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# Effective potential in glassy systems: theory and simulations

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## Abstract

We study the phase diagram of glassy systems in the presence of an attractive coupling among real replicas. We find competition among a localized and a delocalized phase, that are separated by a coexistence line as in ordinary first-order phase transitions. The coexistence line terminates in a critical point. We present numerical simulations for binary glasses in which we show that this scenario is realized. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Supercooled liquids show a dramatic increase of the relaxation time as the temperature is lowered. The glassy transition is met at the temperature  $T_g$  where flowing is not observable and the systems get out of equilibrium. One of the most suggestive ideas to rationalize this behavior can be found in the Gibbs–DiMarzio theory and its elaborations [1]. This relates the observed finite time singularity to a thermodynamic transition due to an entropy crisis, which would be observable only in the infinite time limit. Qualitatively the picture is as follows. Still in the liquid phase, around a crossover temperature  $T_c$ , the time scales for local motion of the molecules (vibrations) and large-scale motion (diffusion) become widely separated, as if the system remained

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trapped for long times in local minima of the free energy. The entropy  $\Sigma$  associated to the large-scale motion, often called configurational entropy or complexity, can be related to the number of free-energy minima  $\mathcal{N}$  by the formula  $\mathcal{N} = \exp(N\Sigma(T))$ , ( $N$  is the number of particles). As a function of temperature,  $\Sigma$  is supposed to vanish at a finite temperature  $T_s$ , which is the ideal point of thermodynamic glass transition. The relaxation time is then related to the escape rate from the free-energy minima and one can argue in favor of Vogel–Fulcher-like relations for the relaxation time as a function of the temperature with a divergence at  $T_s$  [2,3,29–31]. As it was first realized by Kirkpatrick and Thirumalai [2,29,30], the Gibbs–DiMarzio scenario is exactly implemented in a large class of infinite range disordered models, with the difference that the times needed to escape from local equilibrium states (and the corresponding free-energy barriers) diverge when the volume of the system goes to infinity. The value of  $T_c$ , which is to a large extent arbitrary in real systems, can be sharply defined in the mean-field limit. In fact this is the temperature where the mode coupling theory [7,34,35], which is exact in these models, shows a divergent relaxation time. On the contrary in the short-range systems  $T_c$  signals a change in behavior but we cannot assign to it any sharply defined value.

It has been recently shown that if the models are generalized by introducing two coupled replicas of the same system one finds that  $T_c$  corresponds to the edge of a metastability region [5]. In the same way, the complexity is related to the difference of free-energy in the stable and in the metastable phase. In this paper, we show how in the framework of coupled replicas the glass transition can be described as an ordinary phase transition. Enlarging the space of the parameters to include the coupling among replicas we find a first-order transition line, terminating in a critical point. Although our analysis is based on mean-field theory, we will see that, as in ordinary first-order phase transition, the Maxwell construction will allow to extract the qualitative features of the phase diagram of real systems. A sketch of these results has appeared in Ref. [6]. To submit to test our picture in realistic systems, we have simulated coupled replicas of binary mixtures with repulsive interaction [7,8,34,35]. These are known to vitrify for some values of the parameters defining the model. The results of Monte Carlo simulations strongly support the theoretical picture.

This paper is structured as follows. In Section 2 we present some general considerations on the effect of coupling replicas and we predict the behavior of a glass in the presence of two coupled replicas of the same system. We have to distinguish two different cases: the quenched and the annealed ones, which have different properties. In Section 3 we show that the previous arguments are indeed correct in a soluble model for the glassy transition, the  $p$ -spin spherical model. In Section 4 we present the results of the numerical simulations for the binary mixtures. Finally in the last section, we present our conclusions.

## 2. Coupling replicas

### 2.1. The quenched case

In this section we describe the construction of an effective potential in systems where long-range order is absent, but that can remain stuck for a long time in metastable states. Generically, one can expect that all the relevant metastable states at a given temperature are equivalent as far as their macroscopic characteristics are concerned. Consequently, one cannot identify any intrinsic order parameter allowing to distinguish one state from the others. In this situation it is possible to use as order parameter a degree of similarity among different points in the configuration space. The procedure is common in spin glass theory where the “overlaps” among different replicas appear as natural order parameters when one averages over the quenched disorder. Here we discuss an effective potential as a function of the overlap for generic systems, which may or may not, as structural glasses, contained quenched disorder.

Let us describe the construction in the case of a system composed of only one type of particle with coordinates  $x_i$ , for  $i=1, N$ ; the generalization to many kind of particles is trivial. We consider two replicas of the same system, with coordinates  $x$  and  $y$ , respectively, in an asymmetric relation. The replica  $y$  is a typical configuration distributed according to the Boltzmann–Gibbs law with the original Hamiltonian of the system  $H(y)$  at a temperature  $T'$ , and does not feel any influence from the replica  $x$ . The replica  $x$ , instead, feels the influence of the replica  $y$ , and for fixed value of  $y$ , thermalizes at a temperature  $T$  with a Hamiltonian

$$H_\varepsilon(x|y) = H(x) - \varepsilon \sum_{i,k=1}^N w(x_i - y_k). \quad (1)$$

The function  $w$  is different from zero only at short distance, an example is  $w(x) = 1$  if  $|x| < a$  and  $w(x) = 0$  if  $|x| > a$ . An interesting behavior is found when the value of  $a$  is smaller than the typical interatomic distance (e.g.  $a = 0.3$  atomic distances). The quantity  $q(x, y) \equiv N^{-1} \sum_{i,k=1, N} w(x_i - y_k)$  measures then the similarity of the two configurations, and would be close to one when the two replicas stay in similar configurations. Using the same terminology as in spin glasses [9–11]  $q$  can be called the overlap of the two configurations. For positive  $\varepsilon$  the  $x$  variables feel then a potential which pushes them near to the  $y$  variables. We can define a free-energy for  $x$  variables in the presence of the quenched configuration  $y$  as

$$F(T, \varepsilon, y) = (N\beta)^{-1} \ln \left( \int dx \exp \left\{ -\beta H(x) + \beta \varepsilon \sum_{i,k=1}^N w(x_i - y_k) \right\} \right). \quad (2)$$

This quantity should be self-averaging with respect to the distribution of the  $y$  and can therefore be computed as

$$F_Q(T, T', \varepsilon) = \frac{\int dy \exp(-\beta' H(y)) F(T, \varepsilon, y)}{\int dy \exp(-\beta' H(y))}. \quad (3)$$

The temperature  $T'$  of the reference configuration  $y$  can be equal or different from that of the  $x$  configuration ( $T$ ).

The free-energy (3) is a well-defined function that one can envisage to evaluate analytically or numerically. Its practical analytic evaluation can be performed with the aid of the replica method. For systems not containing quenched disorder one just needs to introduce replicas to average the logarithm in Eq. (2). This consists in substituting  $\log(Z)$  in Eq. (2) by  $Z^m$  and evaluate  $\langle \log(Z) \rangle = \lim_{m \rightarrow 0} (\langle Z^m \rangle - 1)/m$ , where  $Z$  is the argument of the log in Eq. (2) and the angular brackets represent the average over the distribution of  $y$ . The formal procedure is similar to that used by Zippelius and coworkers to study vulcanization [12] and the one used by Given and Stell for liquids in random quenched matrix [13,36,37]. The physical meaning of our and their constructions is however very different. Both in the vulcanization and in the liquid cases the replica method is used to average over some kind of real quenched disorder, the random crosslinking occurring at the vulcanization transition in the first case and the quenched matrix in the second. In our case, there is no quenched disorder. The coupling with the reference configuration  $y$  is a theoretical tool that allows to probe regions of configuration space that have zero weight in the usual Boltzmann distribution, and that can allow us to give a description of freezing even in absence of quenched disorder.

Writing explicitly the replicated partition function

$$\begin{aligned} \langle Z^m \rangle &= \int dy \exp(-\beta' H(y)) \int dx_1 \dots dx_n \\ &\times \exp \left[ -\beta \sum_{a=1}^n H(x_a) + N\beta\varepsilon \sum_{a=1}^n q(y, x_a) \right], \end{aligned} \quad (4)$$

we see that the problem is reduced to an  $m + 1$  component system in the limit  $m \rightarrow 0$ . As we will see in the next section, the procedure needs to be modified if the Hamiltonian  $H$  contains some quenched parameters, to take into account the denominator in Eq. (3).

Let us now try to understand qualitatively the behavior of  $F_Q$  for small positive  $\varepsilon$  and  $T_0 < T < T_c$ , in the simpler case where the two temperatures are equal. At  $\varepsilon = 0$  the probability that the replica  $x$  would stay in a same local minimum of the replica  $y$  is exponentially small. While, when  $\varepsilon > 0$ , the case in which the replica  $x$  stays near to the replica  $y$  is energetically favored. The system can therefore stay in two different phases

- Replica  $x$  different from  $y$  ( $q$  very small) and its free-energy  $F(T, \varepsilon) \approx F(T, 0)$ .
- Replica  $x$  near to  $y$  (here  $q \approx 1$ ). The free-energy is given by  $F(T, \varepsilon) \approx F(T, 0) - \varepsilon q + T\Sigma(T)$ .

It is now clear that in this picture there is a first-order phase transition at  $\varepsilon \approx T\Sigma(T)$  with a discontinuity in the internal energy given by  $q$ . Moreover at  $\varepsilon = 0$  the difference in free-energy among the two phases is exactly given by  $T\Sigma(T)$ . For small  $\varepsilon$  one finds that the transition line starts as  $T(\varepsilon) = T_c + \text{Const.} \times \varepsilon$ .

The thermodynamic properties in the  $T$ - $\varepsilon$  plane (for different values of  $T'$ ) are quite interesting. The previous argument tell us something only in the region of small

$\varepsilon$ , the fate of the first-order transition for large  $\varepsilon$  is a very interesting question. In principle such a computation could be done in structural glasses by using the replicated hypernetted chain approach of [14] and work is in progress in this direction [15]. As a first investigation we limit ourselves to study what happens in a generalized spin glass model, the spherical  $p$ -spin models with long-range forces [16,38–40]. We would like to stress another aspect that makes our approach interesting in connection with glass physics. Studying the usual Boltzmann measure of these models in the glassy phase one faces the problem that the configurations that give the dominant contribution at close but different temperatures look very different from each other (the so-called chaotic temperature dependence of the measure). However, it happens in general that metastable states that dominate the measure at a given temperature  $T'$ , that we call  $T'$ -states, remain metastable if the temperature is changed [17]. With our method, if we fix  $T'$  and we varyate  $T$  we can “follow” metastable states in temperature. In other words, we can modify the Boltzmann measure so as to give non-vanishing weight to the  $T'$ -states to different temperatures. This has important connections with cooling experiments in real systems. At a given cooling rate, the system equilibrates within the (super-cooled) liquid phase, until the glassy transition temperature  $T_g$  is reached. This is the last temperature where the system is able to equilibrate. Below that temperature genuine off-equilibrium phenomena as aging and memory effects set in the system. However, one can expect that the system remains confined for a long time in the metastable state reached at  $T_g$ . Indeed this has been observed in recent numerical experiments in [18]. For short enough times after reaching the temperature  $T_g$  the system will be found in local equilibrium in the “analytic continuation” of the state at  $T_g$ . This hypothesis implies reversibility and can be valid only for times such that structural rearrangements can be neglected. In this perspective one would like to define restricted Boltzmann–Gibbs measures in which only the configurations with a given distance from the quenched configuration  $y$  have non-zero weight:

$$P(x|y) = \frac{1}{Z(\beta, y)} e^{-\beta H(x)} \delta(q(x, y) - q). \quad (5)$$

As the constraint on the value of  $q$  in Eq. (5) is a global one, the free-energy associated to the distribution (5),  $V_Q(q) = -T \log Z(\beta, y)$ , is related to  $F_Q(\varepsilon)$  by Legendre transform:

$$V_Q(q) = \min_{\varepsilon} F_Q(\varepsilon) + \varepsilon q. \quad (6)$$

This represents the minimal work required to keep the replica  $x$  at fixed overlap  $q$  from the replica  $y$ . In a situation with exponentially many minima, each one carrying vanishing contribution to the Boltzmann measure, one can expect a two minima structure of  $V_Q$  at the mean field level. It is clear that a minimum should be found at the value of  $q$  characterizing the typical overlap among different states. This corresponds to having the second replica in one of the exponentially many equilibrium states, different from the one where the first replica lies. In addition, if one does not allow for configurations where  $q$  is spatially inhomogeneous there is a minimum corresponding to

the two replicas globally in the same state.<sup>1</sup> Therefore, for  $T = T'$ , the height of this secondary minimum with respect to the primary one has to be equal to the complexity  $\Sigma(T)$  multiplied by  $T$ .

## 2.2. The annealed case

The following is a similar but different construction: we consider two replicas with total Hamiltonian

$$H_\varepsilon(x, y) = H(x) + H(y) - \varepsilon \sum_{i,k=1,N} w(x_i - y_k). \quad (7)$$

The difference with the quenched case is that for  $\varepsilon \neq 0$  both  $x$  and  $y$  may not be equilibrium configurations. This construction, which we will see, gives similar results of the quenched one that might be more advantageous in numerical simulations, where one can thermalize the two replicas at the same time.

Let us see what we can expect in this case if we make the approximation that  $q$  may be zero or 1. For  $T > T_c$  there is a low  $q$  phase in which the free energy and the internal energy are just the same as at  $\varepsilon = 0$ . The most interesting phase is the high  $q$  phase. At  $\varepsilon = 0$  the free energy in the region  $T_c < T < T_d$  can be obtained for each of the two systems by minimizing the total free energy

$$F(f) = 2[f - T\Sigma(f, T)]. \quad (8)$$

If we couple the two systems and we restrict the analysis to the pairs of configurations with  $q \approx 1$ , we have that

$$F(\varepsilon, f) = 2f - T\Sigma(f, T) - \varepsilon. \quad (9)$$

In this case the minimum will be located at  $\Sigma(f, T) = 0$  also be temperatures higher than  $T_c$ , i.e. up to a temperature  $T_{c,2}$  such that

$$T_{c,2} = \left. \frac{\partial \Sigma(f, T)}{\partial T} \right|_{T_{c,2}}. \quad (10)$$

In other words the presence of a term proportional to  $\varepsilon$  stabilizes the glass phase. As far as the difference in free energy of the liquid phase and the glassy phase is of order  $(T - T_c)^2$ , we expect that the second-order phase transition is transmuted into a first-order one with a temperature  $T(\varepsilon) = T_c + \text{Const.} \times \varepsilon^{1/2}$  and a discontinuity in the internal energy proportional to  $\varepsilon^{1/2}$ . This in contrast with the quenched case, where  $T(\varepsilon)$  is linear in  $\varepsilon$ . We see then, that although the symmetric coupling among replicas induces a kind of deformation of the landscape, so that e.g. the various transition

<sup>1</sup> In real, finite-dimensional systems the secondary minimum is washed out by the possibility of having configurations with inhomogeneous  $q$  but the same global overlap and smaller free energy than the homogeneous ones. This kind of configuration with “coexisting phases” lead to conclude that, as in usual systems, the potential has to be convex function of  $q$ .

temperatures are changed, the global situation is similar to that of the quenched case with the main difference in the behavior of the transition line.

### 3. An analytic computation

#### 3.1. The $p$ -spin spherical model

The model that we are going to describe is the so-called  $p$ -spin spherical model, which has become in the last years one of the simple reference mean-field models for the structural glass transition [16,38–40]. It will be clear from the form of the Hamiltonian that this generalized spin glass is microscopically very different from a structural glass. The basis for its use as a model for the glass transition rely basically on the phenomenology of disordered models model with “one step replica symmetry breaking transition”, which is strongly reminiscent to that of structural glasses. This issue, that has been discussed widely in the literature [2,29,30], will be the starting point for the application of our discussion to real glasses. Just to mention a few facts, the model presents an ideal glassy transition to a broken ergodicity phase with an extensive configurational entropy, to a low-temperature zero complexity phase, very much like in the Gibbs–Di Marzio scenario, and its Langevin dynamics maps exactly in the schematic mode coupling theory [1,4,32,33] and its off-equilibrium generalization [19–21], capturing in this way many of the qualitative and some quantitative features of the supercooled and glassy relaxation.

Many studies have shown explicitly that the random nature of the couplings in this model is not essential. In fact there have been found long range models with oscillatory couplings and the same basic physics of the model we are going to describe [19,22,23,41]. We then believe that many of the issues that we will discuss in this paper, and in particular the qualitative features of the phase diagrams in the  $T$ - $\varepsilon$  plane are quite universal and reflect very general properties of the phase space. We can thus conjecture that the phase diagram for real glasses is similar to that of the generalized spin glasses if we only consider the order of the phase transition and the topology of the various transition lines in the  $T$ - $\varepsilon$  plane.

The model is defined in terms of  $N$  real dynamical variables (spins)  $S_i$ , ( $i = 1, \dots, N$ ) subjected to the constraint  $\sum_{i=1}^N S_i^2 = N$  and interacting via the Hamiltonian

$$H_p = - \sum_{i_1 < \dots < i_p}^{1, N} J_{i_1, \dots, i_p} S_{i_1} \dots S_{i_p} \quad (11)$$

with independent centered Gaussian couplings  $J_{i_1, \dots, i_p}$  with variance  $\overline{J_{i_1, \dots, i_p}^2} = p! / (2N^{p-1})$ . The model for  $p > 3$  has a one step replica breaking, the transition pattern which has been repeatedly shown to be deeply related to the Gibbs–Di Marzio entropy crisis mechanism [2,24].

In spin models the natural way to couple two replicas consist in adding to the Hamiltonian a term  $-\varepsilon \sum_i S_i S'_i$  and with the usual definition of the overlap  $q = N^{-1} \sum_{i=1, N} S_i S'_i$ . The overlap  $q$  is equal to one if the configurations of the two systems coincide.

### 3.2. The quenched case

The quenched potential for the model is obtained inserting the Hamiltonian (11) in the general definition (3). The two replicas potential is

$$F_Q(T, T', \varepsilon) = \frac{\overline{\int dS' \exp(-\beta' H(S')) F(T, \varepsilon, S')}}{\int dS' \exp(-\beta' H(S'))},$$

$$F(T, \varepsilon, y) = (N\beta)^{-1} \ln \left( \int dS \exp \left\{ -\beta H(S) + \beta \varepsilon \sum_{i,k=1, N} S_k S'_k \right\} \right),$$

where the bar denotes the average over the  $J$ 's. In addition to the  $m$  replicas needed to average the logarithm  $\overline{\log(Z)} = \lim_{m \rightarrow 0} (\overline{Z^m} - 1)/m$ , in order to average over the quenched parameters  $J_{i_1, \dots, i_p}$  we also need to represent the denominator  $1/z$  in Eq. (12) as  $\lim_{n \rightarrow 0} z^{n-1}$ . As usual the computation is performed continuing from integer  $n$  and  $m$ . We have then  $n$  unconstrained replicas  $S_i^a$ , ( $a = 1, \dots, n$ ) and  $m$  constrained replicas  $S_i^\alpha$ , ( $\alpha = 1, \dots, m$ ). The average over the quenched disorder induces a coupling among replicas, and as usual in this model, the order parameter for the theory is the matrix of the overlaps among all the  $n + m$  replicas of the system. This can be conveniently arranged in three matrices describing respectively the overlaps of the unconstrained replicas  $Q_{a,b} = 1/N \sum_i S_i^a S_i^b$ , ( $a, b = 1, \dots, n$ ), the overlap among the constrained replicas  $R_{\alpha,\beta} = 1/N \sum_i S_i^\alpha S_i^\beta$ , ( $\alpha, \beta = 1, \dots, m$ ) and the mutual overlap among constrained and unconstrained replicas  $P_{a,\alpha} = 1/N \sum_i S_i^a S_i^\alpha$ . In terms of these order parameters, one finds

$$\frac{1}{N} \log Z_2^{(n,m)} = \frac{1}{2} \left[ \sum_{a,b}^{1,n} \beta^2 f(Q_{a,b}) + \sum_{\alpha,\beta}^{1,m} \beta^2 f(R_{\alpha,\beta}) + 2 \sum_{a,\alpha} \beta \beta' f(P_{a,\alpha}) \right]$$

$$+ 2\beta \varepsilon \sum_{\alpha=1}^m P_{1\alpha} + \frac{1}{2} \text{Tr} \log \begin{pmatrix} Q & P \\ P^T & R \end{pmatrix}, \tag{12}$$

where we have written  $f(q) = q^p/2$ . From Eq. (12) one has to extract the terms proportional to  $m$  in order to evaluate the effective potential. The procedure that we have sketched here has been discussed in Refs. [5,17,25], to which we address the interested reader for the details. In the following, we will concentrate on temperatures  $T > T_s$ . In this region the matrix describing the unconstrained replicas has the simple form  $Q_{a,b} = \delta_{a,b}$ , which is valid both in the paramagnetic phase for  $T > T_c$  and in the non-ergodic phase for  $T_s < T < T_c$  with exponentially many states with vanishing weights.

In this condition the constrained replicas have zero overlap only with replica  $a = 1$  and therefore,  $P_{a,\alpha} = \delta_{a,1} q$ . For the matrix  $R$  the most general ansatz needed here

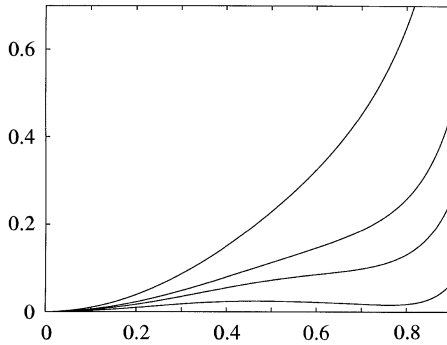


Fig. 1. The potential as a function of  $q$  for the  $p$ -spin model with  $p=4$ ,  $T'=0.523$  and various values of  $T$ , in order of decreasing temperatures from top to bottom. We have chosen  $T_c < T' < T_s$ . For  $p=4$  one has  $T_c=0.503$  and  $T_s=0.544$ . The curves have been normalized in such a way that  $V_Q(0)=0$ .

is a “one step broken” structure [10]. Both the structure and the physical meaning of this ansatz have been discussed widely in the literature, and in standard notations we parameterize it by the three parameters  $q_0, q_1, x$ .

In the following, we will study the phase diagram of the model in the  $\varepsilon$ - $T$  plane in two situations: (a)  $T'=T$ , corresponding to restricting the partition sum to the vicinity of a particular equilibrium state at each temperature. (b)  $T'$  fixed, corresponding to probe the evolution of the free-energy landscape in the vicinity of a fixed configuration of equilibrium at  $T'$  when  $T$  is changed. The Legendre transform of  $F_Q(T, T', \varepsilon)$ ,  $V_Q(q, T, T') \equiv \min_{\varepsilon} F_Q(T, T', \varepsilon) + \varepsilon q$ , admits the following expression in terms of the variational parameters defined above:

$$V_Q(q) = -\frac{1}{2\beta} \left\{ 2\beta\beta' f(q) - \beta^2((1-x)f(q_1) + xf(q_0)) + \frac{x-1}{x} \ln(1-q_1) + \frac{1}{x} \ln(1-(1-x)q_1-xq_0) + \frac{q_0-q^2}{1-(1-x)q_1-xq_0} \right\}, \tag{13}$$

where  $V_Q$  has to be maximized with respect to  $q_0, q_1$  and  $x$ . Depending on the values of  $\beta, \beta'$  and  $q$ , the solution of the saddle-point equations can be either replica symmetric with  $x=0$  or  $x=1$ , or display replica symmetry breaking with  $q_1 \neq q_0$ , and  $x \neq 0, 1$  [17].

We see from Fig. 1 that the shape of the function  $V$  is the characteristic one of a mean-field system undergoing a first-order phase transition. At high enough temperature  $V_Q$  is an increasing and convex function of  $q$  with a single minimum for  $q=0$ . Decreasing the temperature, we find a value  $T_{cr}$ , where for the first time a point  $q_{cr}$  with  $V''_Q(q_{cr})=0$  appears. The potential loses the convexity property and for  $T \leq T_{cr}$  a phase transition can be induced by a field. A secondary minimum develops at  $T_c$ , the temperature of dynamical transition [2,29,30], signaling the presence of long-life metastable states. The minimum of the potential has received a dynamical interpretation in [5,17,26] where it has been shown that its characteristics (internal energy,

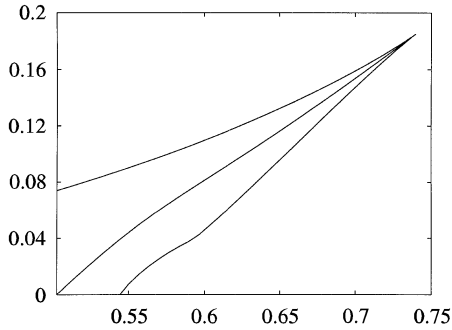


Fig. 2. Phase diagram in the  $\varepsilon$ - $T$  plane for  $p=4$  and  $T'=T$ . The upper curve is the spinodal of the low  $q$  phase, the lower one the spinodal of the high  $q$  state, and the middle curve the coexistence line. The coexistence line touches the axes  $\varepsilon=0$  at  $T=T_s$ , while the spinodal of the high  $q$  phase touches it at  $T=T_c$ . For  $T < T_s$  the spinodal of the low  $q$  phase remains finite and touches the  $T=0$  axes at finite  $\varepsilon$ .

self-overlap, etc.) correspond to the states reached at long times by the evolution at temperature  $T$  starting at an initial time from an equilibrium configuration at temperature  $T'$ . In Fig. 1 we show the shape of the potential in the various regions.

Although the behavior of the potential function is analogous to the one found in ordinary systems undergoing a first-order phase transition the interpretation here is radically different. While in ordinary cases different minima represent qualitatively different thermodynamical states (e.g. gas and liquid), this is not the case in the potential discussed here. In our problem the local minimum appears when ergodicity breaks, and the configuration space splits into an exponentially large number of components. The two minima are different manifestations of the existence of potentially many states with similar characteristics. In the high  $q$  minimum the system  $S$  is in the same microscopic state as  $S'$ , while in the low  $q$  minimum it can be in any other state among the exponentially many that contribute to the Boltzmann measure. The height of the secondary minimum, relative to the one at  $q=0$  measures the free-energy loss to keep the system in the same component of the quenched one. At equal temperatures  $T=T'$  this is just equal to the complexity  $\Sigma$  multiplied by  $T$  and it goes to zero at  $T_s$ , where coexistence in zero coupling takes place without a release of latent heat and both minima lie at the same height. For  $T \neq T'$  the height of the secondary minimum also takes into account the free-energy variation of the equilibrium state at temperature  $T'$  when “followed” (i.e. adiabatically cooled or heated) at temperature  $T$ .

The presence of the field  $\varepsilon$  adds finite stability to the metastable states, and the transition is displaced to higher temperatures. The position of the transition line can be computed via the Maxwell construction. In Fig. 2 we display the phase diagram of the  $p=4$  model in the case  $T'=T$ . The coexistence line departs from the axes  $\varepsilon=0$  at the transition temperature  $T_s$  and reaches monotonically a critical point  $(T_{cr}, \varepsilon_{cr})$ . For the mean-field model under study one can see that the exponents characterizing the critical point are the classical ones. In Fig. 2 we also show the spinodal of the high  $q$  solution, which touches the  $\varepsilon=0$  axes at the dynamical temperature  $T_c$ , and the spinodal

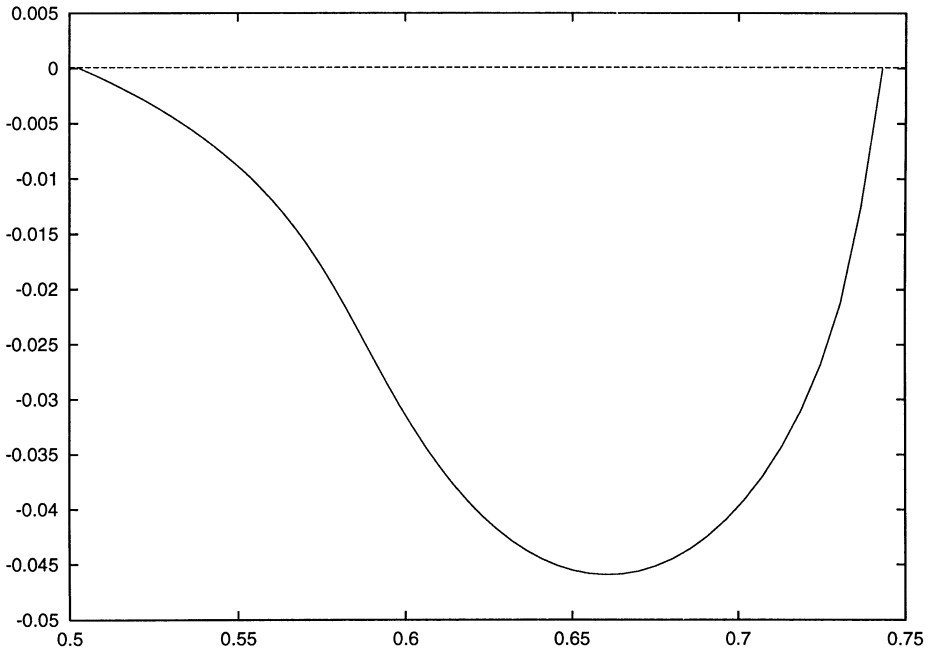


Fig. 3. Latent heat of the transition as a function of the temperature for  $p=4$  and  $T'=T$ .

of the low  $q$  solution for temperatures larger than  $T_s$ . While the transition in zero field is not accompanied by heat release, a latent heat is present in non zero  $\varepsilon$ . In Fig. 3 we show, in the same conditions as Fig. 2, the latent heat  $\mathcal{Q} = E_+ - E_- - \varepsilon(q_+ - q_-)$  where  $E_+(q_+)$  and  $E_-(q_-)$  are the internal energies (overlaps), respectively, of the high and low  $q$  phases. Notice that the latent heat vanishes at the critical point (as it should), and at  $T=0$ . The coexistence line for  $T'$  fixed, in the interval  $T_c \leq T' \leq T_s$  is qualitatively similar to the one of Fig. 2 at high enough temperature, but (for  $T' > T_s$ ) it never touches the axes  $\varepsilon=0$ .

Even at zero temperature there is a first-order phase transition in  $\varepsilon$ , reflecting the fact that the ground state of the system is lower than the energy of the reference state when followed at  $T=0$ . This can be seen in Fig. 4 where we show the phase diagram for a value of  $T'$  such that  $T_c < T' < T_s$ . In Fig. 5 we see that the latent heat for  $T' \neq T$  is qualitatively similar to the one for  $T' = T$  at high temperature, while at low temperature it changes sign and becomes zero only at  $T=0$ .

The high  $q$  phase roughly reflects the properties of the equilibrium states at temperature  $T'$  followed at temperature  $T$ , while the low  $q$  phase reflects the properties of the true equilibrium states at temperature  $T$ . At high temperature the high  $q$  phase is energetically favored, while at low temperature it has an energy higher than the one of equilibrium. The point where  $\mathcal{Q}$  changes sign reflects this fact, and does not correspond to a second-order phase transition. Finally, in Fig. 6 we show, for a fixed temperature the curve of  $q(\varepsilon)$  obtained by the Maxwell construction.

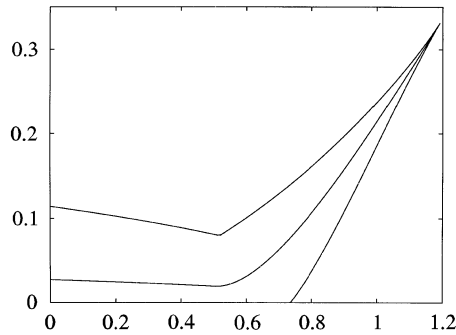


Fig. 4. Phase diagram in the  $\varepsilon$ - $T$  plane for  $p=4$  and  $T'=0.523$ . The upper curve is the spinodal of the low  $q$  phase, the lower one the spinodal of the high  $q$  phase, and the middle curve the coexistence line.

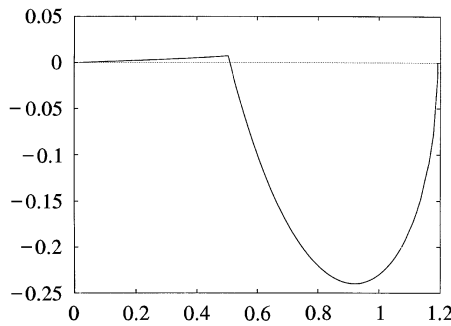


Fig. 5. Latent heat of the transition as a function of the temperature for  $p$  and  $T'$  as in Fig. 4.

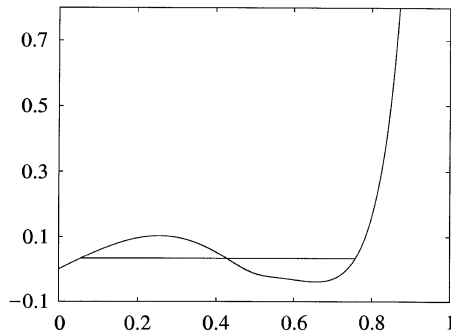


Fig. 6. Equation of state for  $p=4$ ,  $T'=0.523$  and  $T=0.609$ . The horizontal line corresponds to coexistence and is obtained by the Maxwell construction.

In closing this section we would like to comment on the use of the Maxwell construction for finite-dimensional systems. In ordinary systems, the justification of the Maxwell construction is in the phenomenon of phase coexistence. Here we do not know what a supposed coexistence in physical space of the high  $q$  and the low  $q$  phase would mean. This, together with the related problem of finding solutions with inhomogeneous  $q$  to

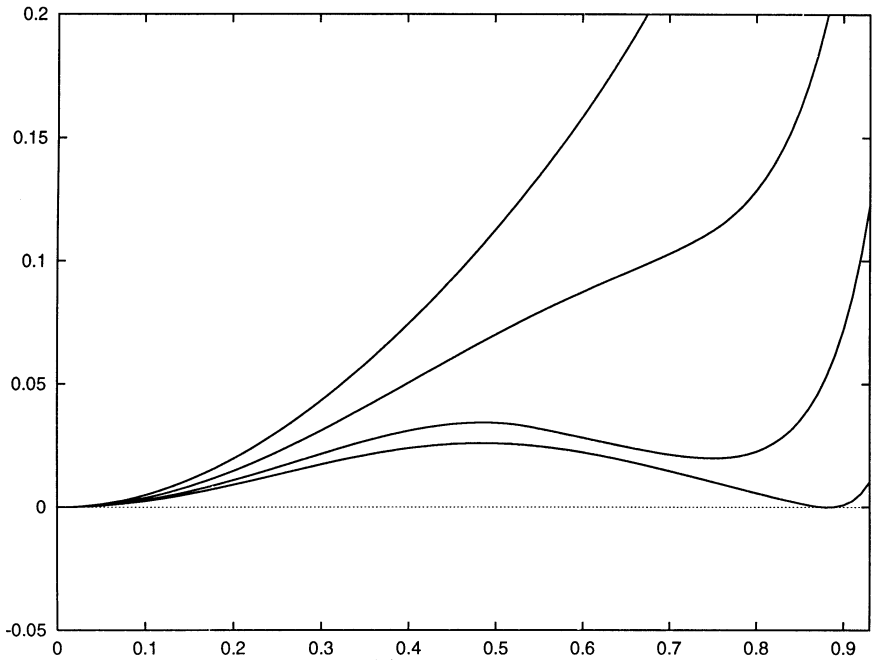


Fig. 7. The annealed potential  $V_A(q)$  as a function of  $q$  for  $p=4$  and various values of  $T$ , in order of decreasing temperatures from top to bottom. For  $p=4$  one has  $T_c=0.503$  and  $T_s=0.544$ . The curves are normalized to have  $V_A(0)=0$ .

the mean-field equations in finite dimensional models is an open problem and needs further investigation. For the time being we limit ourselves to look for support for our construction in numerical simulations. This will be the aim of next section.

### 3.3. The annealed case

The aim of this section is to show rapidly that the annealed potential gives results qualitatively similar to the quenched one. The detailed analysis can be found in [27]. In this case we want to compute the average of the free energy of the two coupled replicas over the quenched couplings. The procedure to do this with replicas is explained in [27,28]. In these cases the overlaps describing the system can be conveniently arranged into three replica matrices  $Q_{a,b} = 1/N \sum_i S_i^a S_i^b$ ,  $Q'_{a,b} = 1/N \sum_i S_i'^a S_i'^b$  and  $P_{a,b} = 1/N \sum_i S_i^a S_i'^b$ . All the matrices have the dimension  $n \times n$  and the symmetry among the two system implies  $Q = Q'$  and  $P_{a,b} = P_{b,a}$ . The most general ansatz needed in the problem is a “one step replica symmetry breaking” form where the matrices  $Q$  and  $P$  are parameterized, respectively, by the parameters  $(q_1, q_0=0, x)$  and  $(\tilde{p}, p_1, p_0=0, x)$ . The resulting free-energy is

$$V_A(q) = -\beta[f(1) + f(q) - (1-x)(f(p_1) + f(q_1))] - \frac{1}{2\beta} \left(1 - \frac{1}{x}\right) [\log(1 + p_1 - q - q_1) + \log(1 - p_1 + q - q_1)]$$

$$\begin{aligned}
& - \frac{1}{2\beta x} [\log(1 + p_1 - q - q_1 + (-p_1 + q_1)x) \\
& + \log(1 - p_1 + q - q_1 + (p_1 + q_1)x)]
\end{aligned} \tag{14}$$

which has to be optimized with respect to  $q_1$ ,  $p_1$  and  $x$ . In Fig. 7 we see that qualitatively the situation resembles the quenched case, with a non-convex potential function at low enough temperature. It is clear that the essential features of the phase diagram or the previous section with a first-order transition line terminating in a critical point are present also in this case, although the actual values of the different characteristic temperatures will be different.

## 4. Real glasses

### 4.1. The model

We have tested the ideas presented in this note for binary fluids. Although we did not perform a systematic study of the phase transition line, we found the evidence for a first-order transition in the presence of coupling among replicas both in the annealed and in the quenched case. The model we consider is the following. We take 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 particle is given by

$$H(x) = \sum_{i < k} \left( \frac{\sigma(i) + \sigma(k)}{|x_i - x_k|} \right)^{12}, \tag{15}$$

where the radii ( $\sigma(i)$ ) depend on the type of particles. This model has been carefully studied in the past [7]. It is known that a choice of the radii such that  $\sigma_B/\sigma_A = 1.2$  strongly inhibits crystallization and the system goes into a glassy phase when it is cooled. Using the same conventions of the previous investigators we consider particles of average diameter 1. More precisely, we set

$$\frac{\sigma_A^3 + 2(\sigma_A + \sigma_B)^3 + \sigma_B^3}{4} = 1. \tag{16}$$

Due to the simple scaling behavior of the potential, the thermodynamic quantities depend only on the quantity  $T^4/\rho$ ,  $T$  and  $\rho$  being respectively the temperature and the density. For definiteness we have taken  $\rho = 1$ .

This is one of the simplest models of glass forming materials and we have chosen it because of its simplicity. The model has been widely studied especially for this choice of the parameters. It is usual to introduce the quantity  $\Gamma \equiv \beta^4$ . The glass transition is known to happen around  $\Gamma = 1.45$  [7,34,35]. It has been shown that aging appears below this temperature, and that the time-dependent correlation and response functions are well in agreement with the prediction of the one step replica symmetry breaking below this temperature [8].

Our simulations are done using a Monte Carlo algorithm, which is easier to deal with than molecular dynamics. Each particle is shifted by a random amount at each step, and the size of the shift is fixed by the condition that the average acceptance rate of the proposal change is about 0.5. Particles are placed in a cubic box with periodic boundary conditions.

Following the discussion in the introduction, we have introduced two copies  $x$  and  $y$  of the same system and have introduced the quantity  $q$  defined as

$$q(x, y) \equiv \frac{1}{N} \sum_{i,k}^{1,N} w(x_i - y_k), \quad (17)$$

where the sum over  $i$  and  $k$  runs over all possible  $N^2/2$  pairs of particles of the same kind. The function  $w$  is chosen in such a way that the quantity  $q$  counts the percentage of particles such that there is a similar particle nearby in the other configuration. The form we have considered is

$$w(x) = \frac{a^{12}}{x^{12} + a^{12}}, \quad (18)$$

with  $a=0.3$ . The function  $w$  is very small when  $x \gg 0.3$  and near to 1 for  $x < 0.3$ . The value of  $q$  will thus be a number very near to 1 for similar configurations (in which the particles have moved of less than  $a$ ) and it will be much smaller value (less than 0.1) for unrelated configurations. The value of  $a$  has been chosen in such a way that  $q$  is insensitive to thermal fluctuations.

#### 4.2. Numerical results for the quenched case

In this case the replica  $y$  is at equilibrium with the Hamiltonian  $H(y)$  while the Hamiltonian of the replica  $x$  is

$$H(x|y) = H(x) - N\tilde{\epsilon}q(x, y), \quad (19)$$

where  $\beta\tilde{\epsilon} = \epsilon$ .

Our aim would be to find out if there is a first-order transition in the plane  $\epsilon-T$  and to locate the transition line. In principle, it is rather difficult to find out the precise position of a first-order phase transition. The reason is quite simple: in a dynamical simulation the mean life in a metastable phase is exponentially large just near the transition.

We have first followed an exploratory approach by monitoring the properties of the system as a function of the coupling, temperature and their time variation, when we go from one phase to the other. In this case the results will be a function of the speed at which we change the parameters and the precise value of the phase transition point will be obtained only in the limit of zero speed.

This gives an approximate information on the position of the transition. We have taken a system with 66 particles and we have thermalized it at a given value of  $T$

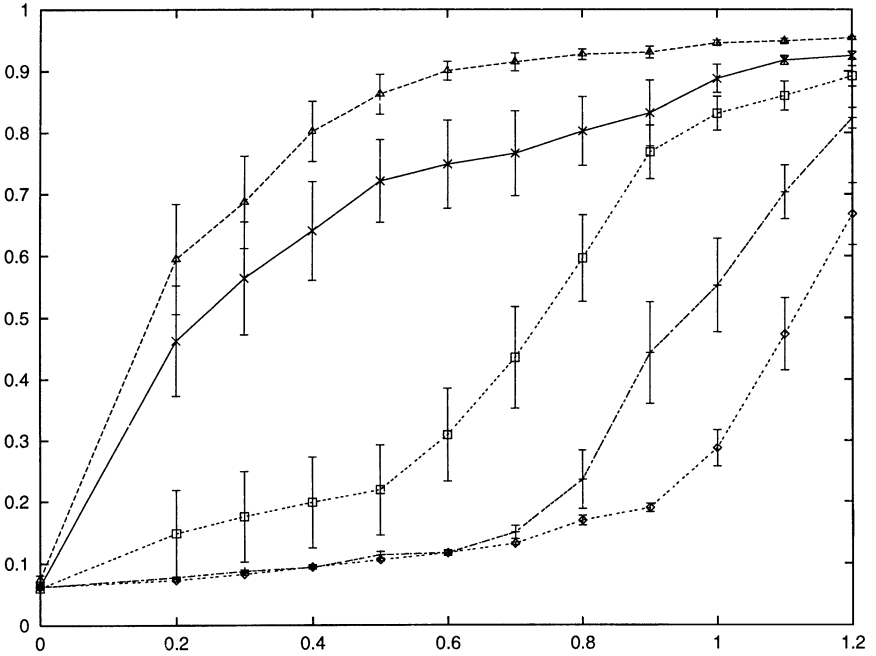


Fig. 8. The overlap as a function of the coupling for various values of  $\Gamma$ , from bottom to top  $\Gamma = 1.25, 1.30, 1.35, 1.40, 1.45$ . The number of particles is 66, the value of  $q$  is averaged over 10 different simulations, and the number of Monte Carlo step for each value of  $\varepsilon$  in each simulation is  $2^{17}$ .

for  $2^k$  Monte Carlo sweeps (we have data for  $k = 7-17$  in order to estimate the  $k$  dependence).

At this point we start the evolution of a second system which is coupled to the configuration reached by the first one ( $y$ ) as in Eq. (19) with a value of  $\varepsilon = 1.2$ , taking as initial condition the quenched configuration  $y$ . We then let the system thermalize for other  $2^k$  steps and we measure the overlap in the last quarter of the run. Starting from the final configuration we decrease the value of  $\varepsilon$  by 0.1 and we perform the  $2^k$  Monte Carlo sweeps. This procedure is repeated up to  $\varepsilon = 0$ .

In Fig. 8 we present the data relative of this procedure for  $k = 17$ . We see that at high temperature (low  $\Gamma$ ) the value of  $q$  drops to nearly zero at already high values of  $\varepsilon$ , while for lower temperature, it persists to high values down to low  $\varepsilon$ . Data at lower value of  $k$  show a much smoother dependence on  $\varepsilon$ . The data are compatible with the possibility that for larger systems and for longer thermalization time a real discontinuity develops. This point deserves to be analysed in much greater detail. On the basis of the data of Fig. 8, in Fig. 9 we give a rough estimate of the transition line in the plane  $\Gamma-\varepsilon$  as the line where  $q = 0.7$ .

There are two alternative methods which should give more accurate estimates of the phase diagram.

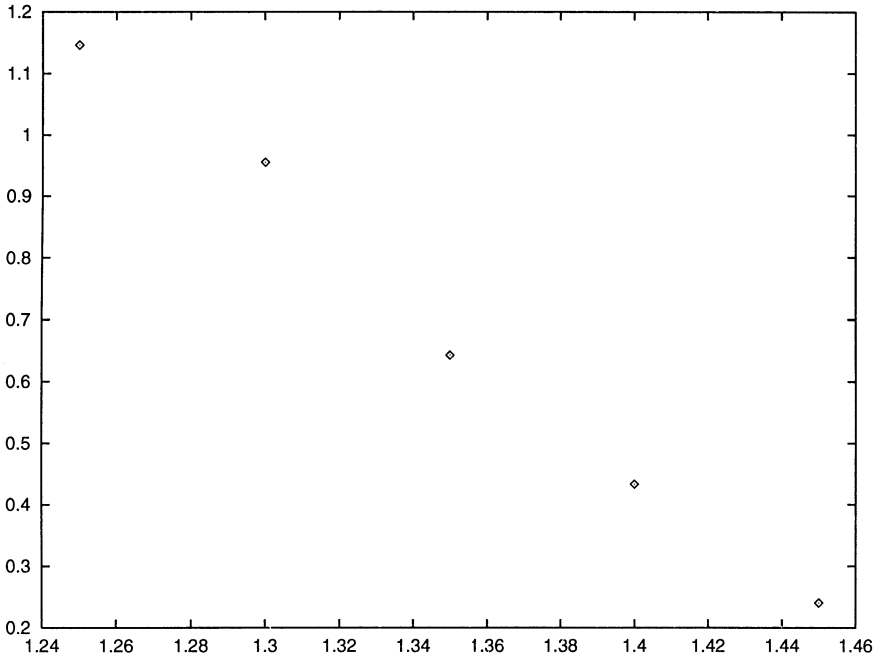


Fig. 9. Rough estimate of the transition line in the  $\varepsilon$ - $\Gamma$  plane, obtained as the value of  $\varepsilon$  at which the overlap shown in the previous figure is equal to 0.7.

- We start from mixed initial conditions, i.e. half of the system in the phase with high overlap, half of the system in the phase with low overlap and we study which of the two phases becomes asymptotically stable.
- We compute the free energy in each of the two phases (apart from a constant) by computing the internal energy and the overlap along a path that starts from a fixed reference point in the  $\varepsilon$ - $\Gamma$  plane up to the final point.

In this note we explore only the first procedure. We first thermalize the system for  $2^k$  iterations. At this point we start the evolution of a second system which is coupled to the configuration reached by the first one ( $y$ ) as in Eq. (19) with a value of  $\varepsilon=4$ , taking as initial condition the quenched configuration  $y$ . The only difference from the previous case is that we substitute in Hamiltonian (19)  $q(x, y)$  by

$$q_G(x, y) = \frac{1}{N} \sum_{i,k} w(x_i - y_k) G(x_i^1), \quad (20)$$

where  $x_i^1$  is the first component of the  $x_i$  and  $G(x) = -1$  for  $x < L/2$  and  $G(x) = 1$  for  $x > L/2$ . In this way, we force the overlap of the particles in the first and second half of the box to small and large values, respectively. In this way, we have prepared the starting point of the runs done (for others  $2^k$  sweeps) at different values of  $\varepsilon$  with the usual Hamiltonian (19). In Fig. 10 we present the data for a system of 512 particles

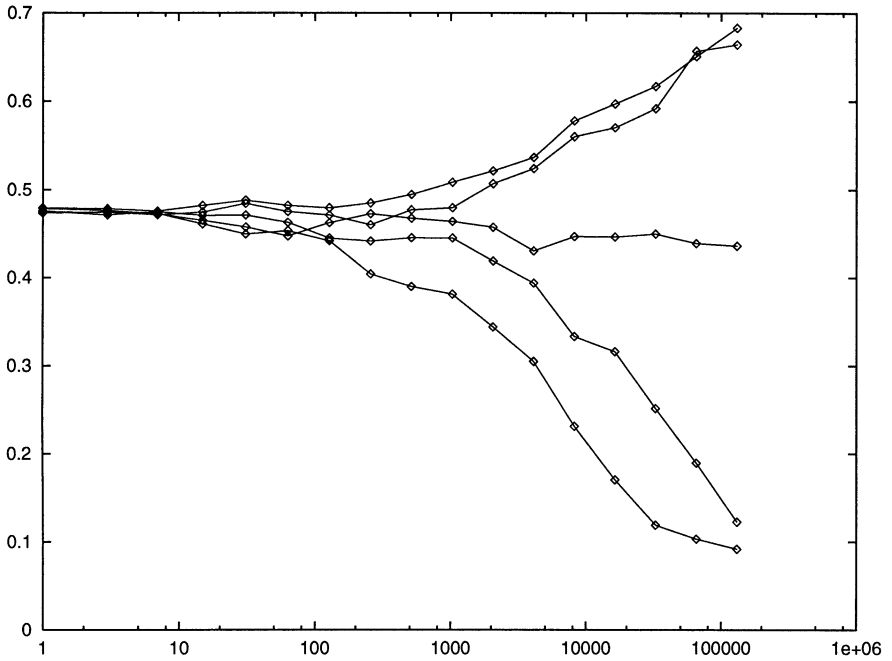


Fig. 10. The value of the overlap for different values of  $\varepsilon$  (from top to bottom  $\varepsilon = 1.5, 1.2, 0.9, 0.6, 0.3$ ), as a function of Monte Carlo time in a logarithmic scale.

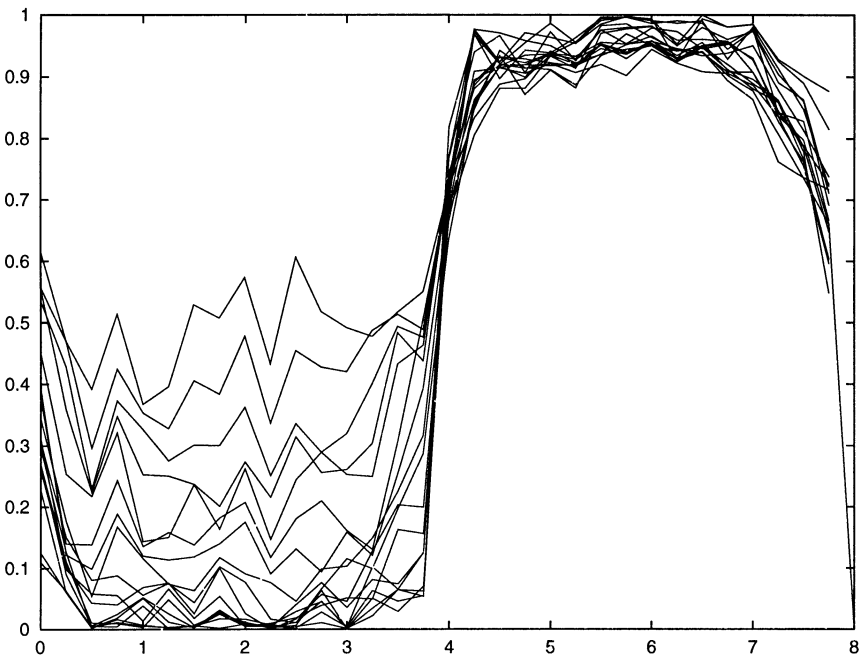


Fig. 11. Time evolution of the space dependent overlap for a system prepared in the low overlap phase for  $0 < x < 4$  and in the high overlap phase for  $4 < x < 8$ . The number of particles is 512, and the box size is 8. The different lines represent the density profile averaged over  $y$  and  $z$  at different times  $t_k = 2^k$ , for  $k = 0, \dots, 17$ . The values of  $\Gamma$  and the coupling, respectively,  $\Gamma = 1.35$  and  $\varepsilon = 1.5$  are such that the stable phase is the one with high overlap. The curves corresponding to higher times are higher in the low  $x$  region.

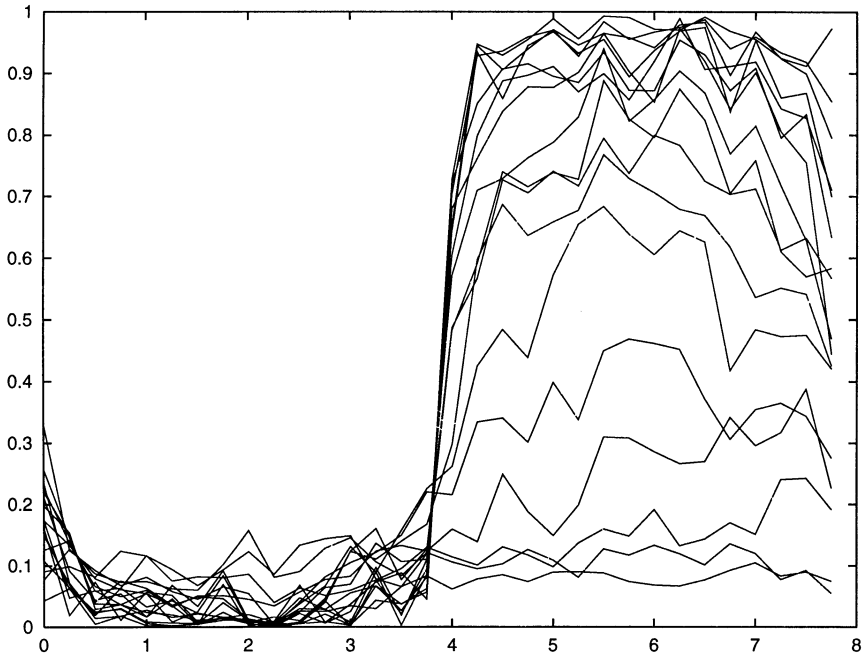


Fig. 12. The same as in Fig. 11 but with a value of the coupling ( $\varepsilon=0.3$ ) such that the stable phase is the one with low overlap. The curves corresponding to higher times are here lower in the high  $x$  region.

for  $\Gamma=1.35$ . We see clearly that for high values of  $\varepsilon$  the system evolves towards high values of  $q$  while for small  $\varepsilon$ ,  $q$  decreases to low values. The value of  $\varepsilon$  that separates the two situations can be estimated to be around  $\varepsilon=0.9$  in this figure.

The dynamics of equilibration from that initial condition presents interesting features. In Fig. 11 we show the overlap profile at times  $t_k=2^k$  for  $\varepsilon=1.5$ , a value such that the high  $q$  phase is stable. Fig. 12 shows the same thing in a case,  $\varepsilon=0.3$ , where the low  $q$  phase is stable. We notice that differently from the usual cases of first-order transitions where the dominating phase grows at the expenses of the metastable one via a surface mechanism, here the dominant dynamics seems to occur in the bulk. The investigation of this kind of dynamics certainly deserves more attention than we have dedicated to it here.

#### 4.3. Numerical results for the annealed case

In this case we have two replicas that evolve in parallel with Hamiltonian

$$H(x, y) = H(x) + H(y) - N\tilde{\varepsilon}q(x, y). \quad (21)$$

To support our first-order transition picture we present hysteresis data during temperature cycles. The procedure consists in first cooling a system in which the two replicas start from independent random condition at a low value of  $\Gamma$ , when a maximum value of  $\Gamma$  is reached, the two configurations are set equal (and equal to one of the two)

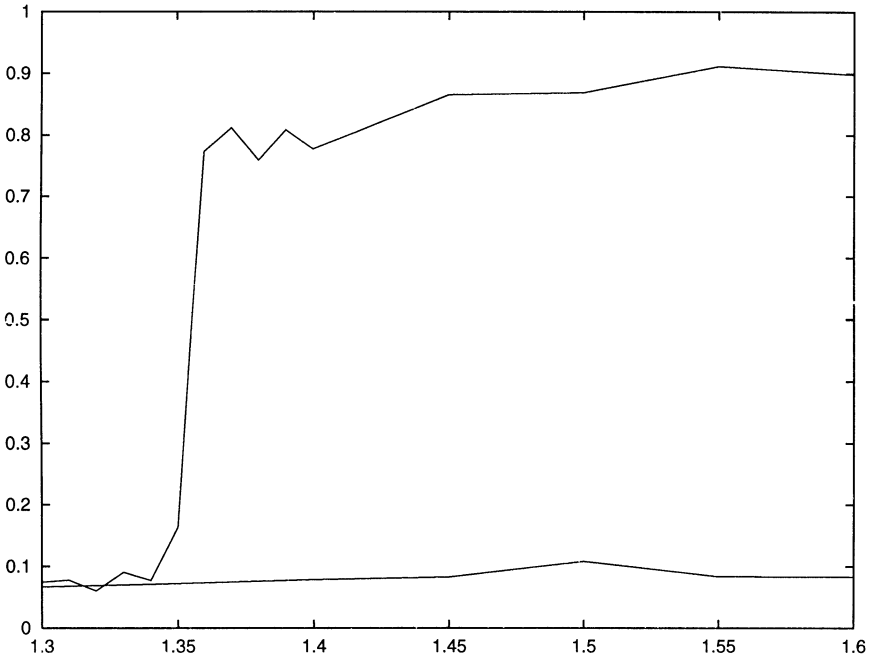


Fig. 13. Overlap  $q$  for two coupled replicas in the annealed case, during a temperature cycle at small coupling  $\varepsilon=0.2$  as a function of  $\Gamma$ . The cooling rate is  $2^{15}$  step for value of  $\Gamma$ , the number of particle is 66. We start from high temperature  $\Gamma=1/3$  we cool down to  $\Gamma=1.6$  (lower curve). At this temperature we set the two configurations equal to one of them and we heat again (higher curve).

and the temperature is raised again. In Figs. 13 and 14 we show data corresponding to  $\varepsilon=0.2$  and  $\varepsilon=0.8$ , respectively. We see in both cases that the low  $q$  phase seems to be metastable for all the probed values of the temperature. On heating the system passes from the high  $q$  phase to the low  $q$  phase with a sharp discontinuity. In Fig. 15 we present data for the internal energy for the same cycle of Fig. 14. The hysteretic behavior found there is an important indication of a first-order phase transition. Notice that the high  $q$  phase, where the entropy is lower, has a lower internal energy and is present also in the liquid phase for  $\Gamma < \Gamma_c$ . Indeed the difference in energy starts to be present just around  $\Gamma_c$ . This behavior is in agreement with the theory. Low energy metastable states exist also for  $T > T_c$ , but they have zero Boltzmann weight in that region. Coupling two replicas together enhance their probability so that their existence can be observed [5,17,26,27].

## 5. Conclusions

In this paper we have given theoretical arguments and numerical support in favor of a description of the ideal glassy transition as the limiting point of a first-order transition line in the plane of the temperature and the coupling among real replicas.

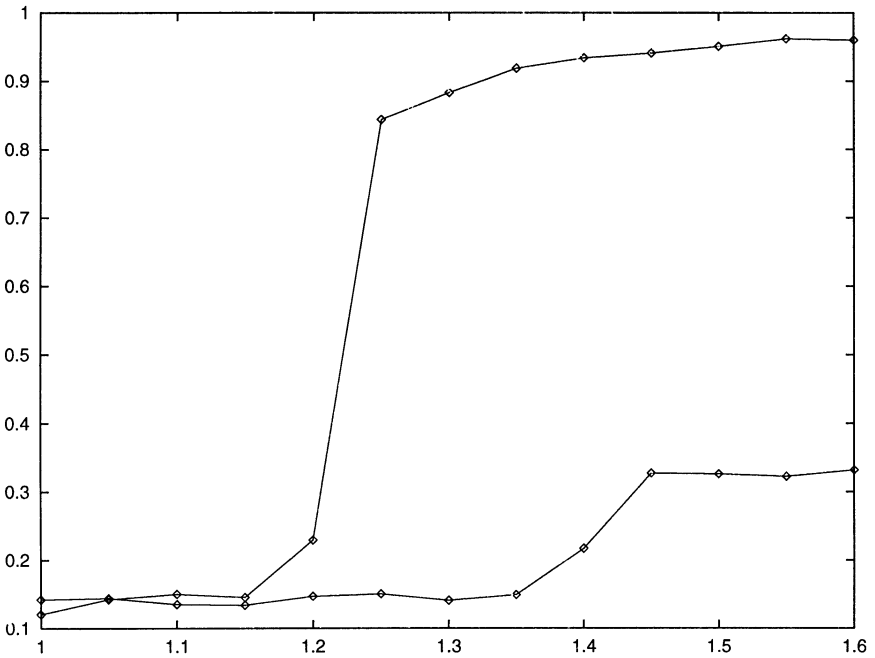


Fig. 14. Overlap  $q$  during a temperature cycle as in the previous figure, at higher coupling  $\varepsilon = 0.8$  as a function of  $\Gamma$  in the region  $\Gamma = 1$ –1.6.

Similar conclusions are obtained in the quenched construction and the annealed one. The first construction studies the implications of a Boltzmann–Gibbs distribution limited to the configurations which have a fixed overlap with a quenched configuration. The second construction studies a Boltzmann–Gibbs distribution of two systems on the same foot and with fixed overlap.

In both formalisms the glassy state is described as a state where there are two phases. A “confined phase” with high value of the overlap, and a “deconfined phase” where there is minimal correlation. We have shown that the glassy transition, which is Ehrenfest second-order for zero coupling, becomes first-order as soon as a non-zero coupling is introduced. A detailed computation in the example of the spherical  $p$ -spin model has shown that there is a first-order transition line in the  $\varepsilon$ – $T$  plane terminating in a critical point. This result should be robust beyond mean field. Indeed, we have discussed how the numerical simulations for binary soft-sphere mixtures at non-zero values of the coupling  $\varepsilon$  support the theoretical picture. A much greater numerical effort would however be needed to locate with precision the transition line and to study the interesting issue of the nature of the glassy critical point. A key point in our analysis, in going from infinite range to short range models, is the possibility to use the Maxwell construction to estimate the topology of the transition line. In ordinary systems the validity of the Maxwell construction is intimately related to the phenomenon of phase coexistence. In the case of glasses we do not know what a supposed coexistence

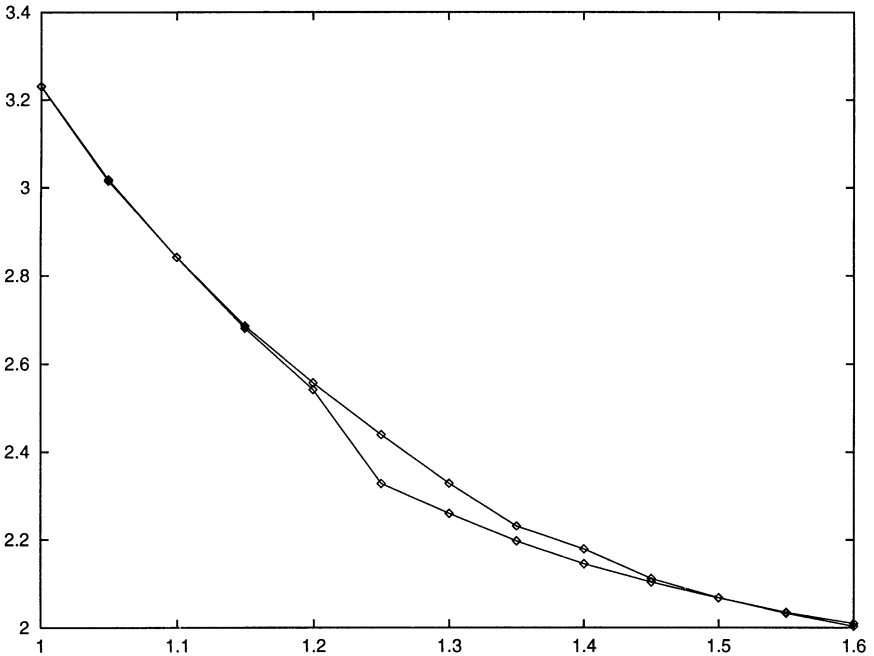


Fig. 15. Internal energy  $E$  during the same temperature cycle as in the previous figure. The high curve corresponds to cooling, the lower one to heating.

of the confined and the deconfined phase would mean. Our numerical simulations, which seem to confirm the first-order transition picture, indicate an overlap dynamics different from the usual domain growth is spinodal decomposition. This question, and the one of the decay of the high  $q$  phase in the metastable regime are deeply related to the problem of restoring of ergodicity when the barriers are finite. This is at the heart of the glassy physics and further numerical and theoretical effort is certainly needed.

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