Glasses, Theory and Simulations

Giorgio Parisi

(CHIMERA.ROMA1.INFN.IT)

A short summary.

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

Gran Sasso, July 1999

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.

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

(i.e. $S(t)$ is the correlation function at zero spatial momentum at different times).

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

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

$\eta \propto (T - T_c)^{-\gamma}$ mode coupling theory (1983)

Avoided transition at T_c

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

Specific heat depends on cooling rate.

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

$S(T = 0)$ versus T_B with $h \neq 0$ (Plank).

Third law $S(T = 0) = 0$. Theorem $S(T = 0) \geq 0$.

Glass $\Longrightarrow$ frozen liquid

Many valley or states

$Z = \sum_a \exp(-\beta N f_a)$

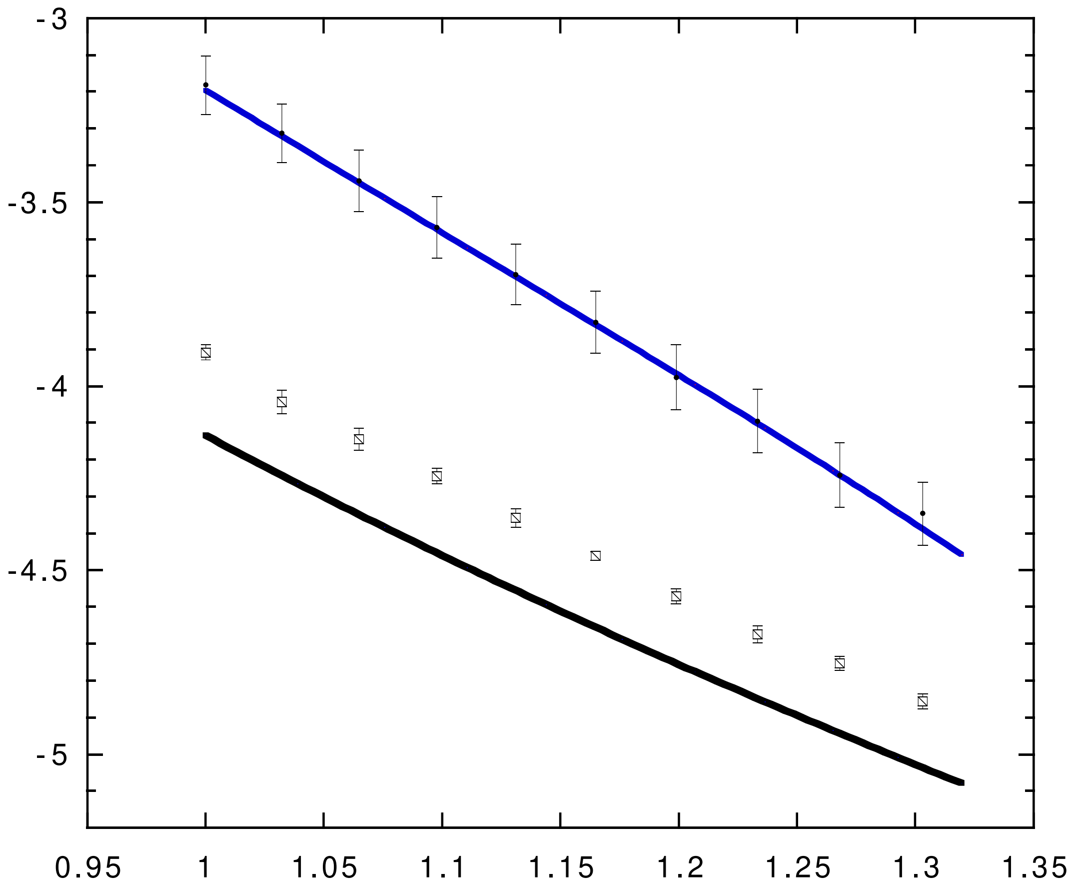
Dominated by $f = f^*(\beta)$

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

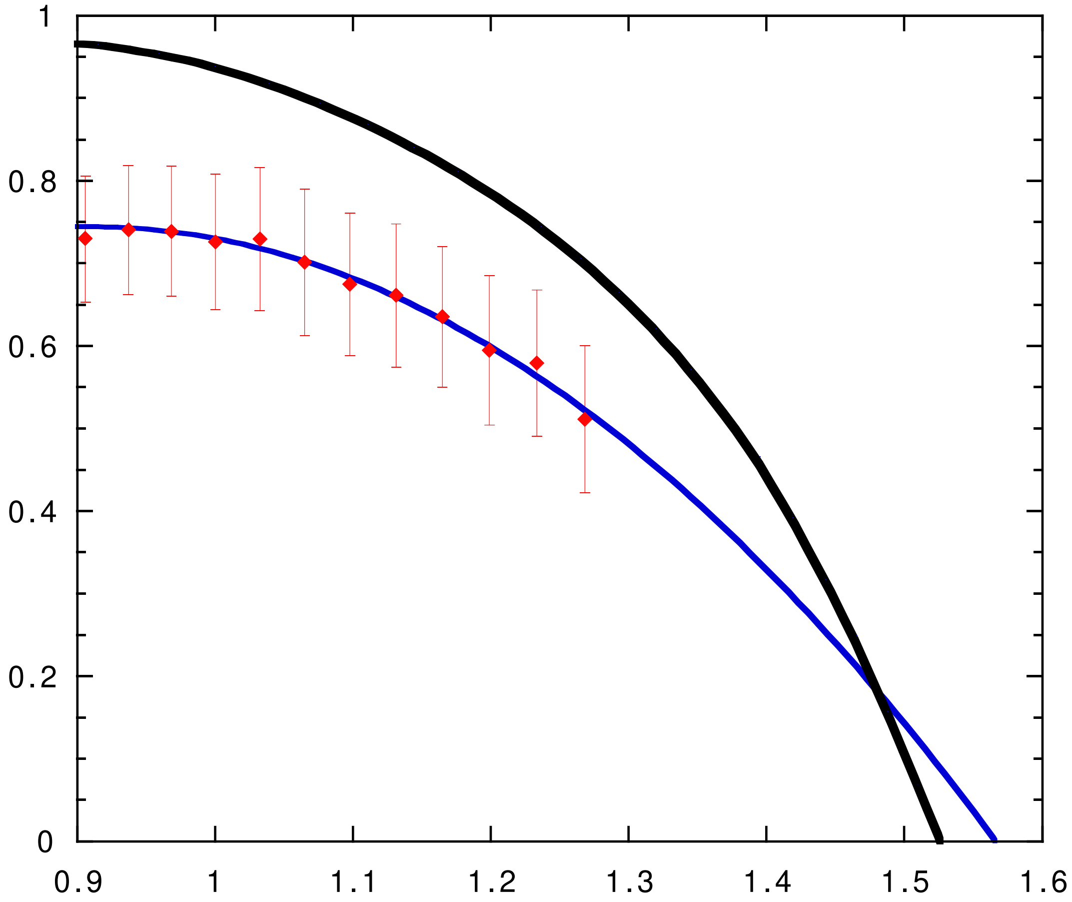
$\Sigma(\beta)$ Configurational entropy or Complexity

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

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



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.

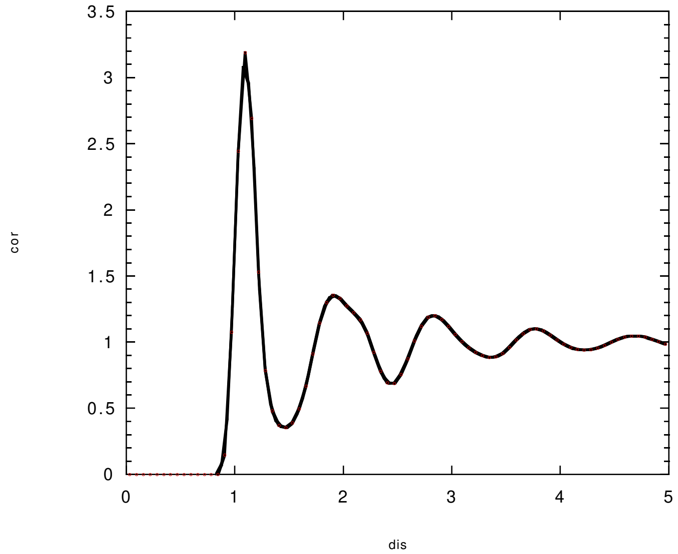
$$\Longrightarrow$$

Replica symmetry breaking

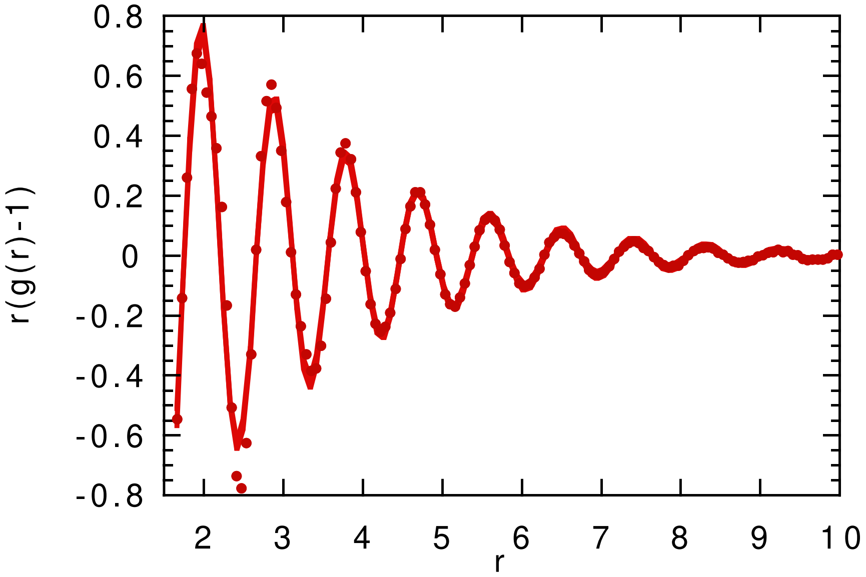
Characteristic violations of Fluctuation Dissipation theorem in off-equilibrium dynamics.

$$\rho(x) = \sum_i \delta(x(i) - x); \; \langle \rho(x) \rangle = \rho = 1.$$

$$\langle \rho(x)\rho(0) \rangle = \delta(x) + g(x)$$



Typical correlation function $g(x)$ near the glass transition or in the glass phase for soft spheres (27.000 particles)



$$x(g(x) - 1) \approx \exp(-Ax)\cos(Bx + C)$$

Divergent dynamical correlation length.

Introduce a lattice (e.g. lattice spacing .4).

$n_i(t)$ = number of particle in the box at i at time t.

$n_i = 0$ or 1 in practice.

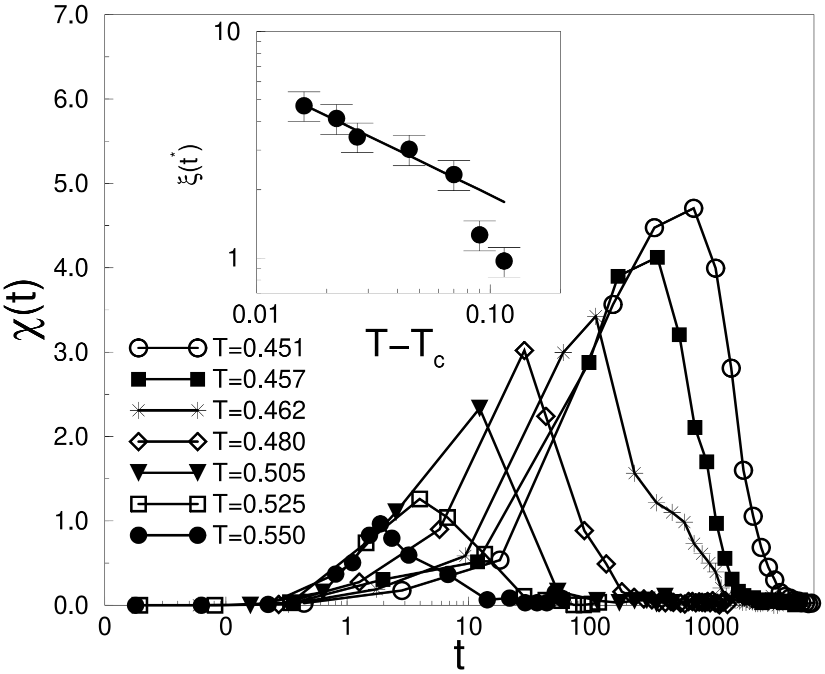
Overlap $q_i(t) = n_i(t)n_i(0)$.

Correlations in overlap $\Longrightarrow$

correlated motion on large scale.

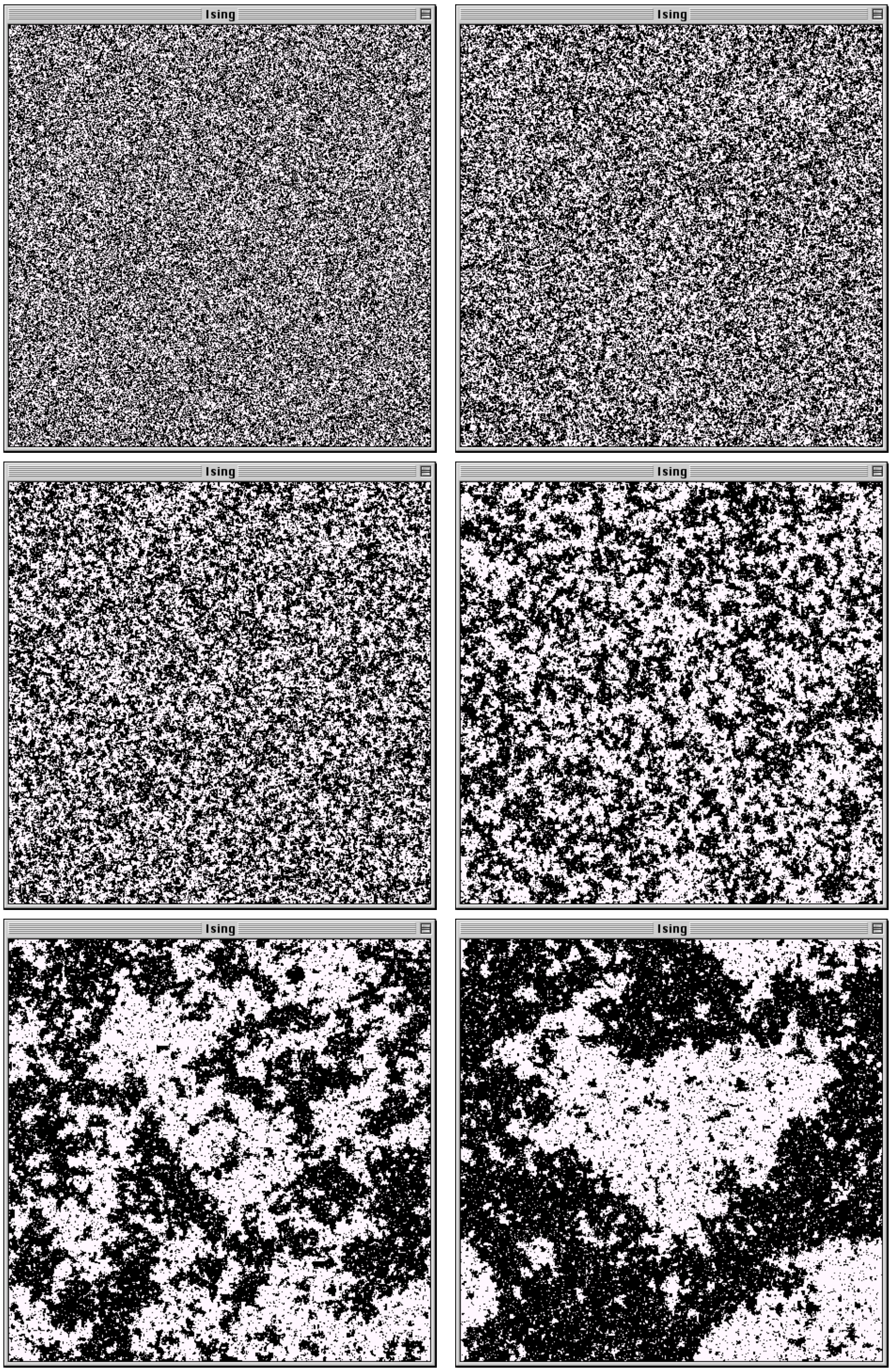
$$C_i(t) = \langle q_i(t)q_0(t)\rangle_c = \langle q_i(t)q_0(t)\rangle - \langle q_0(t)\rangle^2$$

$$\chi(t) = \sum_i C_i(t)$$



At low temperatures: growing correlation length.

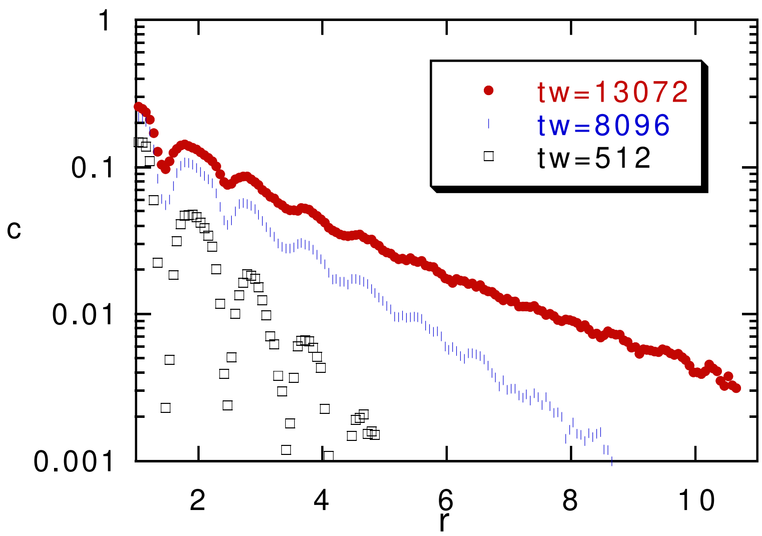
Spinodal decomposition; Ising fast cooled from above to below T_c.

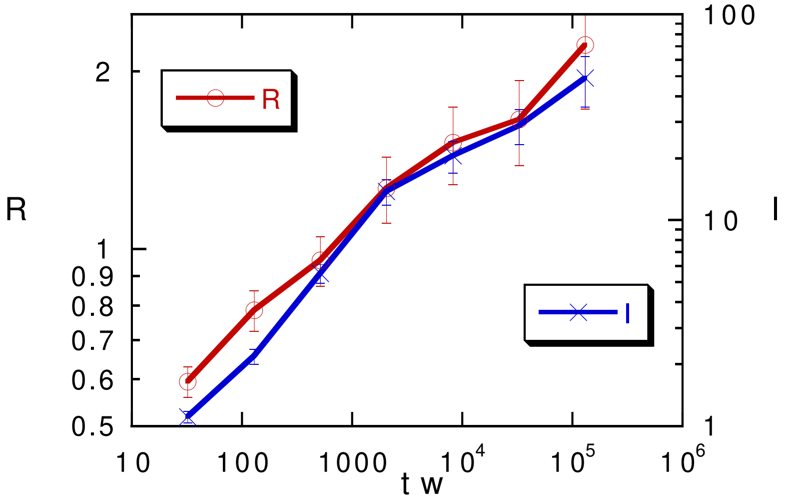


$$D_i(t) = \langle q_i(t) q_0(2t) \rangle_c$$

$$f(x,t) = \frac{D(x,t)}{g(x)}$$

At low temperatures one finds an increasing correlation length





Susceptibility and correlation length versus time

$$R(t) = \xi(t) \propto t^{.16}; \; \chi(t) \propto t^{.5}$$

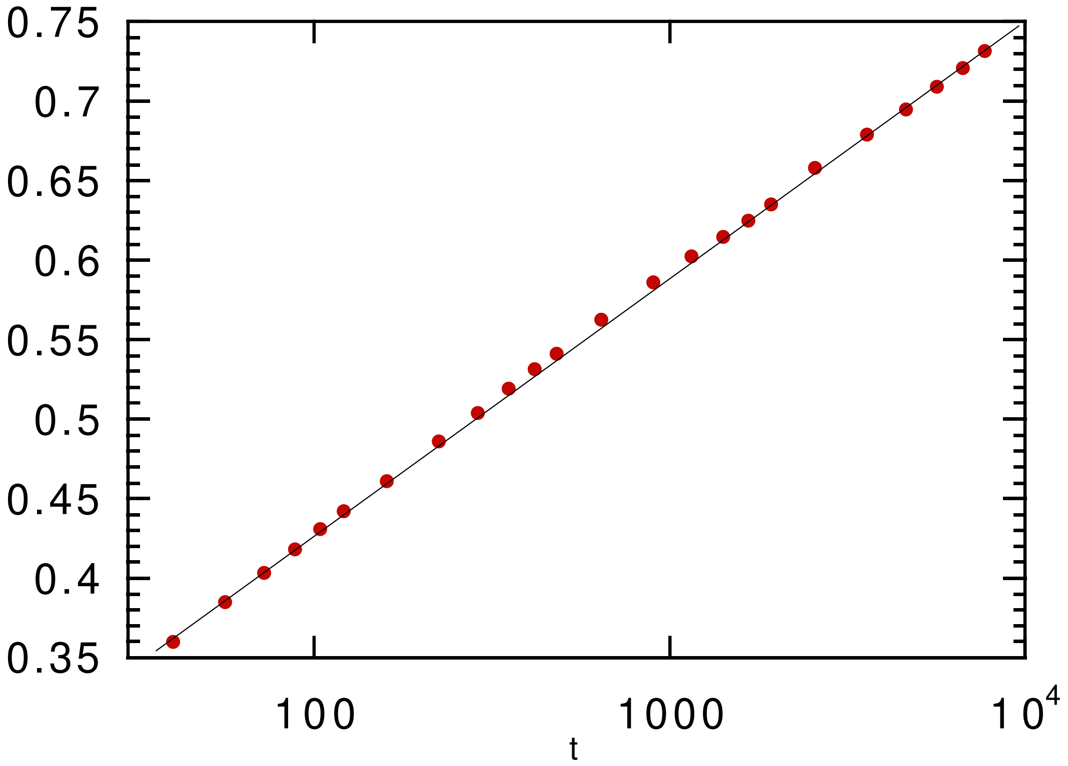
Numbers of spin flips at $T = 0 \propto \ln(t)$.

Numbers of phase changes at $T \neq 0 \propto \ln(t)$.

Squared distance form the original position of a particle

$\propto \ln(t)$

i.e it is the cumulative effect of uncorrelated events that happen with logarithmic frequency.



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?

- cond-mat/9703219: Off-equilibrium fluctuation dissipation relation in binary mixtures

  Authors: Giorgio Parisi

- cond-mat/9807420: Thermodynamics of glasses: a first principle computation

  Author: Marc Mezard, Giorgio Parisi

- cond-mat/9903129 : Thermodynamics of binary mixture glasses

  Authors: Barbara Coluzzi, Marc Mezard, Giorgio Parisi, Paolo Verrocchio

- cond-mat/9906172: The thermodynamical liquid-glass transition in a Lennard-Jones binary mixture

  Authors: Barbara Coluzzi, Giorgio Parisi, Paolo Verrocchio

- cond-mat/9905433 Theory of Non-linear Susceptibility and Correlation Length in Glasses and Liquids

  Authors: Claudio Donati, Silvio Franz, Giorgio Parisi, Sharon C. Glotzer

- cond-mat/9801034: A divergent correlation length in off-equilibrium glasses

  Authors: Giorgio Parisi