Phase Diagram of Coupled Glassy Systems: A Mean-Field Study

Silvio Franz[1] and Giorgio Parisi[2]
[1]*ICTP Strada Costiera 11, P.O. Box 563, 34100 Trieste, Italy*
[2]*Università di Roma "La Sapienza," Piazzale A. Moro 2, 00185 Rome Italy*
(Received 8 January 1997)

In the example of the spherical p-spin model, we study the phase diagram of glassy systems in the presence of an attractive coupling with a quenched configuration. We find competition among two phases, separated by a coexistence line terminating in a critical point, as in ordinary first-order phase transitions. We argue that these results are not an artifact of the mean-field approximation, and may be observed in numerical simulations of realistic glassy models. [S0031-9007(97)04049-0]

PACS numbers: 64.70.Pf

The transition from liquid to glasses presents in many materials highly universal features. These may be qualitatively understood in the framework of the Gibbs-DiMarzio scenario and its generalizations [1]. Roughly speaking, the picture is the following. Still in the liquid phase, when the temperature is smaller than a crossover value (T_d), the system may be trapped for a long time in one of the exponentially large number of local minima of the free energy. In this region the large time dynamics becomes extremely slow because it is dominated by transitions among different local minima. The number ($\mathcal{N}$) of these local minima is related to the complexity (or configurational entropy) $\Sigma(T)$ by the formula $\mathcal{N} = \exp[N\Sigma(T)]$, N being the number of particles. The total entropy S is the sum of two contributions: the entropy of each minimum and the complexity. The complexity is supposed to vanish linearly at a lower temperature (i.e., at a temperature $T_c < T_d$), where the height of the typical barriers becomes infinite. The correlation time diverges at T_c, and one can argue in favor of a Vogel-Fulcher law.

This scenario is exactly implemented in a large class infinite range models, with the only difference that the lifetimes of local equilibrium states (and the corresponding free-energy barriers) diverge when the volume of the system goes to infinity [2,3]. In fact, the correlation time diverges at T_d, as can be seen in the mode coupling approximation which is exact for these models. On the contrary, in short range systems T_d signals a change in behavior, but we cannot assign to it any sharply defined value.

In this Letter we will show that if we generalize the models by introducing two coupled replicas of the same system [4–8], we find that T_d corresponds to the edge of a metastable region. In the same way the complexity is related to the difference of a free-energy in the stable and in the metastable phase. Now, in short range models the properties of a metastable phase can only be approximately computed because of the *finite* mean life of metastable states, and in the mean-field approximation metastable states have an *infinite* mean life. It is now clear that the complexity and T_d can be sharply defined only in the framework of the mean-field approximation. We will see that, as in ordinary first-order phase transition, a kind of Maxwell construction allows us to extract qualitative features of the phase diagram of real systems.

Let us describe the construction in the case of a system composed by only one type of particles 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 [i.e., $H(y)$] 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 a fixed value of y, thermalizes at a temperature T with a Hamiltonian

$$H_\epsilon(x \mid y) = H(x) - \epsilon \sum_{i,k=1,N} w(x_i - y_k). \qquad (1)$$

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 $|x| < 1$. An interesting behavior is present when the value of a is smaller than the typical interatomic distance (e.g., $a = 0.3$ atomic distances). The quantity $q \equiv N^{-1}\sum_{i,k=1,N} w(x_i - y_k)$ measures then the similarity of the two configurations, and would be close to one when the two replicas stay in similar configurations. For positive coupling ϵ the x variables feel a potential which pushes them near to the y variables. We can define a free energy for the x variables in the presence of the quenched y variables as

$$F(T, \epsilon, y) = (N\beta)^{-1} \ln\left(\int dx \exp[-\beta H_\epsilon(x \mid y)]\right), \qquad (2)$$

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

$$F_Q(T, T', \epsilon) = \frac{\int dy \exp[-\beta' H(y)] F(T, \epsilon, y)}{\int dy \exp[-\beta' H(y)]}, \qquad (3)$$

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

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Let us consider what happens for small positive ϵ in the region $T_c < T < T_d$ in the simpler case where the two temperatures are equal. At $\epsilon = 0$ the probability that the replica x would stay in a same local minimum of the replica y is exponentially small. While, when $\epsilon > 0$, the case in which the replica x stay near to the replica y is energetically favored. The system can therefore stay in two different phases: (1) Replica x different from y (q very small) and its free energy $F(T, \epsilon) \approx F(T, 0)$. (2) Replica x near to y (here $q \approx 1$). The free energy is given by $F(T, \epsilon) \approx F(T, 0) - \epsilon q + T\Sigma(T)$.

It is now clear that in this picture there is a first-order phase transition at $\epsilon \approx T\Sigma(T)$ with a discontinuity in the internal energy given by q. Moreover, at $\epsilon = 0$ the difference in free energy among the two phases is exactly given by $T\Sigma(T)$. The thermodynamic properties in the T-ϵ plane (for different values of T') are quite interesting. The previous argument tell us something only in the region of small ϵ, the fate of the first-order transition for large ϵ is a very interesting question. In principle such a computation could be done in structural glasses by using the replicated hypernetted chain approach of [9]; however the computations would be rather involved. Here 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 [10].

It is clear that this generalized spin glass is microscopically very different from a structural glass; however, we believe that many of the issues that we are discussing in this Letter, and in particular the qualitative features of the phase diagrams in the $T - \epsilon$ plane, are quite universal and reflect very general properties of the phase space. We 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 $T - \epsilon$ plane. Indeed, this happens for some of the most significative qualitative prediction for the off-equilibrium dynamics of the p-spin model that have been observed in simulations of more realistic glass models (i.e., soft binary mixtures) [11].

The model is defined in terms of N real dynamical variables (spins) S_i ($i = 1, \ldots, N$), subjected to the constraint $\sum_{i=1}^{N} S_i^2 = N$ and interacting via the Hamiltonian $H_J = -\sum_{i_1<\cdots<i_p}^{1,N} J_{i_1,\ldots,i_p} S_{i_1} \cdots S_{i_p}$ with independent centered Gaussian couplings $J_{i_1,\ldots,i_p}$ with variance $\overline{J^2_{i_1,\ldots,i_p}} = p!/(2N^{p-1})$. The model has been studied extensively during the last few years, and furnishes, for $p > 2$, a good toy model of fragile glasses in mean field. It has been often observed [2] that the Langevin relaxation of this model leads to equations homologous to those of schematic mode coupling theory [12]. In spin models the natural way to couple two replicas consists in adding to the Hamiltonian a term $-\epsilon \sum_i S_i S'_i$. Here we can define $q = N^{-1} \sum_{i=1,N} S_i S'_i$. The overlap q is equal to one if the configurations of the two systems coincide. The two replicas potential is

$$F_Q(T, T', \epsilon) = \left\langle \frac{\int dS' \exp[-\beta' H_J(S')] F(T, \epsilon, S')}{\int dS' \exp[-\beta' H_J(S')]} \right\rangle,$$

$$F(T, \epsilon, S') = (N\beta)^{-1} \ln\left[\int dS \exp\left(-\beta H_J(S) + \beta\epsilon \sum_{k=1}^{N} S_k S'_k \right) \right].$$

where the $\langle\,\rangle$ denotes the average over the J's.

In the following we will study the phase diagram of the model in the ϵ-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 $F(T, T', \epsilon)$, $V(q, T, T') \equiv \min_\epsilon F(T, T', \epsilon) + \epsilon q$, which corresponds physically to constraining the value of the overlap to q, was studied in detail in [8] with the aid of the replica method. The interested reader can find there details about the general method and the analytic expression for V.

The shape of the function V turned out to be characteristic of a mean-field system undergoing a first-order phase transition. At high enough temperature V is an increasing and convex function of q with a single minimum for $q = 0$. Decreasing the temperature to a value T_f, the potential loses the convexity property and a phase transition can be induced by a finite coupling. A secondary minimum develops at T_d, the temperature of dynamical transition [2], signaling the presence of long-life metastable states. The minimum of the potential has received a dynamical interpretation [8,13] as corresponding to the states reached at long times by the evolution at temperature T starting at time zero from an equilibrium configuration at temperature T'. The height of the secondary minimum reaches the one of the primary minimum at $T = T_s$ and coexistence in zero coupling takes place. This is the usual statical transition point in zero coupling, and it is not accompanied by the release of latent heat. In Fig. 1 we show the shape of the potential in the various regions. (The attentive reader would have noticed that with respect to the curves presented in [8] only one secondary minimum is present at low temperature. The results we present here are corrected, taking into account replica symmetry breaking effects, the meaning of which has been discussed in [14].)

Although the behavior of the potential function is analogous to the one found in ordinary systems undergoing a first-order phase transition, the interpretation is here

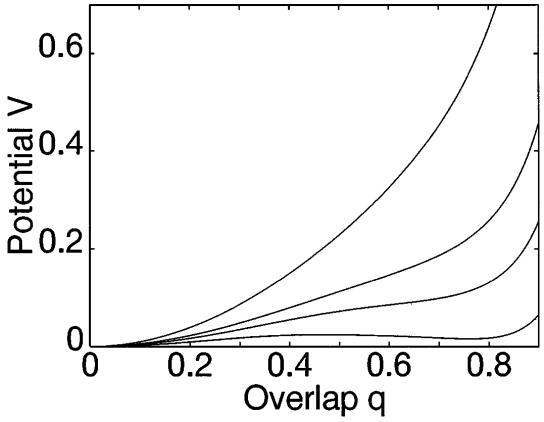

FIG. 1. The potential as a function of q for $p = 4$, $T' = 2T_sT_d/(T_s + T_d) = 0.523$, and various values of T, in order of decreasing temperatures from top to bottom (i.e., $T = 0.7, 0.6., 0.56, 0.523$). For $p = 4$ one has $T_s = 0.503$ and $T_d = 0.544$.

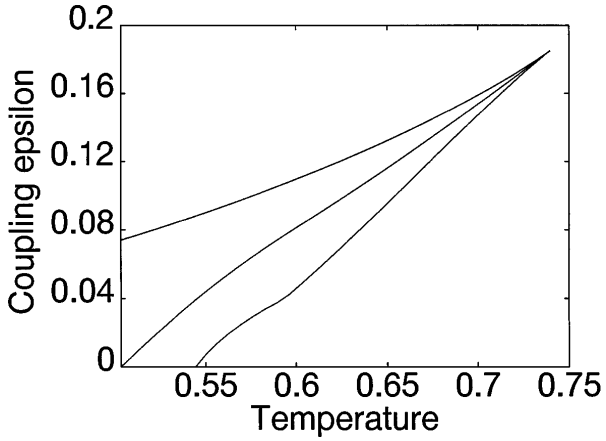

FIG. 2. Phase diagram in the ϵ-T plane for $p = 4$ and $T' = T$. The upper curve is the spinodal of the low q phase, the lower one the spinodal of the high q state, and the middle curve the coexistence line. The coexistence line touches the axes $\epsilon = 0$ at $T = T_s$, while the spinodal of the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

radically different. While in ordinary cases different minima represent qualitatively different thermodynamical states, this is not the case in the potential discussed here. In our problem the local minimum appears when ergodicity is broken, and the configuration space splits into an exponentially large number of components. The two minima are different manifestations of states with the same characteristics. 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 the complexity $T\Sigma$. For $T \neq T'$ it also takes into account the free-energy variation of the equilibrium state at temperature T' when *followed* (i.e., adiabatically cooled or heated) from the temperature T' to the temperature T. The presence of ϵ adds finite stability to the metastable state, and the transition is displaced at higher temperatures. 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 $\epsilon = 0$ at the transition temperature T_s and reaches monotonically a critical point $(T_{\rm cr}, \epsilon_{\rm cr})$. We also show the spinodal of the high q solution, which touches the $\epsilon = 0$ axes at the dynamical temperature T_d, and the spinodal of the low q solution for temperatures larger than T_s. The coexistence line for T' fixed, in the interval $T_s \leq T' \leq T_d$, is qualitatively similar to the one of Fig. 2 at high enough temperature, but (for $T' > T_s$) it never touches the axis $\epsilon = 0$.

Even at zero temperature there is a first-order phase transition in ϵ, reflecting the fact that the energy of the ground state is lower than the energy of the reference state (S') when followed at $T = 0$. This can be seen in Fig. 3 where we show the phase diagram for $T' = 2T_sT_d/(T_s + T_d)$. At the critical point the transition is second order. While the transition in zero coupling is not accompanied by heat release, a latent heat is present for nonzero ϵ. In Fig. 4 we show, in the same conditions of Fig. 3, the latent heat $\mathcal{Q} = E_+ - E_- - \epsilon(q_+ - q_-)$, where E_+ (q_+) and E_- (q_-) are the average H_J (overlaps), respectively, of the high and low q phases. Notice that (as it should) the latent heat is zero at the critical point and 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. We see that at high temperature the high q phase is energetically favored, while at low temperature it has an energy higher than the one of equilibrium.

Finally, in Fig. 5 we show for a fixed temperature the curve of $q(\epsilon)$ obtained by the Maxwell construction.

Although we have based our discussion on a mean-field model, we expect that the qualitative features of the phase diagrams presented survive in finite dimension,

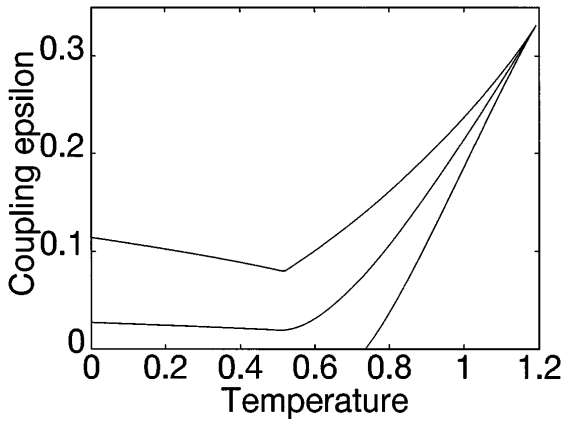

FIG. 3. Phase diagram in the ϵ-T plane for $p = 4$ and $T' = 2T_sT_d/(T_s + T_d)$. The upper curve is the spinodal of the low q phase, the lower one the spinodal of the high q phase, and the middle curve the coexistence line.

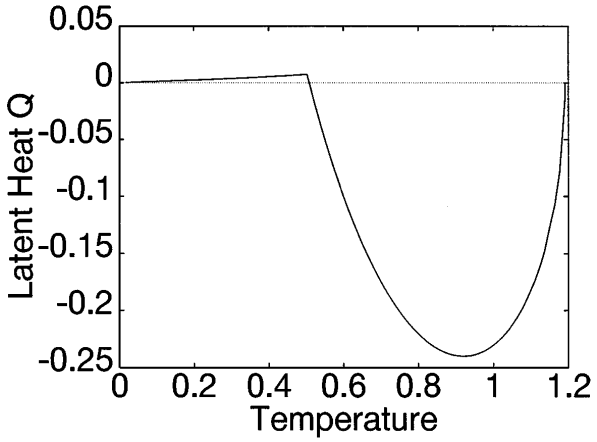

FIG. 4. Latent heat of the transition as a function of the temperature for p and T' as in Fig. 3. The latent heat changes sign in the point where the transition becomes reentrant.

where the potential can be estimated, complementing the mean-field results with the Maxwell construction. We believe that the existence of a coexistence line, terminating in a critical point, is a constitutive feature of systems whose physics is dominated by the existence of long-lived metastable states. The predictions of this Letter can be submitted to numerical test in glassy model systems such as, e.g., Lennard-Jones, or hard spheres, or polymer glasses. The phase diagram starts to have nontrivial features at temperatures greater than T_s, and in this region the thermodynamical properties can be computed by using standard numerical simulations for small samples. It is possible that better results could be obtained using algorithms *parallel tempering* [15] that have been tested for spin glasses and allow for equilibration in the low temperature region at least for not too large samples. For example, the identification of the complexity Σ as the free-energy difference between the stable and the metastable phases could allow a direct measure of this quantity in a simulation. Indeed the ending of the transition lines in a critical point implies that the metastable state can be reached via closed paths in phase diagram leaving always the system in (stable or metastable) equilibrium, and the free-energy difference of the two phases computed integrating the specific heat along the loop. The absence of a first-order phase transition at large coupling is an important prediction of the analogy with p-spin model whose validity is crucial for an accurate determination of the free energy in the low temperature phase.

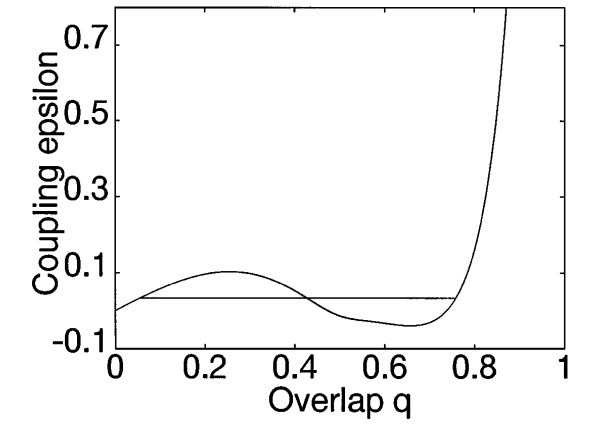

FIG. 5. Equation of state for $T' = 2T_sT_d/(T_s + T_d)$ and $T = 0.609$. The horizontal line corresponds to coexistence and is obtained by the Maxwell construction.

The authors benefited from the stimulating environments of the conferences of Sitges (10–14 June 1996) and Lyon (30 September–3 October 1996). S. F. thanks the "Dipartimento di Fisica dell' Università di Roma La Sapienza" for kind hospitality during the elaboration of this work.

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