Slightly off-equilibrium dynamics

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Many progresses have recently done in understanding system who are slightly off-equilibrium because their approach to equilibrium is quite slow.

In this talk I will shortly discuss:

• A mini introduction to structural glasses.

• Aging in glasses

• The replica potential as a distinctive tool.

• Fluctuation dissipation relations.
Spin glasses and structural glasses.

The main differences between spin glasses and structural glasses are the following:

- In structural glasses the Hamiltonian is translational invariant: there is no quenched disorder.

- In spin glasses a quenched disorder is present and the system is no more translational invariant.

Glasses and spin glasses have many qualitative features in common; moreover different spin glasses may belong to quite diverse universality classes.

Let me start with structural glasses, however the same toolbox can be used for spin glasses.
An impressive increase of the viscosity (Angell’s Plot)

Strong glasses: $\eta \propto \exp \left( \frac{B}{T} \right)$

Fragile glasses: $\eta \propto \exp \left( \frac{B}{T-T_K} \right)$
(Time dependent specific heat)

\( C \) vs \( T \)

\( \Delta S \) vs \( T \)
Schematic view of the internal energy as function of the temperature:

The position of the dynamic line slightly (on a logarithmic scale) depends on the cooling speed.
Artistic views of the free energy landscape:

In the transition region.

Deep in the many valleys region.
Collective Behaviour

Slowing down is a collective phenomena. $\xi(T)$ is the size of collective rearranging regions.

The correlation time diverge with $\xi(T)$. This leads to dynamical heterogeneities.

Mean field Scenario

- Conventional slowing down

$$\tau \propto \xi^z$$

- Activated barriers:

$$\tau \propto \exp(\beta \Delta E) \quad \Delta E \propto \xi^\theta.$$ 

if $\xi^{-1} = \frac{B}{T-K} \text{ and } \theta = 1$, then

$$\tau \propto \eta \propto \exp\left(\frac{B}{T-K}\right)$$
Mean field scenario

Many soluble models with long range forces where correlations can be neglected or tamed.

Loop expansion around the mean field solution.

Renormalization group computations.
Strong slowing down appears when decreasing the temperature

Two time scales: the first one to thermalize in one valley the other one for going from one valley to an other valley.

We plot some correlation function approaching the glass temperature. We see the formation of a plateaux that becomes longer and longer.
What happens if we do experiments at time scales smaller than $\tau_{eq}$. We are naturally in this condition when $\tau_{eq} > 100$ years.

We have to consider Aging (aging of the sample, not of the observer!). If we measure something at time $t_w$ it depends on $t_w$.

If we do a measurement of something (e.g. $\chi(t_w, \omega)$) we may expect that the $t_w$ dependence is stronger at small $\omega$.

Naive aging:

$$\chi(t_w, \omega) = F(\chi(t_w \omega))$$

We study the correlation between two different configuration: $C(t_w + t, t_w)$ is the correlation between the configuration at at time $t_w$ and the configuration at time $t + t_w$. Naive aging:

$$C(t_w + t, t_w) = B(t/t_w)$$

Similar things for response and relaxation functions.
Molecular dynamics of binary liquids.

Aging: $C(t_w + t, t_w) \approx G(t/t_w)$. The correlations with a configuration of age $t_w$ decays with a time scale that is roughly proportional to $t_w$. 
Aging in Monte Carlo simulations of a 3-d spin glass (Janus collaboration).

$10^{11}$ time steps
A key concept is the overlap.

We define an overlap $q$ between two configurations. For example in spin models

$$q(\sigma, \tau) = \frac{\sum_i \sigma_i \tau_i}{N}.$$  

We can normalize the overlap in such a way that $q = 1$ for identical configurations and $q = 0$ for uncorrelated configurations.

Often the two-times correlation function is the overlap of the configuration at time $t_w$ with the configuration at time $t + t_w$

$$C(t_w + t, t_w) = q(\sigma(t_w + t), \sigma(t_w)).$$

The overlap can be used to define the order parameter also in usual cases.
The overlap and the order parameter.

- Let us consider a case where the ground state of the system is unique (apart a group transformation, if there is a symmetry group). If \( \sigma^* \) is a ground state, the order parameter is just \( q(\sigma, \sigma^*) \). In a ferromagnet the ground state is \( \sigma_i^* = 1 \) and the overlap with the ground state is the spontaneous magnetization.

- The previous definition works if the configurations at \( T = 0 \) are very similar to those at \( T \neq 0 \). For a real material the lattice spacing depends on the temperature and the previous definition fails.

- In this last case we can define the order parameter for a crystal by taking two configurations (\( \sigma \) and \( \tau \)) and looking to

\[
q_{\text{max}} \equiv \max_{\text{translations}} q(\sigma, \tau_{\text{translated}}).
\]

- The previous quantity \( (q_{\text{max}}) \) is large also when the systems have a unique disordered ground state.
The replica potential

We consider an equilibrium configuration $\sigma$. We consider a restricted partition function $Z(q)$ where we sum over all the configurations that are at an overlap $q$ with the configuration $\sigma$.

$$\frac{Z(q)}{Z} = \exp(-NW(q)) .$$

$W(q)$ is $\beta$ times the increase in free energy for restricting to those configurations with overlap $q$ with a generic configuration.

In other word:

$\exp(-NW(q))$ is the typical probability of finding a configuration with overlap $q$. 

For sake of precision

\[ W(q) = - \lim_{N \to \infty} \frac{1}{N} \int d\sigma P_B(\sigma) \log \left( \int d\tau P_B(\tau) \delta(q(\sigma, \tau) - q) \right), \]

where \( P_B(\sigma) \) is the Boltzmann probability of \( \sigma \).

In the nutshell \( W(q) \) is the derivative respect to \( n \) (at \( n = 0 \)) of the partition function of \( 1 + n \) replicas where all the replicas (but the first one) have overlap \( q \) with the first replica.

\[ W(q) = \frac{d}{dn} \left( \lim_{N \to \infty} \frac{1}{N} \log \left[ \left( \prod_{i=1,n} d\sigma_i P_B(\sigma_i) \right) \left( \prod_{k=2,n} \delta(q(\sigma_1, \sigma_k) - q) \right) \right] \right) \bigg|_{n=0} \]
The dynamical transition

The value of $W(q^*)$ at the secondary minimum is the configurational entropy $\Sigma_C$. Indeed the probability of a given valley is $\exp(-NW(q^*))$ and their number is $\exp(NW(q^*))$. 
Schematic behaviour of the Configurational Entropy $\Sigma_C$

$\Sigma_C$ is sometime called Complexity.
Numerical and theoretical estimates of the configurational entropy for three dimensional soft spheres:

\[
\text{Total Entropy} = \text{Harmonic Entropy} + \text{Configurational Entropy}
\]
Two temperatures: Cugliandolo Kurchan

- Short times: the standard temperature measured with fast thermometers.
- Long times: jumping between valleys: an higher temperature.

Number of valleys as function of the free energy of the valley $F$.

$$\mathcal{N}(F) \propto \exp(\beta'(F - F_0))$$

The higher temperature is $T' = 1/\beta'$. 
Fluctuation dissipation theorem equilibrium.

We have a response (relaxation function) $R(t)$ and the correlation function $C(t)$. We eliminate the time $t$ in a parametric way: we define $R(C)$. FDT implies that

$$\frac{dR}{dC} = -\frac{1}{T}$$

Off-equilibrium fluctuation dissipation relations (Cugliandolo Kurchan)

We have $R(t_w, t)$ and $C(t_w, t)$. For large values of $t_w$ we eliminate the time $(t)$ in a parametric way: we find

$$\frac{dR}{dC} = -\frac{1}{T(C)}$$

Two temperatures scenario

- For $C > C_{plateaux}$ $T(C) = T$
- For $C < C_{plateaux}$ $T(C) = T^*(T)$
Simulations (spin glasses)
and absolute theoretical prediction.

Experiments (spin glasses)
Numerical simulations in glasses (Silica)

\[ x(T) \equiv \frac{T}{T^*} \]

i.e. \( T^* \) is temperature independent from \( T \) at small \( T \) as theoretical expected.
Open problems

- Renormalization group computations for dynamics heterogeneities (partially done).
- Better observation of dynamics heterogeneities.
- Analytic computation of the critical exponents neat $T_K$ and their measurement.
- Careful experimental study of fluctuation dissipation relations.
- Detailed theoretical predictions and comparison with observations.


arXiv:0903.4264: Supercooled Liquids for Pedestrians, Andrea Cavagna