Aging

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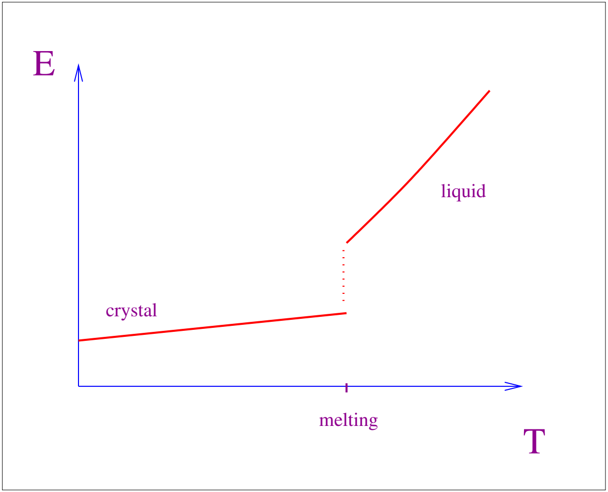
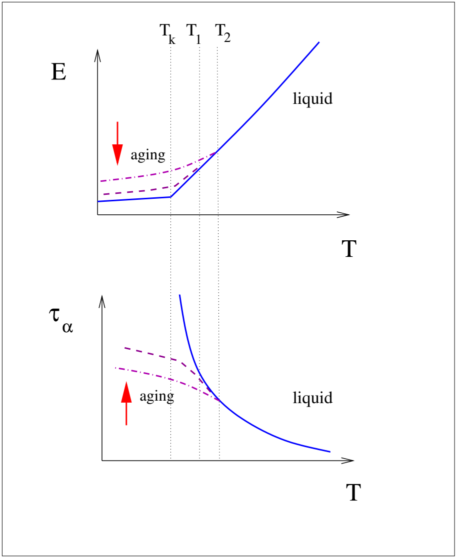
Aging

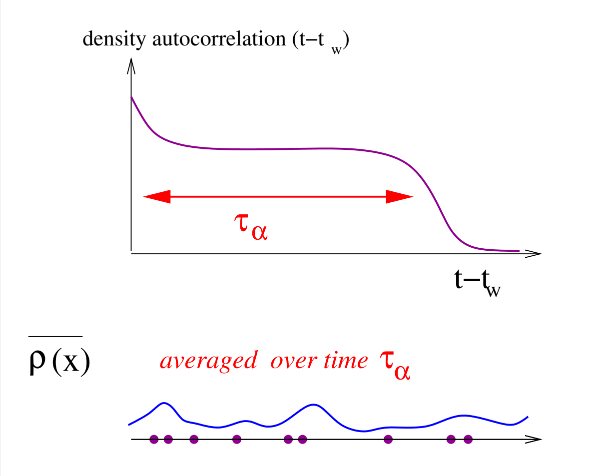


E versus T – or V versus $1/P$.

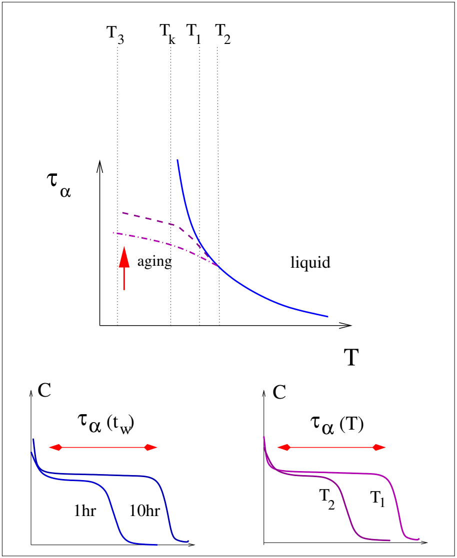
Glassy solid:

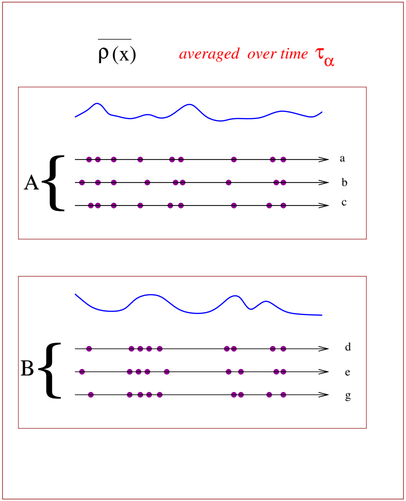


(less and less) transient density profiles

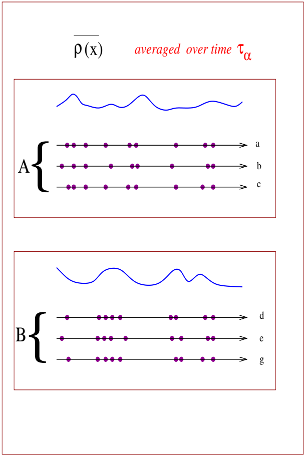


The α scale, in and out of equilibrium

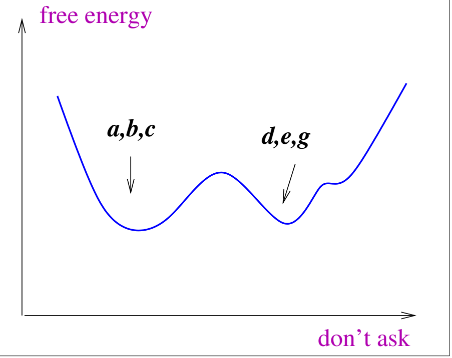




If $\tau_\alpha = \infty$ we have true states


$\overline{\rho(x)}$
averaged over time τ_α
A
a
b
c
B
d
e
g

landscape

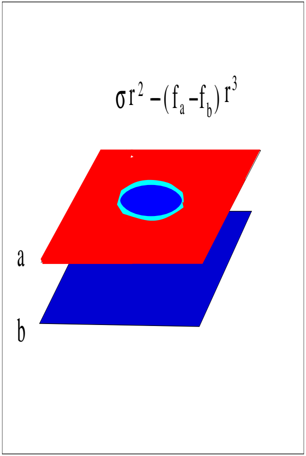

free energy
a,b,c
d,e,g
don't ask

Two nucleation arguments show that it is impossible to have stable states

- **with free energy density higher than equilibrium**

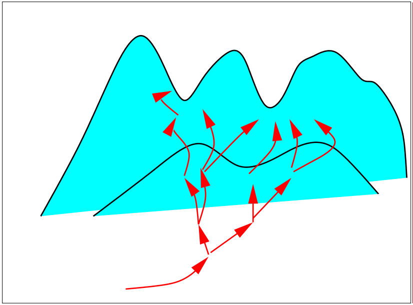
or

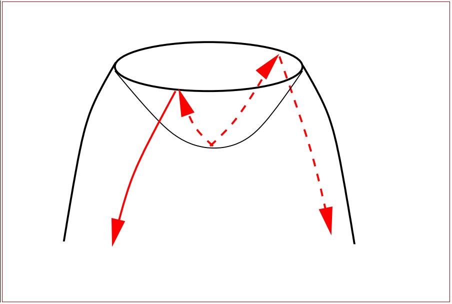
- **exponential in number**



$$r^* = \frac{(2)\sigma}{3(f_a - f_b)} \quad \rightarrow \quad f(r^*) \propto \frac{\sigma^3}{(f_a - f_b)^2}$$

Entropic pressure: multiplication of possibilities helps climb high mountains





$$V_{eff} = V(r) - T(d-1)\ln r$$

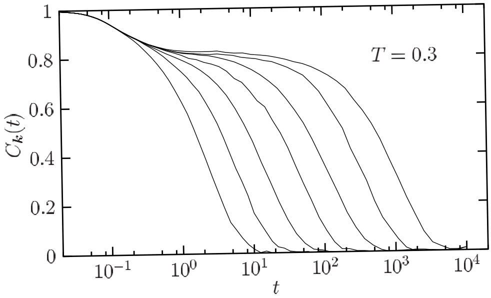
Glasses in this non-ideal world ***age***

they are continuously evolving into more and more equilibrated configurations

or, alternatively, they are continuously nucleating better and better equilibrated phases

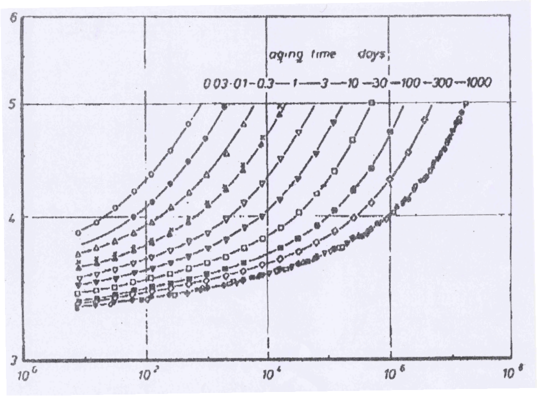
evolution becomes slower as time passes

Aging



Autocorrelation of density fluctuations (Lennard-Jones system, Kob-Barrat)

Aging



the stretching of a plastic bar, from an hour to four years old (Struik)

correlations and responses

A quantity:

$$\rho_k(t) = \int dx\ cos(kx)\rho(x,t)$$

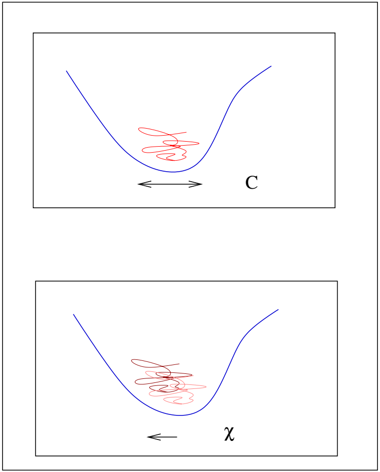
The correlation of its fluctuations:

$$C_k(t,t_w) = \langle \rho_k(t)\rho_k(t_w) \rangle$$

The response at time t to a conjugate field $h\rho_k$ acting from time $-\infty$ to t_w

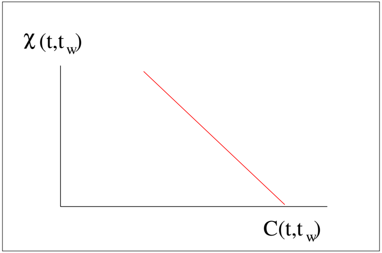
$$\chi(t,t_w) = \frac{\delta \langle \rho_k(t) \rangle}{\delta h}$$

In equilibrium one should expect χ and C to be related:



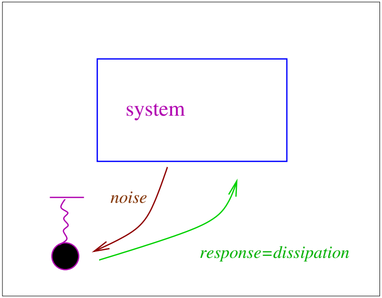
indeed:

$$T\chi(t,t_w) = C(t,t) - C(t,t_w) \qquad \text{or} \qquad T\frac{\partial\chi(t,t')}{\partial t'} = -\frac{\partial C(t,t')}{\partial t'}$$



the fluctuation-dissipation theorem says something important about thermalisation:

$$\mathbf{E}^* = E + x\rho_k + \frac{p_x^2}{2} + \frac{\omega^2 x^2}{2}$$



the fluctuation-dissipation theorem says something important about thermalisation:

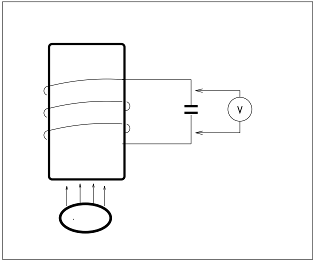
$$\mathbf{E}^* = E + x\rho_k + \frac{p_x^2}{2} + \frac{\omega^2 x^2}{2}$$

$\ddot{\mathbf{x}} = -\omega \mathbf{x} - \rho_\mathbf{k}$ **but** $\rho_k = \underbrace{[\rho_k]_o}_{bare} + \underbrace{\int_\infty^t dt' \; \frac{\partial \chi(t,t')}{\partial t'} x(t')}_{back\ reaction}$

$$\ddot{\mathbf{x}} = -\omega \mathbf{x} + [\rho_\mathbf{k}]_\mathbf{o} + \int_\infty^\mathbf{t} \mathbf{dt}' \; \frac{\partial \chi(\mathbf{t},\mathbf{t}')}{\partial \mathbf{t}'} \mathbf{x}(\mathbf{t}')$$

... an oscillator in a good thermal bath of temperature T **provided that** $\langle [\rho_k]_o(t)[\rho_k]_o(t')\rangle = -T\frac{\partial \chi(t,t')}{\partial t'}$

A concrete example for a magnetic system:



cf. Grigera Israeloff

Density functional theory $\longleftrightarrow$ Random First Order

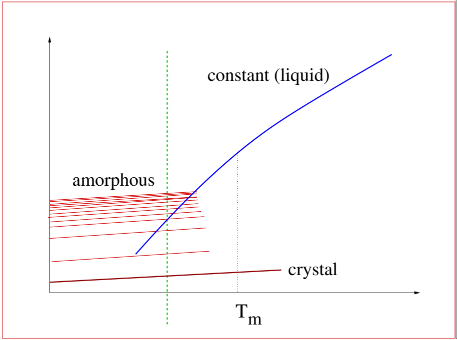
a mean-field free energy

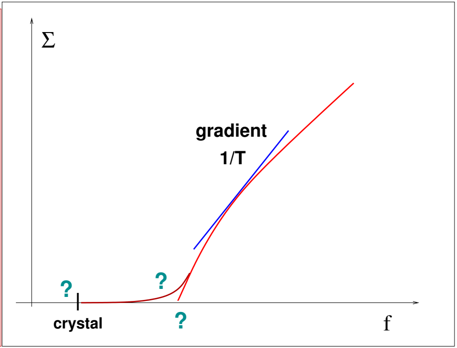
$$F[\rho(\mathbf{x})] = \int d^3\mathbf{x}\ \rho[\ln\rho(\mathbf{x}) - 1] - \frac{1}{2}\int d^3\mathbf{x}\ d^3\mathbf{x}'\ [\rho(\mathbf{x}) - \rho_o] C(\mathbf{x}-\mathbf{x}') [\rho(\mathbf{x}') - \rho_o]$$

has many local minima, solutions of

$$\frac{\delta F[\rho(\mathbf{x})]}{\delta \mathbf{x}} = \ln\rho(\mathbf{x}) - 1 - \int d^d\mathbf{x}'\ C(\mathbf{x}-\mathbf{x}', \rho_o)[\rho(\mathbf{x}') - \rho_o] = 0$$

liquid – crystal + many amorphous





$$\mathbf{Z = \Sigma_{solutions} \quad e^{V[\Sigma(f) - \beta f]}}$$

$$\mathbf{\frac{d\Sigma}{df} = \frac{1}{T}}$$

Density functional theory ⟷ Random First Order

we may simplify even further, just as going from Landau theory to Curie-Weiss:

$$F[\rho(\mathbf{x})] = \int d^3\mathbf{x}\ \rho[\ln \rho(\mathbf{x}) - 1] - \frac{1}{2} \int d^3\mathbf{x}\ d^3\mathbf{x}'\ [\rho(\mathbf{x}) - \rho_o] C(\mathbf{x} - \mathbf{x}')[\rho(\mathbf{x}') - \rho_o]$$

$$\downarrow$$

$$E[\rho_1, ..., \rho_N] = \sum_{ijk} J_{ijk} \rho_i \rho_j \rho_k$$

has similar phenomenology

Here, I am cutting a long story short.

- This form of density functional theory was introduced long ago (70's), and used to study crystallisation

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- Later the existence of amorphous solutions, and hence the relevance for glasses, was remarked (1984).

- Random First Order theory started from the observation that spin glass-like models with quenched disorder $E = \sum_{ijk} J_{ijk} s_i s_j s_k$ where mean-field models of glasses (late 80's)

- This led to an explosion of results (mainly in the 90's), because well established techniques *(and technicians)* where now available.

- Finally, one may come back to a local mean-field (Landau) theory for $\rho(x)$, which will be a better-understood and consistent form of density functional theory. The phenomenological (for the moment) extension beyond mean-field is the subject of the mosaic theory.

What is relevant here is that the dynamics associated with these models

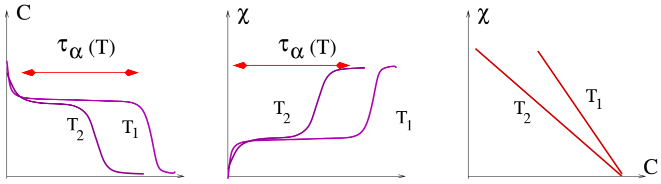
$$\ddot{\rho}_i = -\frac{\partial E}{\partial \rho_i} \; + \; thermal\ bath$$

is also exactly solvable

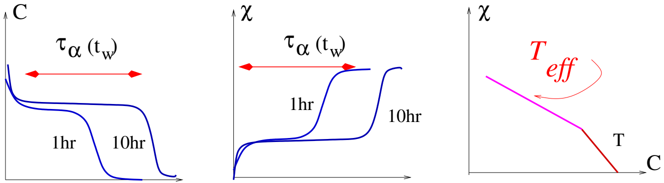
- Above T_c the system equilibrates in finite time - Mode Coupling Equations
- Below T_c the system never equilibrates. It ages.

- **The appearance of effective temperatures:**

Aging in the correlations and the response

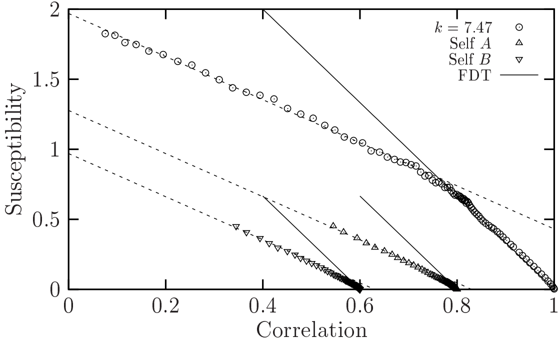


constant temperature T



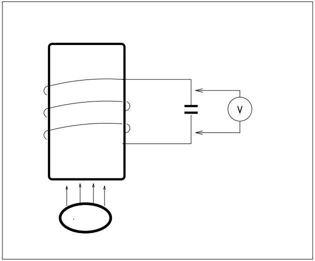
This, in turn, led to the search of effective temperatures in realistic models

all the temperatures in a given timescale should coincide!



Binary Lennard-Jones glass, simulation L. Berthier and JL Barrat

...and in experimental systems:



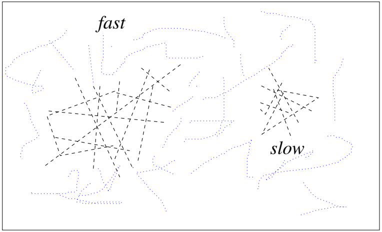
cf. Grigera Israeloff

And poses the question of *fictive temperatures*, introduced long ago (Tool) **phenomenologically**

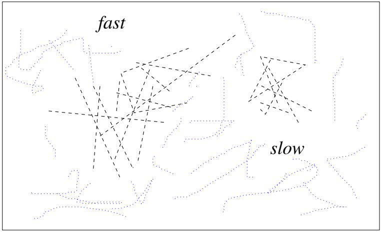
is this the same thing? It seems difficult to avoid identifying them, yet:

it is difficult to compare a definition within a theoretical framework with a phenomenological idea. Certainly many formulas applied to fictive temperatures do not apply to effective temperatures...

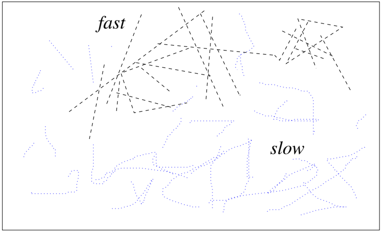
Dynamic heterogeneities and effective temperatures



Dynamic heterogeneities and effective temperatures



Dynamic heterogeneities and effective temperatures



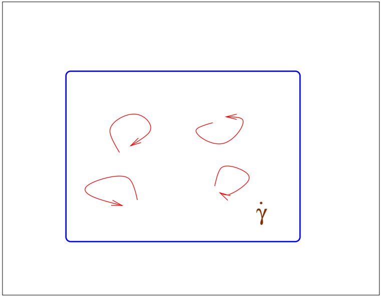
- **Paradoxically, slow regions are responsible for T_{eff}**

- **T_{eff} is not the result of heterogeneities left over from the quench**

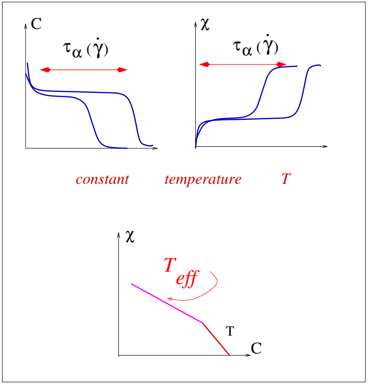
- **The reason why $T_{eff} \sim T_g$ is more subtle!**

Rheology and shear thinning:
the other face of aging

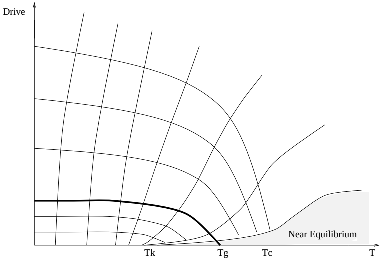
shear-thinning: stirring a liquid makes τ_α smaller, and kills aging



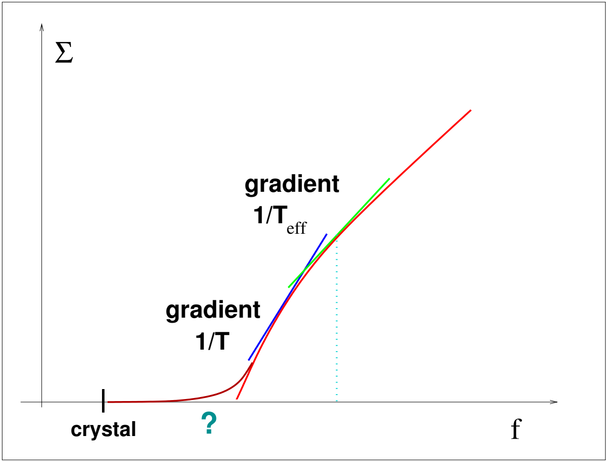
but surprisingly, effective temperatures are still there (for small $\dot{\gamma}$)



iso-τ_α and iso-T_{eff} lines



flat exploration of states (why?)



Amazingly, one has 'laws' for the out-of equilibrium regime, quite independent of what the system will do at infinite times

This is a new way of thinking, and it is not well established yet