

Testing replica predictions in experiments^(*)

G. PARISI

*Dipartimento di Fisica, Università di Roma I "La Sapienza", INFN, Sezione di Roma I
Piazzale Aldo Moro, 00185 Roma, Italy*

(ricevuto il 23 Gennaio 1998; approvato il 19 Febbraio 1998)

Summary. — We review the predictions of the replica approach both for the statics and for the off-equilibrium dynamics. We stress the importance of the Cugliandolo-Kurchan off-equilibrium fluctuation-dissipation relation in providing a bridge between the statics and the dynamics. We present numerical evidence for the correctness of these relations. This approach allows an experimental determination of the basic parameters of the replica theory.

PACS 61.20.Lc – Time-dependent properties; relaxation.

PACS 02.70.Ns – Molecular dynamics and particle methods.

PACS 64.70.Pf – Glass transitions.

PACS 01.30.Ee – Monographs and collections.

When we suddenly decrease the temperature in a Hamiltonian system, many interesting phenomena happen if the initial and the final temperatures correspond to different phases. When the low-temperature phase can be characterized by a simple order parameter (*e.g.*, the magnetization for ferromagnets) we find the familiar phenomenon of spinodal decomposition characterized by growing clusters of different phases. There is a dynamical correlation length (*i.e.* the size of the clusters), which increases as a power of the time t after the quench, and the energy approaches equilibrium with power-like corrections (*e.g.*, $E(t) \approx E_\infty + At^{-1/2}$). In this region aging phenomena are also present [1].

The situation is more intriguing in the case of structural glasses and spin glasses where the low-temperature phase cannot be characterized in terms of a simple order parameter. Remarkable progress in understanding the off-equilibrium dynamics and its relations to the equilibrium properties has been done by noticing that a crucial off-equilibrium feature is the presence of deviations from the well-known *equilibrium* fluctuation-dissipation relations. On the basis of analytic results for soluble models it has been conjectured that we can define a function $X(C)$, C being an autocorrelation function at different times [2-4]. This function characterizes the violations of the fluctuation-dissipation theorem (which is correct only at equilibrium). It is remarkable that (at least in the case of spin glasses) the

(*) In honour of Prof. Gianfranco Chiarotti on the occasion of his 70th birthday.

function $X(C)$ is equal to the function $x(q)$ (q being the overlap of two spin configurations) which plays a central role in the equilibrium computation of the free energy [5].

Let us first recall the description of these glassy systems at equilibrium according to the predictions of the replica theory. We consider a system and we denote by \mathcal{C} a generic configuration of the system. For simplicity we will assume that there are no symmetry in the Hamiltonian, in the presence of symmetries the arguments must be slightly modified. It is useful to introduce an overlap $q(\mathcal{C}, \mathcal{C}')$. There are many ways in which an overlap can be defined; for example in a spin system we could define

$$(1) \quad q = \frac{\sum_{i=1, N} \sigma_i \tau_i}{N},$$

N being the total number of spins or particles and σ and τ are the two spin configurations. In a liquid a possibility is given by

$$(2) \quad q = \frac{\sum_{i=1, N} \sum_{k=1, N} f(x(i) - y(k))}{N},$$

where f is a function which decays in a fast way at large distances and is substantially different from zero only at distances smaller than the interatomic distance (x and y are the two configurations of the system).

In the high-temperature phase for very large values of N the probability distribution of the overlap ($P_N(q)$) is given by

$$(3) \quad P_N(q) \approx \delta(q - q^*).$$

In the low-temperature phase $P_N(q)$ depends on N (and on the quenched disorder, if it is present). When we average over N we find a function $P(q)$ which is not a simple delta-function. In all known cases one finds that

$$(4) \quad P(q) = a_m \delta(q - q_m) + a_M \delta(q - q_M) + p(q),$$

where the function $p(q)$ does not contain delta-function and its support is in the interval $[q_m, q_M]$.

The non-triviality of the function $P(q)$ (*i.e.* the fact that $P(q)$ is not a single delta-function and consequently q is an intensive fluctuating quantity) is related to the existence of many different equilibrium states. Moreover the function $P_N(q)$ changes with N and its statistical properties (*i.e.* the probability of getting a given function $P_N(q)$) can be analytically computed [5, 6].

In this equilibrium description a crucial role is given by the function $x(q)$ defined as

$$(5) \quad x(q) = \int_{q_m}^q P(q') dq'.$$

In the simplest case the function $p(q)$ is equal to zero, *i.e.* the function $P(q)$ has only two delta-functions without the smooth part. In this case, which corresponds to one-step replica symmetry breaking, there are many equilibrium states, labeled by α , and the overlaps among two generic configurations of the same state and of two different states are,

respectively, q_M and q_m . The probability of finding a state with total free energy f is proportional to

$$(6) \quad \exp [m\beta(f - f_R)] ,$$

where f_R is a reference free energy and m is the value of $x(q)$ in the interval $[q_m, q_M]$.

In the more complicated situation where the function $p(q)$ is non-zero, couples of different states may have different values of the overlaps. The conjoint probability distribution of the states and of the overlaps can be described by formulae similar to eq. (6), but more complex [5].

Although these predictions are quite clear, it is not so simple to test them for many reasons:

- They are valid at thermal equilibrium, a condition that is very difficult to reach for this kind of systems.

- Experimentally it is extremely difficult to measure the values of the microscopic variables, *i.e.* all the spins of the system at a given moment. These measurements can be done only in numerical simulations, where the observation time cannot be very large.

Very important progress has been done when it was discovered [2] that the function X , which describes the violations of the fluctuation dissipation theorem, is equal to the function x which is relevant for the statics. This equality is very interesting because function $X(C)$ can be measured relatively easily in off-equilibrium simulations [7].

The temperature dependence of the function $X(C)$ (or equivalently $x(q)$) is interesting also because rather different systems can be classified in the same universality class according to the behaviour of this function. It was conjectured long time ago that the equilibrium properties of glasses are in the same universality class as some simple generalized spin glass models [8, 9].

Let us be more precise. We concentrate our attention on a quantity $A(t)$. We suppose that the system starts at time $t = 0$ from an initial condition and subsequently it remains at a fixed temperature T . If the initial configuration is at equilibrium at a temperature $T' > T$, we observe an off-equilibrium behaviour. We can define a correlation function

$$(7) \quad C(t, t_w) \equiv \langle A(t_w)A(t + t_w) \rangle$$

and the response function

$$(8) \quad G(t, t_w) \equiv \left. \frac{\delta \langle A(t + t_w) \rangle}{\delta \epsilon(t_w)} \right|_{\epsilon=0} ,$$

where we are considering the evolution in the presence of a time-dependent Hamiltonian in which we have added the term $\int dt \epsilon(t)A(t)$.

The usual equilibrium fluctuation-dissipation theorem (FDT) tells us that

$$(9) \quad G^{\text{eq}}(t) = -\beta \frac{dC^{\text{eq}}(t)}{dt} ,$$

where

$$(10) \quad G^{\text{eq}}(t) = \lim_{t_w \rightarrow \infty} G(t, t_w) , \quad C^{\text{eq}}(t) = \lim_{t_w \rightarrow \infty} C(t, t_w) .$$

It is convenient to define the integrated response

$$(11) \quad R(t, t_w) = \int_0^t d\tau G(t - \tau, t_w + \tau), \quad R^{\text{eq}}(t) = \lim_{t_w \rightarrow \infty} R(t, t_w),$$

$R(t, t_w)$ is the response of the system at time $t + t_w$ to a field acting for a time t starting at t_w . The usual FDT relation becomes

$$(12) \quad R^{\text{eq}}(t) = \beta(C^{\text{eq}}(t) - C^{\text{eq}}(0)).$$

The off-equilibrium fluctuation-dissipation relation [2] states that the response function and the correlation function satisfy the following relation for large t_w :

$$(13) \quad R(t, t_w) \approx \beta \int_{C(t, t_w)}^{C(0, t_w)} X(C) dC.$$

If we plot R vs. βC for large t_w the data collapse on the same universal curve and the slope of that curve is $-X(C)$. The function $X(C)$ is system dependent and its form tells us interesting information in the case of three-dimensional spin glasses.

We must distinguish two regions:

- A short-time region where $X(C) = 1$ (the so-called FDT region) and C belongs to the interval I (*i.e.* $C_1 < C < C_2$).

- A large-time region (usually $t = O(t_w)$) where $C \notin I$ and $X(C) < 1$. In the same region the correlation function often satisfies an aging relation, *i.e.* $C(t, t_w)$ depends only on the ratio $s \equiv t/t_w$ in the region where both t and t_w are large: $C(t, t_w) \approx C^a(t/t_w)$.

In the simplest non-trivial case, *i.e.* one-step replica symmetry breaking [5, 9], the function $X(C)$ is piecewise constant, *i.e.*

$$(14) \quad X(C) = m \quad \text{for } C \in I, \quad X(C) = 1 \quad \text{for } C \notin I.$$

One-step replica symmetry breaking for glasses has been conjectured in ref. [8].

In all known cases in which one-step replica symmetry holds, the quantity m vanishes linearly with the temperature at small temperatures. It often happens that $m = 1$ at $T = T_c$ and $m(T)$ is roughly linear in the whole temperature range.

Let us consider the case of spin glasses at zero magnetic field (in this case the replica symmetry is fully broken [10]). The natural variable to consider is a single spin ($A = \sigma_i$). In this case the correlation $C(t, t_w)$ is equal to the overlap among two configurations at time t and t_w :

$$(15) \quad C(t, t_w) = \frac{\sum_{i=1}^N \sigma_i(t) \sigma_i(t_w)}{N}.$$

The response function is just the magnetization in the presence of an infinitesimal magnetic field. In this case the situation is quite good because there are reliable simulations for the system at equilibrium [10].

In fig. 1 (taken from [11]) we plot the prediction for the function R vs. C , obtained at equilibrium (*i.e.* using the equilibrium probability distribution of the overlaps, $P(q)$) by means of a simulation of a 16^3 lattice using parallel tempering [12, 10]. The simulation has

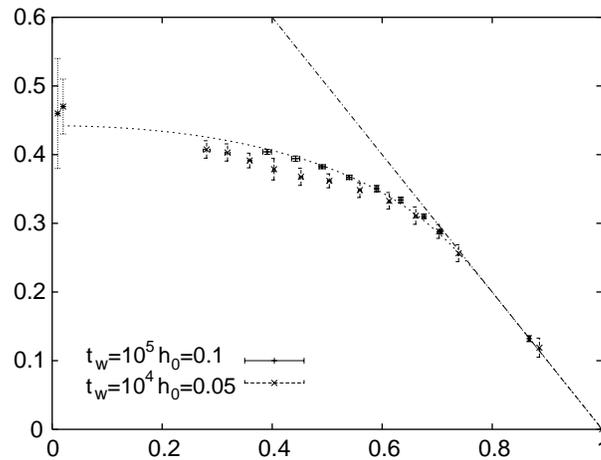


Fig. 1. – The response R times T vs. C at $T = 0.7$ for the three-dimensional Ising spin glass [10]. The curve is the prediction for function $R(C)$ obtained from the equilibrium data. The straight line is the FDT prediction. We have plotted the data of the two runs: $t_w = 10^5$ and $t_w = 10^4$.

been done with the help of the APE100 supercomputer [13] and involves the study of 900 samples of a $L = 16$ lattice.

During the off-equilibrium simulations [11] in a first run without magnetic field the autocorrelation function has been computed. In a second run from $t = 0$ until $t = t_w$ the magnetic field is zero and then (for $t \geq t_w$) there is a uniform magnetic field of small strength h_0 . The starting configurations were always chosen at random (*i.e.* the system is suddenly quenched from $T = \infty$ to the simulation temperature T).

In fig. 1 there are the results of the off-equilibrium simulations [11], where $t_w = 10^5$ and $t_w = 10^4$, with a maximum time of 5×10^6 Monte Carlo sweeps. The lattice size was 64, and $T = 0.7$ (well inside the spin glass phase, the critical temperature is close to 1.0). We plot the response function R times T (in this case R is equal to m/h_0) against $C(t, t_w)$. We have plotted also a straight line with slope -1 in order to control where the FDT is satisfied. Finally we have plotted two points, on the left of the figure, that are obtained with the infinite time extrapolation of the magnetization.

The agreement among the absolute theoretical predictions (no free parameters) coming from the statics and the dynamical numerical data is quite remarkable. These data show the correctness of the identification of the functions x of the statics and X of the dynamics.

Let us now go to the case of glass forming materials. I will present the data for binary mixture of soft spheres [14]. Theoretically there have been many speculations suggesting that the glass transition is described by one-step replica symmetry breaking [8, 9, 16, 17]. Here the equilibrium properties are not so well known as in spin glasses, although there are some evidence that the homologous of the function $P(q)$ is non-trivial [6]. On the other side, as we shall see, off-equilibrium simulations [15] show that the function $X(C)$ seems to be given by the one-step formula (14) with an approximate linear dependence of m on the temperature.

We consider a mixture of soft particles of different sizes. Half of the particles are of

type A , half of type B and the interaction among the particles is given by the Hamiltonian

$$(16) \quad H = \sum_{i < k} \left(\frac{(\sigma(i) + \sigma(k))}{|\mathbf{x}_i - \mathbf{x}_k|} \right)^{12},$$

where the radius (σ) depends on the type of particles. This model has been carefully studied in the past [14, 15]. The choice $\sigma_B/\sigma_A = 1.2$ strongly inhibits crystallisation and the system goes into a glassy phase when it is cooled. Using the same conventions as the previous investigators we consider particles of average radius 1 at unit density. It is usual to introduce the quantity $\Gamma \equiv \beta^4$. For quenching from $T = \infty$ the glass transition is known to happen around $\Gamma_c = 1.45$ [14].

The best quantity we can measure to show off-equilibrium effects is the diffusion of the particles

$$(17) \quad \Delta(t, t_w) \equiv \frac{\sum_{i=1, N} \langle |\mathbf{x}_i(t_w) - \mathbf{x}_i(t_w + t)|^2 \rangle}{N}.$$

The usual diffusion constant is given by $D = \lim_{t \rightarrow \infty} \Delta(t, t_w)/t$.

The other quantity we measure is the response to a force. At time t_w we add to the Hamiltonian the term $\epsilon \mathbf{f} \cdot \mathbf{x}_k$, where \mathbf{f} is vector of squared length equal to $d = 3$ and we measure the response

$$(18) \quad R(t_w, t) = \left. \frac{\partial \langle \mathbf{f} \cdot \mathbf{x}_k(t_w + t) \rangle_\epsilon}{\partial \epsilon} \right|_{\epsilon=0} \approx \frac{\langle \mathbf{f} \cdot \mathbf{x}_k(t_w + t) \rangle_\epsilon}{\epsilon}$$

for sufficiently small ϵ . The usual fluctuation theorem tells that at equilibrium $\beta \Delta^{\text{eq}}(t) = R^{\text{eq}}(t)$.

In the following we will look for the validity in the low-temperature region of the generalized relation $\beta X(\Delta) = \partial R / \partial \Delta$. This relation (with $X \neq 1$) can be valid only in the region where the diffusion constant D is equal to zero. Strictly speaking also in the glassy region $D \neq 0$, because diffusion may always happen by interchanging two nearby particles (D is different from zero also in a crystal); however if the times are not too large the value of D is so small in the glassy phase that this process may be neglected in a first approximation.

The simulations we present are done using a Monte Carlo algorithm, which is a discretized form of a Langevin dynamics. In fig. 2 we show R vs. $\beta \Delta$ at $t_w = 2048$ and $t_w = 8192$ for $\Gamma = 1.6$ and $t \leq 4t_w$ at $N = 66$. We also show the data for $t_w = 2048$ at $N = 130$. We do not observe any significant systematic shift in this plot among three data sets. We distinguish two linear regions with different slope as expected from one-step replica symmetry breaking. The slope in the first region is compatible with 1, as expected from the FDT theorem, while the slope in the second region is near 0.62. Also the data at different temperatures for all values of $\Gamma \geq 1.5$ show a similar behaviour. The value of R , in the region where the FDT relation does not hold, can be very well fitted by a linear function of Δ as can be seen in fig. 2. The region where a linear fit (with $m < 1$) is quite good corresponds to $t/t_w > 0.2$.

The fitted value of $m \equiv \partial R / \partial (\beta \Delta)$ is displayed in fig. 3. When m becomes equal to 1, the fluctuation-dissipation theorem holds in the whole region and this is what happens

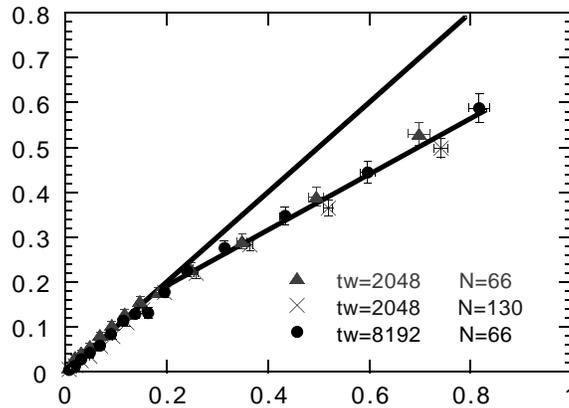


Fig. 2. - R vs. $\beta\Delta$ at $\Gamma = 1.6$ for $t_w = 8192$ and $t_w = 2048$ at $N = 66$ and for $t_w = 2048$ at $N = 130$. The two straight lines have slope 1 and 0.62, respectively.

at higher temperatures. The straight line is the prediction of the approximation $m(T) = T/T_c$, using $\Gamma_c = 1.45$.

All the results are in very good agreement with the theoretical expectations based on our knowledge extracted from the mean-field theory for generalized spin glass models. The approximation $m(T) = T/T_c$ seems to work with an embarrassing precision. We can conclude that the ideas developed for generalized spin glasses have a much wider range of application than the models from which they have been extracted. It is likely that they reflect quite general properties of the phase space and therefore they can be applied to cases which are very different from the original ones.

The most interesting development would be to measure experimentally the function X both in spin glasses and in structural glasses. Clearly the most difficult task is the measurement of the fluctuations. In spin glasses it is clear how it should be done: the

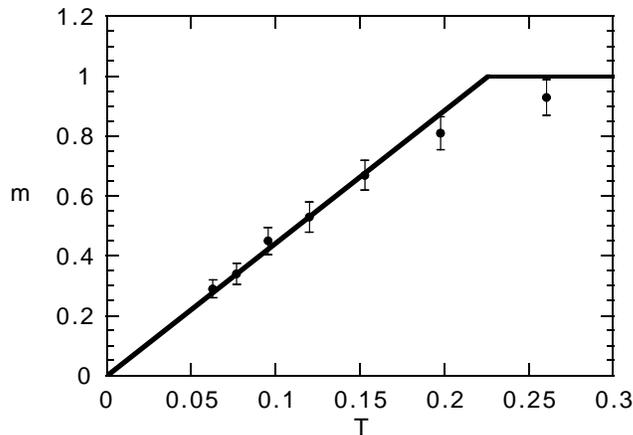


Fig. 3. - The quantity $m \equiv \frac{\partial R}{\partial \beta\Delta}$ as $t_w = 2048$ as a function of temperature. The straight line is the prediction of the approximation $m(T) = T/T_c$.

measurement of the thermal fluctuations of the magnetization is a delicate, but feasible experiment. In the case of structural glasses some ingenuity is needed in planning the experiments. An open interesting possibility would be to do the measurements in the case of rubber, where a transition with similar characteristics should take place.

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