

Constrained Boltzmann-Gibbs measures and effective potential for glasses in hypernetted chain approximation and numerical simulations

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By means of an effective potential associated with a constrained equilibrium measure and apt to study frozen systems, we investigate glassy freezing in simple liquids in the hypernetted chain (HNC) approximation. Unlike other classical approximations of liquid theory, freezing is naturally embedded in the HNC approximation. We give a detailed description of the freezing transition that is analogous to the one given in a large class of mean-field long range spin glass. We compare our findings with Monte Carlo simulations of the same system and conclude that many of the qualitative features of the transition are captured by the approximated theory. © 1999 American Institute of Physics. [S0021-9606(98)51529-2]

I. INTRODUCTION

Cooled at a fixed rate, supercooled liquids stop flowing on observable time scales when the glassy transition temperature T_g is met.¹ At that cooling rate dependent temperature, these systems get out of equilibrium. The large scale motion of the molecules is frozen, and consequently the entropy (in the sense of the logarithm of the phase space accessible to the system) is discontinuously reduced. This discontinuity is equal to the configurational entropy at temperature T_g and is supposed to vanish if the system can be kept in equilibrium down to the point of the ideal glass transition T_0 . This would be observable only for infinitely slow cooling, and would be a real thermodynamic transition.

At temperatures smaller than T_g these systems find themselves in a region of the configuration space having vanishing weight in the Boltzmann distribution,² the values of the extensive quantities being far from these at equilibrium. One can also expect that they will remain conformationally close to the configuration γ reached at T_g where flow stopped. On the other hand, small scale vibrations of the atoms are free to thermalize at the actual temperature T of the thermal bath. This situation, with extreme separation of time scales would be naturally described by a statistical ensemble where the slow degrees of freedom are quenched, and the fast degrees of freedom thermalize at temperature T . One can then define a conditional statistical ensemble, as a Boltzmann-Gibbs measure for fixed distance from the point γ . The free-energy associated with this distribution is a function of the constrained distance, and is a natural "effective potential" for glassy systems. This effective potential can be

computed with the replica method even in nondisordered models, the role of the quenched variables being played by the reference configuration γ . This reduces the problem to the study of the free-energy of a multicomponent mixture, in which an analytic continuation on the number of components has to be performed at the end of the computation.

In previous work,³⁻⁵ the shape of the potential, and the implications for the glass transition in long-range spin glasses were studied and the generality of the picture in numerical simulations of a binary mixture model were supported.⁵ In this paper we extend the analysis to models of simple liquids in the HNC approximation, and show how this approximation, devised to study the liquid phase, naturally describe glassy freezing.⁶ The same would not be true for other classical approximations of liquid theory such as the Percus-Yevick or the mean spherical approximations. The implementation of the replica formalism for the effective potential in the HNC approximation is similar to the one used by Given and Stell⁷ to study liquids in random quenched matrices. It also bears resemblance with the one used by Zippelius and co-workers to implement random crosslinking in models of vulcanization. The main difference is that, while in these cases the replica method is used to deal with external quenched disorder, in our case we use quenched degrees of freedom to probe the configuration space of systems that freeze even in absence of quenched disorder.

The approach of this paper is complementary to the one put forward recently in Ref. 6. There it was shown how, combining HNC and replicas, one could reveal the glassy transition and find the properties of the system below the glass temperature. In this paper we will discuss the nature of the freezing in the HNC approximation finding a scenario very similar to that of mean-field spin glasses. The approximation is constructed in such a way that the critical density

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automatically coincides with the one obtained in Ref. 6. The advantage of the “effective potential” framework with respect to that of Ref. 6 is to make conceptually clear the introduction of the replicas in the theory and to make testable predictions on the behavior of the system at density less than the critical one (as we shall see below) when we introduce a potential among two copies of the system. On the other hand, we will see that for high values of the density, the simpler approach of this paper, where we neglect replica symmetry breaking, leads to inconsistency, and there one needs to resort to the approach of Ref. 6 for a coherent theory.

The explicit computations are performed for the hard sphere potential. We support our findings with Monte Carlo simulations of the same system. A short account of our result has appeared in Ref. 8.

We organize the paper as follows: in Sec. II we discuss the construction of the effective potential and we briefly review the results obtained for long-range spin glasses. In Sec. III we discuss the potential for simple liquids in the HNC approximation. Section IV is devoted to the presentation of the theoretical results on the hard sphere system, that in Sec. V we compare with the numerical simulations. Finally, in Sec. VI we present some conclusions and perspectives.

II. THE EFFECTIVE POTENTIAL

In this section we review the construction of the effective potential.³⁻⁵ We discuss the case of a simple liquid composed by N identical pointlike particles in a volume V , described by their coordinates $x = (x_1, \dots, x_N)$, and interacting via a pair potential $\phi(x_i - x_j)$. Suppose that, undergoing a cooling process from the liquid phase, the system falls out of equilibrium at a temperature T_g and remains stuck in a region of the configuration space having vanishing weight in the Boltzmann-Gibbs measure. This commonly happens at the glassy transition of supercooled liquids, where the liquid stops flowing: Large scale motion is frozen, while small scale motion of the atoms (vibration) can still equilibrate even below T_g . In these conditions the observed values of extensive quantities can be far from their canonical equilibrium values, while keeping the external parameter constant, they do not vary over the laboratory time scale. It is appropriate then to restrict the measure in configuration space to the vicinity of the configuration y reached when crossing T_g .

In order to do that we need to define a notion of similarity (or codistance) among configurations, $q(x, y)$, that, with reference to spin glass terminology, we call overlap. The appropriate definition of the overlap depends on the problem at hand, and it has to be such that to similar configurations correspond high values of q [with normalization $q(x, x) = 1$] and to very different configurations values close to zero.

In our particle system an appropriate definition can be

$$q(x, y) = \frac{1}{N} \sum_{i,j} w(|x_i - y_j|), \quad (1)$$

where $w(r)$ is a function close to one for $r \leq \sigma r_0$ and close to zero for $r \geq \sigma r_0$, with r_0 being the radius of the particles and σ a number, e.g., of the order of 0.3, such that couples of

particles at small distances in the two configurations contribute positively to q . Specifically in the unit radius hard sphere problem of Sec. IV we will use $w(r) = \theta(r - 0.3)$. As $q(x, x) = 1$ and $q(x, y) \leq 1$, we can define a sort of distance as $d(x, y) = 1 - q(x, y)$. In the following we will speak indifferently about the two quantities, remembering that high overlap means small distance and vice-versa.

Having now the definition of $q(x, y)$ we can define a restricted Boltzmann-Gibbs distribution as

$$P(x|y) = \frac{1}{Z(\beta, y)} \exp(-\beta H(x)) \delta(q(x, y) - q), \quad (2)$$

where $Z(\beta, y)$ is the integral over x of the numerator of Eq. (2).

Three comments are in order.

- (1) The value of q that appears in Eq. (2) is at this stage arbitrary. However, the system at temperature T will tend to adjust itself and select a given natural distance from the configuration y , according to local free-energy minimization. The selection of q can be well understood in a mean-field picture, and has been discussed in the case of long range spin glasses in Ref. 3. At low temperatures one expects metastable states in configuration space. This corresponds to a two-minima structure of the effective potential, with one minimum at low q representing the typical overlap among configurations belonging to different metastable states, and one minimum at high q representing the typical overlap among configurations in the same metastable state. This last is the q that would be naturally chosen by the system.
- (2) The second comment concerns the dependence of the measure (2) on the reference configuration y . At a first sight, as different cooling experiment would produce different configuration y , it would appear that the measure (2) could be hardly of any use. However, y is supposed to be a configuration *typical* with respect to the Boltzmann-Gibbs probability at temperature T_g , $\mu(y) = \exp(-\beta_g H(y))/Z(\beta_g)$, and we can expect the extensive quantities computed from Eq. (2) to be self-averaging (i.e., y independent) in the thermodynamic limit. The role of the configuration y is analogous in this construction to the one of the quenched variables in disordered systems. In this sense, the measure (2) is an implementation of the idea of “self-generated disorder” often advocated for structural glasses.^{10,13}
- (3) The third comment concerns the selection of the temperature T_g . For that we do not have any *a-priori* criterion, as it is a quantity that in experiments depends on the cooling rate. We have thought to the temperature of the configuration y , that we will call T' in the following, as the glass transition temperature in the purpose of illustrating the physical situation that we have in mind. As a matter of fact our construction is well defined for arbitrary T' , and interesting results are obtained even for $T' = T$. In this paper we will limit our analysis to this case using the measure (2) as powerful probe of configuration space. We insist, however, on the conceptual importance of considering two temperatures, and we will

often refer to results obtained in spin glasses for this more complicated case. In the previous discussion and part of the following we have considered the temperature as the only external parameter. It is clear that *mutatis mutandis* analogous considerations hold for any other control parameter, as the density of Sec. V.

The object on which we will concentrate our attention is the free-energy associated with the distribution (2) that, invoking the self-averaging property we can write as

$$V(q, \beta, \beta') = -\frac{T}{N} \frac{1}{Z(\beta')} \int dy \exp(-\beta' H(y)) \times \log \left\{ \int dx \exp(-\beta H(x)) \delta(q(x, y) - q) \right\}. \quad (3)$$

As the constraint implied by the delta function is global, we can enforce it through a Lagrange multiplier; and considering the quantity

$$F(\epsilon, \beta, \beta') = -\frac{T}{N} \frac{1}{Z(\beta')} \int dy \exp(-\beta' H(y)) \times \log \left\{ \int dx \exp(-\beta [H(x) - \epsilon q(x, y)]) \right\} \quad (4)$$

we find that V and F are related by the Legendre transform

$$V(q, \beta, \beta') = \min_{\epsilon} (F(\epsilon, \beta, \beta') + \epsilon q). \quad (5)$$

For practical purposes it is more convenient to work with F than with V , while the data are more easily interpreted in terms of V . We will pass freely from one representation to the other in the following.

In order to deal with the average of the logarithm in Eq. (4) we resort to the replica method. This consists in evaluating the moments $\overline{Z^r}$ for integer r and computing the average logarithm from an analytic continuation to non integer r from the formula $\overline{\log Z} = \lim_{r \rightarrow 0} (\overline{Z^r} - 1)/r$. Explicitly we can write

$$\overline{Z^r} = -T \int dx_0 \exp(-\beta' H(x_0)) / Z(\beta') \int dx_1 \dots dx_r \times \exp \left(-\beta \left[\sum_{a=1}^r H(x_a) - \epsilon \sum_{a=1}^r q(x_a, x_0) \right] \right), \quad (6)$$

where we have written $y = x_0$. The problem is reduced to the computation of thermodynamics for a mixture of $r+1$ components in the limit $r \rightarrow 0$. Notice the nonsymmetric role played by the replica x_0 and the replicas x_a for $a \geq 1$. This implies that while there is symmetry under permutation of replicas with positive index there is not symmetry under interchange of the replica x_0 with the others. Although we have $r+1$ replicas, the symmetry of the problem is only S_r , becoming S_{r+1} only for $\epsilon \rightarrow 0$. Technically, our approach is similar to the one of Goldbart and Zippelius¹⁴ in their study of the vulcanization of rubber and the one of Stell *et al.* for liquids in random quenched matrices, where also one finds a number of replicas that tends to one. However, in their case

real quenched disorder is present, while in our case we use the auxiliary configuration y to restrict the Boltzmann-Gibbs measure to small regions of configuration space.

Before discussing in the next section the application of the present formalism to simple liquids in the hypernetted chain approximation, let us describe briefly what one can expect for the effective potential when a glassy transition occurs, considering for simplicity the case $T' = T$. In the supercooled phase the diffusion constant becomes lower and lower as the temperature is lowered. The ‘‘cage effect’’ takes place: The molecules get trapped for long times before they can diffuse. When the glass transition is met diffusion is completely stopped, at least on human time scale. The entropy associated to diffusion is lost at the transition. Ergodicity is broken and the configuration space is effectively split into an exponentially large number of practically mutually inaccessible regions.

Making the approximation that the time to jump out of these regions is infinite, it is natural to expect the effective potential (2) to have two minima. One corresponding to the typical (low) overlap among configurations belonging to different regions in configuration space, and another corresponding to the typical overlap (high) of different configurations belonging to the same region. The number of these regions, or metastable states \mathcal{N} is related to the configurational entropy Σ by the relation: $\mathcal{N} = \exp(N\Sigma)$. The probability of x to be in the same metastable state of y will be in such conditions $1/\mathcal{N} = \exp(-N\Sigma)$. Consequently the relative height of the high q minimum with respect to the low q one has to be equal to $T\Sigma$. This picture is realized and it has been discussed in Refs. 3 and 4 in a large class of long range spin glass model. The analysis of these models tells us that the picture has to be refined a little. To each disconnected region one can associate a free-energy f , with an energetic part and an entropic part. Defining $\Sigma(T, f)$ the logarithm of the number of these regions as a function of f , one finds that, at low enough temperature, Σ is different from zero in a finite temperature dependent interval $I(T) = [f_m(T), f_M(T)]$. The states that dominate the partition function at temperature T are such if the quantity

$$F = f - T\Sigma(T, f) \quad (7)$$

is minimum.¹⁵ The study of the effective potential for $T \neq T'$ shows that individual states do not disappear when the temperature is changed, but remain stable for large ranges of temperatures.^{3,16,17} As the temperature is lowered, states with lower and lower Σ are selected in Eq. (7) until, for a temperature T_s with $\Sigma = 0$ are reached and the partition starts to be dominated by the lowest states.

III. THE HNC APPROACH

Let us now discuss of the implementation of the HNC approximation in the approach outlined in the previous section. As we stressed the use of the replica method reduces the problem of the evaluation of the effective potential to the one of an $r+1$ component liquid mixture, in which there is a privileged component with which all the other replicas interact via the potential

$$-N\epsilon \sum_{a=1}^n q(x_a, x_0) = -\epsilon \sum_{a=1}^n \sum_{i,j}^{1,N} w(x_i^0 - x_j^a). \quad (8)$$

The basic quantities of the theory are the pair correlation functions among replicas

$$\rho_a \rho_b g_{ab}(x, y) + \rho_a \delta_{ab} \delta(x - y) = \sum_{i,j} \delta(x_i^a - x) \delta(x_j^b - y). \quad (9)$$

A partial resummation of the Mayer expansion allows us to write a self-consistent expression for the free-energy^{18,19,6}

$$\begin{aligned} -2\beta F_{\text{HNC}} = & \int d^d x \sum_{a,b=0}^r \rho_a \rho_b g_{ab}(x) [\log g_{ab}(x) - 1 \\ & + \beta_a \phi(x) \delta_{ab}] + 2\beta \epsilon \sum_{a=1}^r \rho_0 \rho_a g_{0a}(x) w(x) \\ & + \text{Tr } \mathbf{L}(\rho h), \end{aligned} \quad (10)$$

where $h_{ab} = g_{ab} - 1$ is the connected correlation function and \mathbf{L} is an operator in physical and replica space, defined by

$$\mathbf{L}(u) = u - u^2/2 - \log(1 + u). \quad (11)$$

We have also put $\beta_0 = \beta'$, $\rho_0 = \rho'$ and $\beta_a = \beta$, $\rho_a = \rho$ for $a > 1$. The free-energy (10) has to be extremized with respect to the g_{ab} 's and the terms of order r have to be extracted. The extremum conditions can be cast in the form

$$\begin{aligned} g_{ab}(x, y) = & \exp(-\beta_a \phi(x, y) \delta_{ab} + \{\delta_{0a}(1 - \delta_{0b})\beta_b \\ & + \delta_{0b}(1 - \delta_{0a})\beta_a\} \epsilon w(x) + h_{ab}(x) - c_{ab}(x)) \end{aligned} \quad (12)$$

with g and c related by the Ornstein-Zernike relation

$$h_{ab}(x) = c_{ab}(x) + \sum_{c=0}^r \int dy h_{ac}(x - y) \rho_c c_{cb}(y). \quad (13)$$

As usual in the replica method one needs a parameterization of the matrix g_{ab} that allows the analytic continuation to $r \rightarrow 0$. On the basis of symmetry considerations analogous to the one of Ref. 3, one can propose the structure

$$g_{ab} = \begin{cases} g_{00} & a = b = 0 \\ g_{10} & a = 0, \quad b \neq 0 \quad \text{or} \quad b = 0, \quad a \neq 0. \\ g_{ab}^* & a, b \neq 0 \end{cases} \quad (14)$$

The $r \times r$ submatrix g_{ab}^* can be either replica symmetric or have an ultrametric structure,²⁰ in the following we will limit ourselves to the replica symmetric structure:

$$g_{ab}^* = \begin{cases} g_{11} & a = b \\ g_{12} & a \neq b \end{cases} \quad (15)$$

which coincides with the choice of Given and Stell.⁷ In the case of the p-spin model, the replica symmetric choice gives the correct result for the effective potential in the high and in the low q regions and in particular around the minima. However, an intermediate q region where ‘‘one step replica symmetry breaking’’ in the matrix g_{ab}^* was necessary to correctly compute the effective potential was found. Although we do not explore here the possibility of solutions with a structure

more complicated than Eq. (15) and we limit ourself to the study of the high and low q parts of the effective potential, we warn the reader that replica symmetry breaking is also to be expected in this case for intermediate q .

The interpretation of the different elements of the g_{ab} matrix with the replica symmetric ansatz is straightforward. The element g_{00} represents the pair correlation function of the free system; as such the equation determining it decouples from the other components in the limit $r \rightarrow 0$. In turn, g_{11} represents the pair correlation function of the coupled system. g_{10} is the pair correlation among the quenched configuration and the annealed one, while g_{12} represents the correlation between two systems coupled with the same quenched system. This is the analogous to the Edwards-Anderson order parameter in disordered systems, and represents the long time limit of the time dependent autocorrelation function at equilibrium.³

Straightforward algebra shows that Eqs. (13) reduce to the ones proposed in Ref. 7. In particular one finds that, as it should be, the equation for g_{00} , describing the correlation function of the quenched replica decouples from the other and coincides with the usual HNC equation in absence of replicas

$$\begin{aligned} h_{00}(x) = & c_{00}(x) + \int d^d y [\rho_0 h_{00}(x - y) c_{00}(y) \\ & + r \rho_1 h_{11}(x - y) c_{11}(y)], \\ h_{10}(x) = & c_{10}(x) + \int d^d y [\rho_0 h_{00}(x - y) c_{10}(y) + \rho_1 h_{10}(x - y) \\ & \times (c_{11}(y) - c_{12}(y)(1 - r))], \\ h_{11}(x) = & c_{11}(x) + \int d^d y [\rho_0 h_{10}(x - y) c_{10}(y) \\ & + \rho_1 (h_{11}(x - y) c_{11}(y) - h_{12}(x - y) c_{12}(y)(1 - r))], \end{aligned} \quad (16)$$

$$\begin{aligned} h_{12}(x) = & c_{12}(x) + \int d^d y [\rho_0 h_{10}(x - y) c_{10}(y) \\ & + \rho_1 (h_{11}(x - y) c_{12}(y) + h_{12}(x - y) c_{11}(y) \\ & - h_{12}(x - y) c_{12}(y)(2 - r))]. \end{aligned}$$

The overlap can be expressed in terms of the correlation function g_{10} , and reads

$$q = \rho \int dx w(x) g_{10}(x) = 4\pi\rho \int_0^\infty r^2 w(r) g_{10}(r). \quad (17)$$

According to the discussion of the previous section, we will associate glassy behavior with nonconvexity of the function $V(q)$, and in particular to the existence of multiple solutions $q(\epsilon)$ for $\epsilon \rightarrow 0$. In the liquid phase we can expect instead $q(\epsilon)$ to be a single value function and a convex effective potential with a minimum at $q = q_0 = \rho \int dx w(x)$, corresponding to the absence of any structure in g_{10} , i.e., $g_{10}(x) = 1$ for all x . A strong coupling ϵ , attracting the system towards the configuration y will force a structure in the g_{10} , which will have a higher peak in $x = 0$ the higher the cou-

pling is. Similarly, g_{12} will acquire a structure: If two different systems are similar to the configuration y they will also be similar to each other. When the system freezes, a solution to the HNC equations will exist in which g_{10} and g_{12} will have a structure even for small and vanishing ϵ .

The value of ϵ at which we find a solution with nonzero g_{12} coincides with dynamical critical density of Ref. 6 and it corresponds to the phase transition point in a mode-coupling approach.¹ Indeed, in this mean-field approach ergodicity starts to break exactly at this point.

IV. RESULTS FOR HNC HARD SPHERES

In this section we discuss the picture coming from the integration of Eqs. (12) and (13) in three dimension. We present systematic data in the case of the hard sphere potential

$$\phi(r) = \begin{cases} 1 & r < 1 \\ 0 & r > 1 \end{cases} \quad \text{and with } w(r) = \begin{cases} 1 & r < 0.3 \\ 0 & r > 0.3 \end{cases} \quad (18)$$

The hard sphere potential has been chosen for practical convenience; the glassy transition picture that will emerge can be strongly expected to be very general. We have verified in nonsystematic investigations that the same picture indeed holds for soft sphere systems with $\phi(r) = r^{-12}$. The value 0.3 that appears in the definition of w has obviously nothing fundamental, and we have checked that the picture is insensitive to its precise value. The hard sphere model has no temperature, and the control parameter is the density. Numerical work report a glassy phase for values of the density higher then 1.15 (we use a normalization of the density such that $\rho = \sqrt{2}$ for f.c.c. packing).

We have solved the saddle point equation (12) and (13) by iteration for various values of the density and the coupling. For fixed density we start the integration of the equation at low (respectively, high) coupling ϵ where we know the solution and we increase (respectively, decrease) it at small steps. In this way we can find the curves of q as a function of ϵ , and reconstruct from Eq. (10) the effective

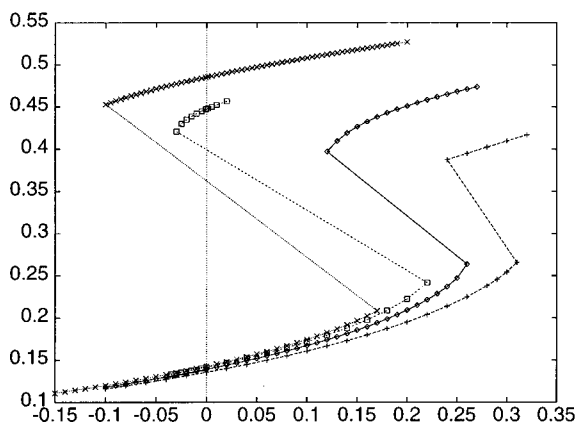


FIG. 1. The behavior of q as a function of ϵ for HNC hard spheres for $\rho = 1.14, 1.17, 1.19, 1.20$. For high enough density q is a multivalued function of ϵ . We have shown only a portion of the curve in the region where it is multivalued. For clarity in this and the next figure we have joined with a line the branches corresponding to the same density.

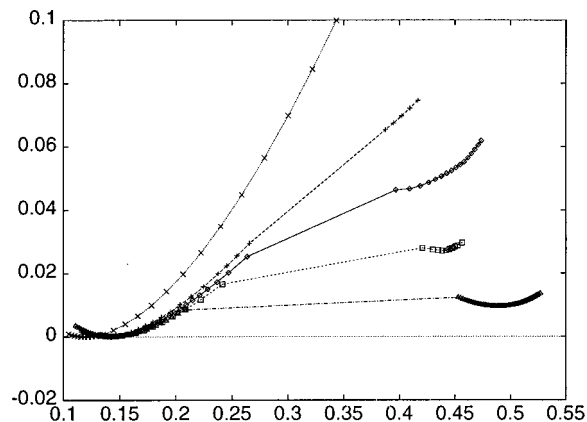


FIG. 2. The effective potential for HNC hard spheres. From top to bottom $\rho = 1.0, 1.14, 1.17, 1.19, 1.20$. For low density, high up in the liquid phase the potential is convex. In the glass phase two minima are present.

potential $V(q)$. We checked that up to a constant $V(q) = \int^q dq' \epsilon(q')$. In the low density region we were able in this way to fully reconstruct the shape of the potential. For higher densities, we could just reconstruct in this way the high and the low parts of the effective potential. This is, however, enough to get a fully detailed picture of the freezing in the system. In Fig. 1 we present the curves of q as a function of ϵ for various values of the density, while in Fig. 2 we plot the corresponding curves $V(q)$.

At low density ϵ is a monotonic function of q , testifying to ergodic behavior of the system. The potential $V(q)$ is convex and has a single minimum for $\epsilon = 0$, where the value of the overlap is $q_0 = \rho 4 \pi (0.3)^3 / 3 = \rho \times 0.113$, corresponding to $g_{10}(x) = 1$ for all x .

Interesting behavior appears for densities higher or equal to $\rho_{cr} \approx 1.14$. At ρ_{cr} the function $q(\epsilon)$ begins to be multivalued, the potential loses the convexity property and a phase transition among a low q and a high q phase can be induced by a coupling. The point $(\rho_{cr}, \epsilon_{cr})$, with $\epsilon_{cr} = 0.305$ is a critical point of second order phase transition, from which it departs a first order phase transition line $\epsilon_{tr}(T)$ (Fig. 3). The term $-N\epsilon q(x, y)$ in the Hamiltonian implies an energetic advantage for the configurations x close to y and induces a transition between a high q “confined” phase with high en-

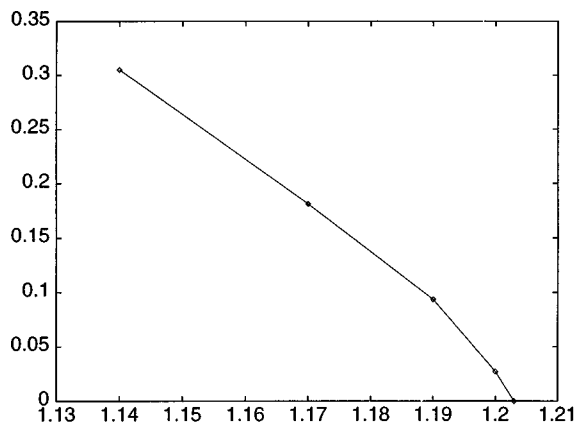


FIG. 3. Phase diagram in the plane $\epsilon - \rho$. A first order transition line terminating in a critical point separates a low q from a high q phase.

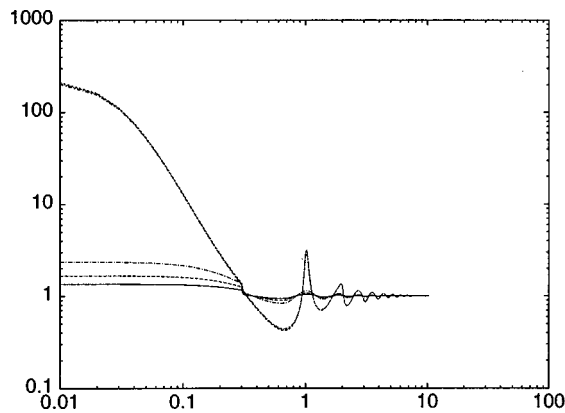


FIG. 4. The function $g_{10}(r)$ for $\rho=1.20$ and $\epsilon=0.10,0.15,0.20$. The three curves on the top correspond to the high q solution; the three curves on the bottom to the low q one.

ergy and a low q “deconfined” phase with high entropy. The transition line tells us that generic equilibrium configurations lie in metastable states for densities higher than ρ_c . For $\rho_{cr} < \rho < \rho_c = 1.17$ the metastable states have a finite life, and a coupling $\epsilon \geq \epsilon_{cr}(T)$ is needed to stabilize them. At ρ_c a minimum develops in the potential, and the metastable states have an infinite time life. The equation $q = q(\epsilon = 0)$ has more than one solution. It has been shown by explicit calculation in Ref. 3 that a second minimum in the effective potential implies that in the equilibrium dynamics the system remains confined in a region with a large overlap with the initial state. In Fig. 4 we plot the function $g_{10}(r)$ for $\rho=1.20$ and various values of ϵ in the high q and the low q solutions. We see how the low q solution has little structure ($g_{10} \approx 1$) while the high q solution has a very pronounced peaks for integer values of r .

In ordinary cases multiple minima in the effective potential as a function, the order parameter signal the presence of different (stable or metastable) phases with different qualitative characteristics (e.g., liquid and gas). Here the implications of the two minima structure are different. The appearance of the secondary minimum signals the breaking of the ergodicity, i.e., the split of the support of the Boltzmann-Gibbs measure into many, mutually inaccessible, regions. It is easy to realize the link among the two minima structure and such nonergodic situation. If we suppose that the different regions have typically all the same distance, one shall have a minimum corresponding to that distance, and another minimum corresponding to the typical distance among configurations in the same region. In this perspective the minima are different manifestations of the same phase. Coherently with this picture, the internal energy in the two minima should be the same. Obviously this last sentence has no meaning for hard spheres where the internal energy is not defined, but it can be easily checked in soft sphere systems. The difference of height between the two minima, ΔV can also be understood in this perspective as being due to the fact that the number of regions in which the configuration space has split (\mathcal{N}) is exponentially large in the number of particles $\mathcal{N} = \exp(N\Sigma)$, and each region carries a vanishing weight in the measure. In that condition, choosing y in a

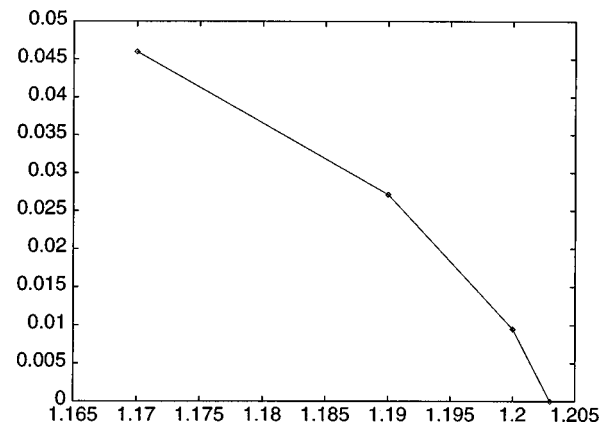


FIG. 5. The configurational entropy Σ as a function of ρ .

region at random, the probability that x falls in the same region, which should be $\exp(-\beta\Delta V)$ is equal to $\mathcal{N}^{-1} = \exp(-N\Sigma)$.

We find then that Σ , to be identified with the configurational entropy, is related to ΔV by²¹

$$\Delta V = T\Sigma. \quad (19)$$

We have then a method to compute the configurational entropy, that we plot in Fig. 5. An equivalent method has been proposed in Ref. 22. We see that Σ is a decreasing function of the density and vanishes at a density $\rho_s \approx 1.203$,²³ according to the scenario of Gibbs and Di Marzio of the glass transition, and analogously to long range spin glasses. At each value of the density one chooses these states such that the total balance between f the internal free-energy of the region and the configurational entropy is such to minimize the total free-energy. Above ρ_s the equations we are considering give the clearly unacceptable result of a negative configurational entropy, and the approach must be modified. Previous experience in spin glasses tells us that the paradoxical behavior has to be ascribed to an incorrect description of the quenched replica y . For $\rho > \rho_s$, the lowest f states are chosen. These carry a finite Boltzmann weight and a correct description has to take this into account. In the correct HNC approach to the high density regime, the quenched replica should be described by the replica formulation of Mézard and Parisi with replica symmetry breaking.⁶ The HNC approximation, originally devised to study liquids at equilibrium, naturally embeds glassy behavior in a glassy transition scenario completely analogous to the one of disordered models with “one step replica symmetry breaking.”

In many senses the picture is genuinely mean-field-like. In fact, it has been stressed many times that in real systems metastable states with an infinite lifetime do not exist, and a mechanism should restore ergodicity between ρ_c and ρ_s . Moreover it is easy to realize that the effective potential we have defined must be convex beyond mean field. This can be seen constructing configurations with overlap inhomogeneous in space and with a free energy lower or equal to the convex envelope of the potential. We expect, however, a reflex of the mean-field structure in real systems. What is seen as a sharp transition in the mean field can still be observed as a crossover in real life and some of the predictions

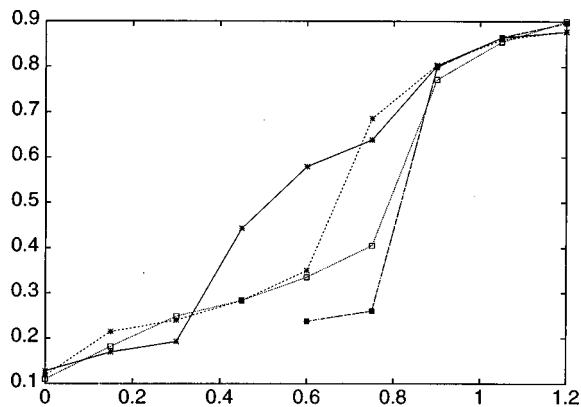


FIG. 6. The behavior of q as a function of ϵ for a system of 258 particles and $\rho=1.04$. The different curves correspond to different thermalization times 2^k for each value of ϵ . From top to bottom $k=17, 19, 21, 23$. For larger thermalization times the system seem to develop a first order jump in q .

of the mean field can be expected to hold in finite dimensional systems. In particular, the existence of a first order transition line in the plane $\rho - \epsilon$, which depends on the existence of metastable states, regardless if their life is finite or infinite we expect to hold in real (or realistic) systems. In the next section we will submit that to test.

Before leaving this section let us remark that (we show how in some detail in the Appendix), the possibility of a glass transition, associated with nontrivial $g_{10}(x)$ for $\epsilon \rightarrow 0$ is excluded by other classical approximations of liquid theory, the Percus-Yevick approximation and the mean spherical approximation.

V. NUMERICAL SIMULATIONS

In order to test the predictions of the transition scenario of the previous section we have performed Monte Carlo simulations of a system of hard spheres in three dimension coupled with a quenched configuration. We have done simulations with a number of particles N ranging from 256 to 1024 and we have not observed any significant dependence on the volume.

To generate the quenched equilibrium configurations at fixed density we start with N particles of zero radius in a box with periodic boundary conditions, and we let the radii grow until two particles do not get in contact. At that point we make a Monte Carlo sweep, i.e., we move the particles of random amount and we accept the change if two spheres do not overlap; the size of the proposed move is fixed in such a way to have 0.4 average acceptance. We iterate the procedure until the desired density is reached. The volume and the radius (r) are at the point rescaled in order to have $r=1$. We thermalize then the system for 4000 Monte Carlo sweeps and use the configuration y reached as external field for our coupled replicas experiment. The relatively short thermalization is chosen in order to avoid crystallization. We have carefully verified that the *equilibrium* configuration does not have any signs of crystallization by monitoring this correlation function, which has a smooth minimum around 1.4, as it should do in the liquid phase.

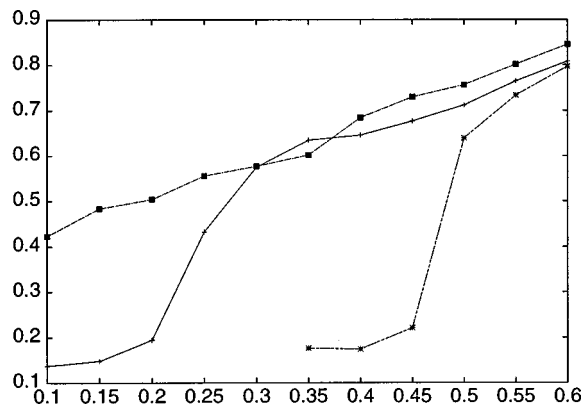


FIG. 7. The same as Fig. 6 but with a higher density, $\rho=1.10$ and $N=1024$. The values are $k=17, 19, 21$. Notice that for $k=17$ the system has not relaxed to the low q value even for $\epsilon=0.1$.

Having generated the configuration y , we start the evolution of a coupled system x . For various densities, we start the evolution from the configuration y with a high value of ϵ and decrease the value of ϵ in units of $\delta\epsilon$, making 2^k Monte Carlo iterations for each value of ϵ . In Figs. 6–8 we plot q as a function of ϵ for various values of the density and different values of k . We see that, as expected for a system undergoing a first order phase transition, the curves are smooth for low k and tend to develop a discontinuity for large k . For low density the discontinuity occurs at high ϵ , while it is pushed toward small ϵ for high density.

A different numerical experiment is presented in Fig. 9 where we plot the overlap as a function of the number of Monte Carlo sweeps in a logarithmic scale. Here we let the system evolve at fixed ϵ starting at time zero from $x=y$. Again, we observe a behavior compatible with a discontinuity of q as a function of ϵ .

The same picture can be also observed directly in the behavior of the function $g_{10}(r)$. In Figs. 10 and 11 we can see that while g_{11} does not vary too much as a function of ϵ ,²⁴ one observes qualitatively different regimes in the high and in the low ϵ regime with a discontinuity in $g_{10}(0)$.

For high ϵ we observe a strong oscillatory structure in g_{01} , which is very similar to g_{11} , with the only difference

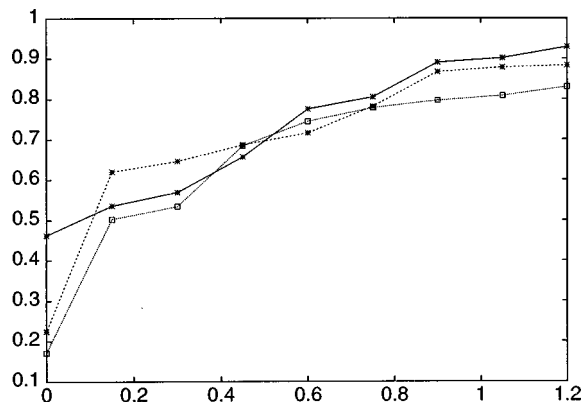


FIG. 8. The same as Fig. 6 with $\rho=1.14$ and $N=256$. The values are $k=17, 19, 21$. As expected, for higher densities the transition is pushed to lower values of ϵ .

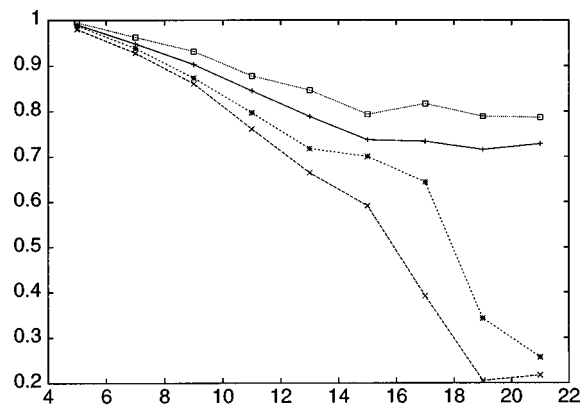


FIG. 9. The overlap as a function of logarithm (in base 2) of the time (i.e., the number of Monte Carlo sweeps) starting from y at time 0 and evolving for fixed ϵ .

being the peaks are smoothed and by the presence of the large peak at $x=0$. On the contrary in the low ϵ regime g_{10} is very close to one for $r>0.3$ and has almost no structure. Notice the striking similarity of this picture with the one that we get from the theory.

VI. CONCLUSIONS

In this paper we have shown that by constraining the Boltzmann-Gibbs measure to small regions of the configuration space we can study the transition from liquid to glass. We have studied, in particular, the case of the simple liquids in the HNC approximation. This model predicts a glassy transition in the lines of the Gibbs-Di Marzio scenario. The physical picture seen from the present analysis is fully consistent with the one obtained from mean-field spin-glass models, although the HNC approach allows us to get information on the structure function of the supercooled liquid. The HNC approach, which consists in neglecting the so-called bridge diagrams in the Mayer expansion turns in this way to be equivalent to a kind of mean-field theory, where the glass transition is associated with a nonconvex effective

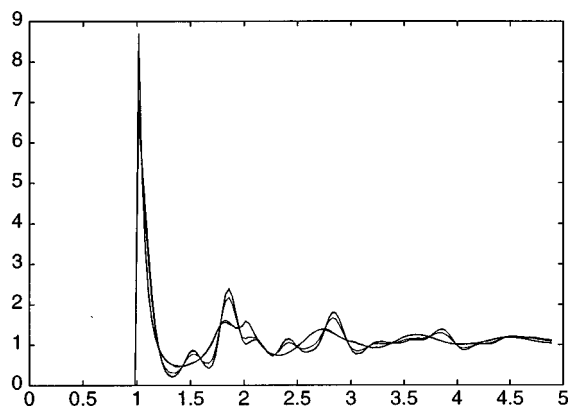


FIG. 10. The function $g_{11}(r)$ for a system with $\rho=1.10$, $N=1024$ and coupling ranging from 0.35 to 0.6 in steps of $\delta\epsilon=0.05$. The curves do not vary too much with ϵ , except the two with the lowest values of ϵ . This could be a spurious effect due to partial crystallization as seen from the small peak around $r=1.4$.

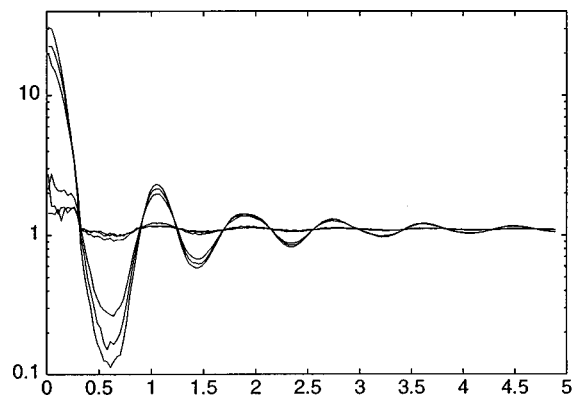


FIG. 11. The function $g_{10}(r)$ for the same system as Fig. 10. We see a net discontinuity in behavior from the high to the low ϵ regions.

potential. Many of the predictions from the theory are expected to be valid in real systems. In particular the picture of first order phase transition in presence of a coupling, which is associated to the presence of metastable regions in configuration space. The picture has been positively tested in numerical simulations on hard sphere systems.

Growing evidence shows that a good starting point for describing the glass transition of supercooled liquids is the scenario met in long-range spin glasses with “one step replica symmetry breaking” transition, which is the static counterpart of the schematic mode coupling theory. Beyond these models this kind of transition pattern is met in mean-field glass models without disorder,^{9–11} and simulations of realistic glass models confirm many aspect of the picture.¹² Finally the HNC approach of Ref. 6 and with a different profile this paper also confirms this scenario.

We believe that the mean-field theory of the glass transition is now on firm ground. On the one hand, we have the mode coupling theory that allows us to extract the dynamical behavior of supercooled liquids not too far from the glass transition. On the other, this theory has been repeatedly observed to be exact in mean-field spin glasses, whose study enriches the picture with a static view of the topography of the configuration space. In this paper we show that the same picture also holds for the realistic model of liquid obtained by the HNC approximation.

Finally we would like to comment once more on the limitation of the theory. As a genuine mean-field theory, the HNC predicts the existence of infinite life metastable states analogously to what happens in long range models and in the mode coupling approximation. According to this picture the system, after having froze into a metastable state at T_g , would “follow” it down and back up in temperature in a completely reversible manner. While this can be true for short times, irreversible effects are observed on large time scales in glasses.²⁵ The issue is related to the barrier jumping processes that restore ergodicity below T_c . Unfortunately, at present the physics of these dynamical problems is unclear. We hope that insight in this problem will come from numerical and theoretical study of disordered models.

ACKNOWLEDGMENT

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APPENDIX

We show here that the mean spherical (MSA) and Percus-Yevick (PY) approximations do not give any glass transition. The MSA deals with hard core interactions, for which $\phi(x) = \infty$ for $|x| < r_0$ and $\phi(x) = \phi_1(x)$ for $|x| > r_0$. In the canonical formalism the exact partition function can be written as a functional integral over the density field $n(x)$

$$Z = \int Dn(x) \exp \left\{ \int dx [-\beta \phi(x-y)n(x)n(y) - \delta(x-y)] - n(x) \log n(x) \right\} \delta \left(\int dx n(x) - \rho \right). \quad (\text{A1})$$

In the MSA one may substitute the entropic part $-\int dx n(x) \log n(x)$ in the exponent of Eq. (A1) by the impenetrability constraint $\int dx n(x)n(x+y) = 0$ if $|y| < r$.²⁶ Expressing the constraint through a set of Lagrange multipliers $\lambda(x)$ one gets a Gaussian integral that can be computed exactly.

In the formalism explained in the text the density variables are replicated, and the constraint takes the form

$$\int dx n_a(x)n_a(x+y) = 0 \quad \text{for } |y| < r_0 \text{ and all } a. \quad (\text{A2})$$

Notice that the replica index in the two densities appearing in Eq. (A2) is the same, as, obviously, there is no impenetrability constraint for different replicas like there would be in a multicomponent fluid. Introducing now a set Lagrange multipliers $\lambda_a(x)$ to enforce Eq. (A2) and exploiting the properties of Gaussian integrals one finds that the correlation function

$$\langle n_a(x)n_b(y) \rangle - \langle n_a(x) \rangle \langle n_b(y) \rangle = A_{ab}^{-1}(x-y) \quad (\text{A3})$$

can be found inverting the relation

$$A_{ab}(x) = \delta_{ab} \lambda_a(x) + V_{ab}(x), \quad (\text{A4})$$

where

$$V_{ab}(x) = \phi_1(x) \delta_{ab} - \{ \delta_{0a}(1 - \delta_{0b}) \beta_b + \delta_{0b}(1 - \delta_{0a}) \beta_a \} \epsilon w(x). \quad (\text{A5})$$

It is clear that for $\epsilon \rightarrow 0$, A_{ab} , and therefore its inverse, becomes diagonal in the replica indices, implying $g_{ab}(x) = 1$ for all x if $a \neq b$.

Analogous reasonings apply to the PY approximation (see, e.g., Ref. 19) where one has

$$c_{ab}(x) = -g_{ab}(x) [e^{\beta V_{ab}(x)} - 1]. \quad (\text{A6})$$

For $\epsilon \rightarrow 0$, c_{ab} becomes diagonal, and the Ornstein-Zernike relation (13) shows that $g_{ab}(x) = 1$ if $a \neq b$.

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²Strictly speaking, in the metastable region the liquid has zero weight, the Boltzmann distribution being concentrated on crystal configurations. In this paper we simply neglect the existence of the crystal and we imagine that in the supercooled region the measure is concentrated on liquid configurations. This situation can also be realized by not considering in the partition sum the crystal-like configurations or by modifying the potential in such a way that the crystal get a high free energy.

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²¹The previous considerations should be modified for $T' \neq T$ or $\rho' \neq \rho$. In that case the secondary minimum reflects the properties of the states of equilibrium at the primed values of the parameters when ‘‘followed’’ at the non primed values.

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²³The values of ρ_c and ρ_s are compatible with those found in Ref. 6, indeed the potential method reproduces the results of replica symmetry breaking for the static and the dynamic critical density.

²⁴Notice the small peak at $r \approx \sqrt{2}$ for the curves with small ϵ . This could signal some crystallization in the system. In any case this effect is present only at high density and is absent in the simulations at lower density. It seems that in the region where the overlap becomes quite small, the system crystallizes in very long runs, while crystallization is obviously forbidden at higher values of the overlap.

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