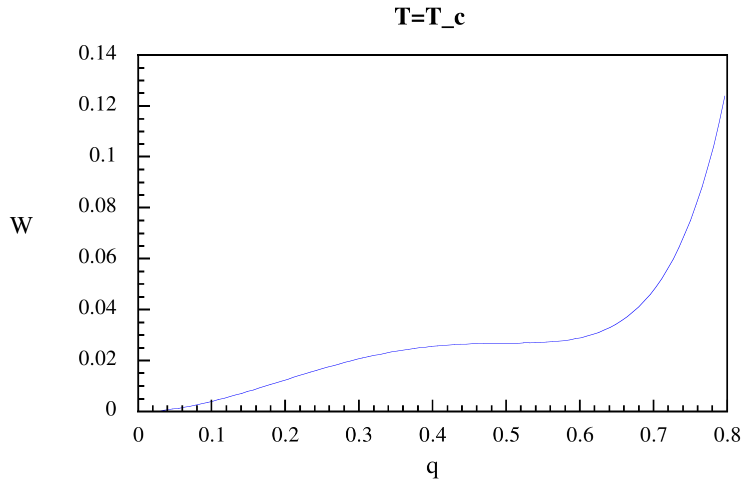
We introduce the Legendre transform $W(q)$ of the free energy

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

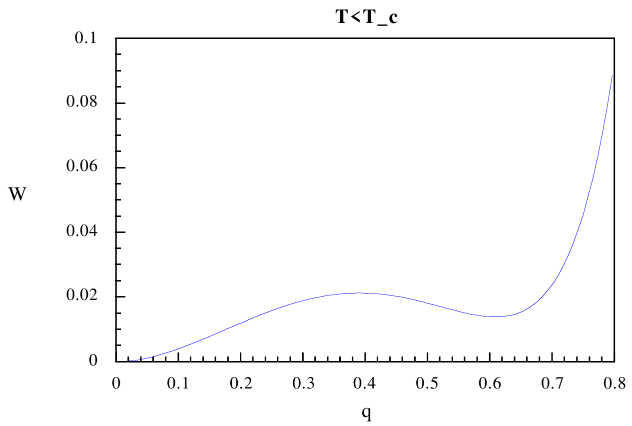
Different shapes of $W(q)$ as function of the temperature.



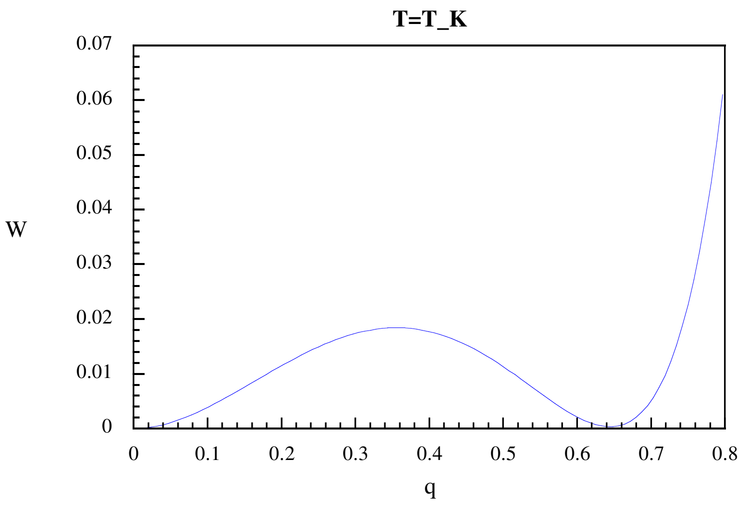
$W(q)$ for $T > T_c$.



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



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



$W(q)$ 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

$$\beta F(0,m)) = \gamma\Phi(\gamma;\beta)),$$

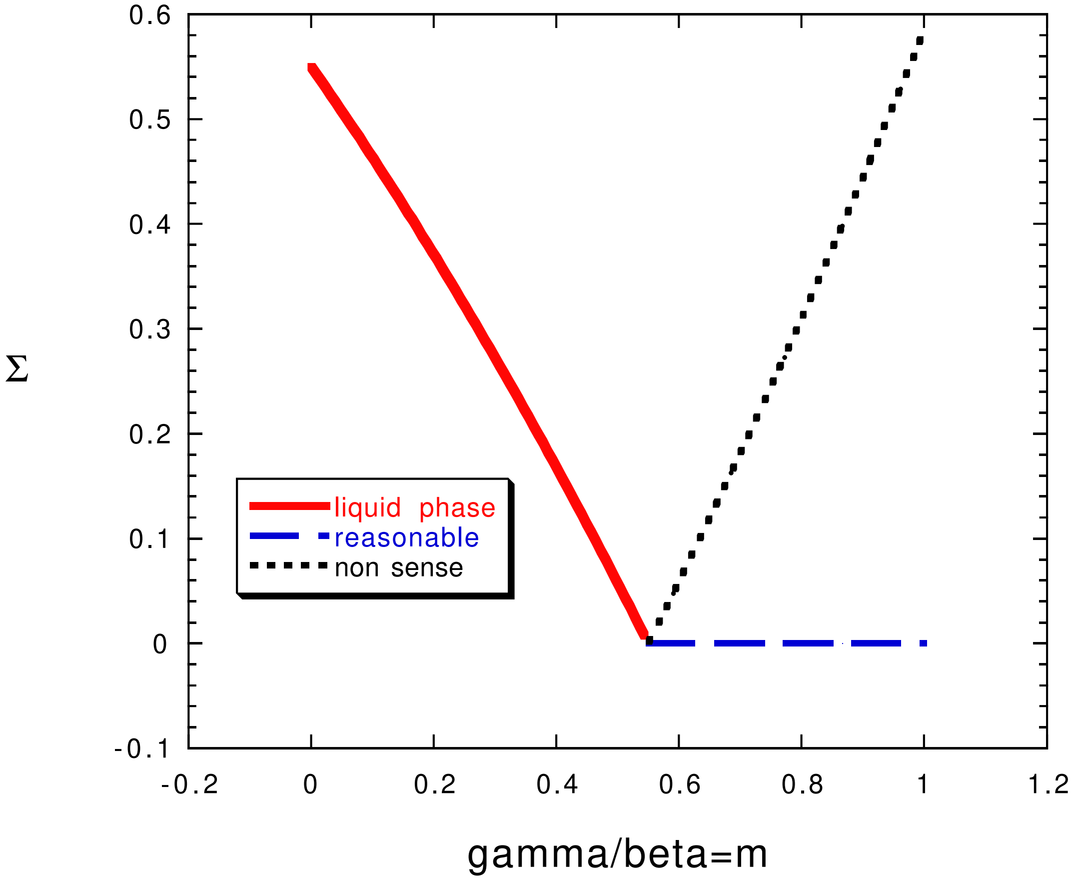
where $\gamma = m\beta$.

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

A POSSIBLE SCENARIO

We compute in the liquid phase $\Phi(\gamma;\beta))$ and $\Sigma(\gamma;\beta))$.

We find for $\gamma > \gamma_c$ (we stay in the liquid phase)



$$\Sigma(\gamma_c;\beta) = 0 \Longleftrightarrow \frac{\partial\Phi(\gamma;\beta)}{\partial\gamma}|_{\gamma_c}$$

If $\Sigma(\gamma;\beta) = 0$ for $\gamma > \gamma_c$

$$\Phi(\gamma;\beta) = \Phi(\gamma;\beta) = \Phi(\beta;\beta) \text{ for } \gamma > \gamma_c.$$

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

This is the old replica recipe (Monasson)

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.

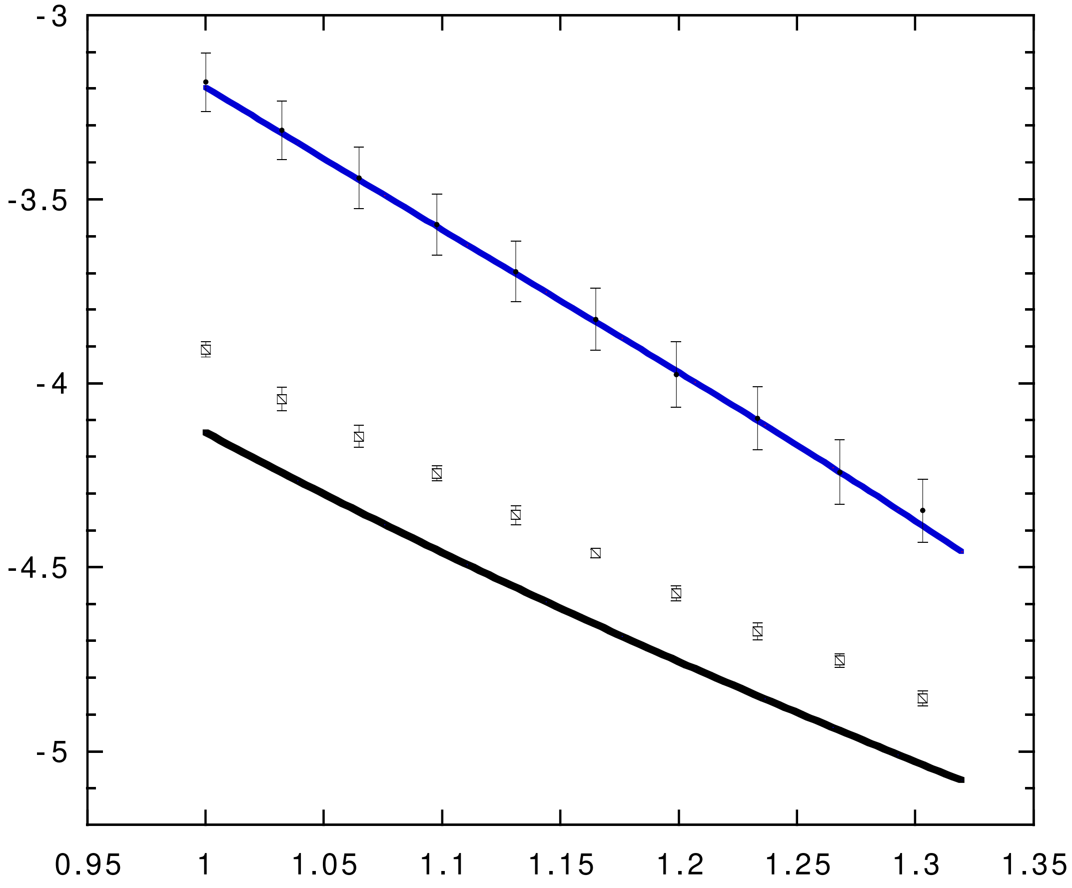
  (i.e. no linear term).

SOME RESULTS

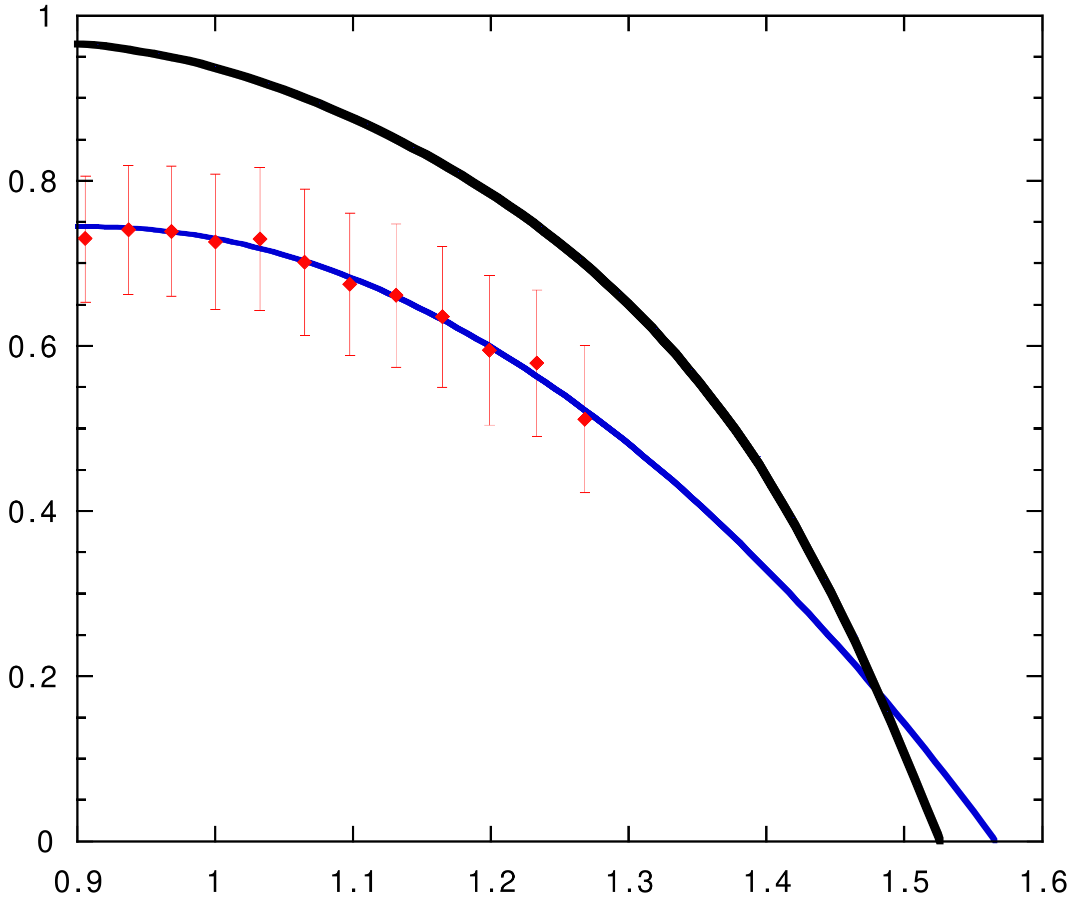
LJ 20-80 binary mixture

$$\Sigma(\beta)) = S_{liquid}(\beta) - S_{harmonic}(\beta) + \dots$$

$$S_{harmonic} = \frac{1}{2} \ln \det \left(\frac{\partial^2 H}{\partial x(i) \partial x(k)} \right)$$



Analytic and numerical entropies as function of $T^{-.4}$



Analytic and numerical complexity as function of $T^{-.4}$

Transition characterized by vanishing of the complexity.

At low temperature below T_K the system stays only in a few valleys.

$$\Longrightarrow$$

Replica symmetry breaking

Characteristic violations of Fluctuation Dissipation theorem in off-equilibrium dynamics.

OPEN PROBLEMS

I would like to know more on:

- No static divergent length (four particle correlations)?
- Barriers among valleys.
- Overlap distributions on small (and larger) systems.
- Phase diagrams with coupled replicas.
- Violations of fluctuation dissipation theorem in off-equilibrium dynamics.
- Strong glasses ?
- Quantum glasses: low temperature behaviour. A quantum phase transitions at a few milliKelvins?

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