

**Dynamical arrest and replica symmetry breaking in attractive colloids**A. Velenich,<sup>1</sup> A. Parola,<sup>2</sup> and L. Reatto<sup>3</sup><sup>1</sup>*Physics Department, Boston University, Boston, Massachusetts 02215, USA*<sup>2</sup>*Dipartimento di Fisica e Matematica, Università dell'Insubria, Como, Italy*<sup>3</sup>*Dipartimento di Fisica, Università di Milano, Milano, Italy*

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Within the replica symmetry breaking framework developed by Mézard and Parisi we investigate the occurrence of structural glass transitions in a model of fluid characterized by hard sphere repulsion together with short-range attraction. This model is appropriate for the description of a class of colloidal suspensions. The transition line in the density-temperature plane displays a reentrant behavior, in agreement with mode coupling theory and recent molecular dynamics simulations. Quantitative differences are found, together with the absence of the predicted glass-glass transition at high density. We also perform a systematic study of the pure hard-sphere fluid in order to ascertain the accuracy of the adopted method and the convergence of the numerical procedure.

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**I. INTRODUCTION**

Understanding the physical conditions leading to dynamical arrest in colloidal suspensions and protein solutions is still attracting considerable interest [1]. Colloidal systems are often modeled as simple fluids of (large) spherical particles interacting via the hard-core repulsion plus, possibly, a short-range attraction. The latter contribution may have diverse physical origins, according to the specific system considered, like the depletion mechanism or steric effects.

This simple model has been investigated by simulation methods [2] and liquid-state theories [3]. The key dimensionless parameter governing the physics of the system is the ratio between the range of attraction ( $\Delta$ ) and the hard-sphere diameter ( $d$ ) which, in the following will be taken as the unit of lengths. The equilibrium phase diagram is now well known in a wide range of  $\Delta$  and the stability of the fluid phase as a function of  $\Delta$  has been extensively discussed in the literature. If the range  $\Delta$  is such that at high densities many particles lie within the respective ranges of attraction, the overall effect of the attractions is expected [4] to be just a shift in the ground-state energy of the system, while the dynamical and thermodynamical properties are mostly determined by the hard cores of the particles. Conversely, if the range of the attractive well is short enough, small displacements of the particles can break one or more “energetic bonds” and cause significant variations in the energy of the microscopic state. While the hard-sphere fluid is a purely entropic system, in this case we have both energetic and entropic contributions to the free energy whose relative importance can be tuned by varying the temperature and/or density.

The possible occurrence of dynamical arrest in this model has been studied via mode coupling theory (MCT) which indeed predicts the existence of two distinct glassy states, called “attractive” and “repulsive” glass, separated in the phase diagram by a first-order transition line terminating in a critical point [5,6]. This finding might have relevant consequences on the experimentally accessible systems, and it is therefore important to investigate the problem by alternative techniques.

The occurrence of glassy states in statistical physics was studied mostly by use of the replica approach in the framework of spin glasses [7]. When considering a system with quenched disorder, it is natural to introduce the whole ensemble of possible realizations of the quenched variables. For a variety of models it turns out that the values of many quantities of physical interest equal, in the thermodynamic limit, their average over the quenched variables. Subsequent studies revealed that in order to produce glassy behavior, an externally imposed quenched disorder is not essential because the frustration necessary for slow dynamics and dynamical arrest can be self-generated by the interparticle interaction.

Throughout the formalism, different replicas are in principle indistinguishable and the equations for a replicated system are symmetric with respect to permutations of replicas; yet replica symmetry breaking (RSB) solutions have proved to be the appropriate solutions for the low-temperature phases of several models. For such solutions, the correlation functions between different replicas do depend on the replica indices.

A general framework often used to account for the slow dynamics of glasses is based on the analysis of a free energy  $F$ , considered as a functional of the *averaged* density profile [8]. The key feature is that at low temperatures  $F$  is expected to develop a multimimum structure and, if the free energy barriers are high enough with respect to  $k_B T$ , the configuration space becomes essentially disconnected, leading to a nonergodic behavior. The basic assumption underlying the mean-field approach presented in this paper is the modeling of the glassy nonequilibrium dynamics through such a free energy landscape. Hence, since the whole formalism of equilibrium thermodynamics promptly applies, we can refer to a glassy state as a proper *phase* of the system. The dynamical crossover observed experimentally is correspondingly replaced by a sharply defined phase transition. Although the modeling through an equilibrium free energy landscape does not necessarily imply the absence of a dynamics ([9] and references therein), in the present approach we deal only with static correlation functions and neglect every time de-

pendence of eventual relaxation processes occurring in the liquid side of the phase diagram.

In this context, the introduction of replicas is a procedure intended to unveil a possible multimimum structure of the free energy: it is natural to expect that for two replicas in the same local minimum of  $F$  the correlation is larger than for replicas in different minima. Hence, the appearance of a non-trivial pattern of correlation among replicas (i.e., the breaking of the replica symmetry) is the signature of the complex free energy landscape characteristic of a glassy phase. In the following, by studying the correlation functions between different replicas of a fluid system, we confirm the existence of a RSB phase transition. The comparison of the resulting phase diagram with experimental and numerical data on dynamical arrest in systems with short-range attractive interactions strongly supports the interpretation of such a transition as an ideal glass transition.

We point out that by “ideal” glass transition it is usually meant a transition defined by a thermodynamic singularity [10]. With the replica method, *two* critical densities are obtained: the lower density signals the appearance of a complex free energy landscape [11] with no thermodynamic singularity. At the higher density the complexity vanishes non-smoothly and this gives a true thermodynamic transition. In [12] it was shown that the replica approach we are going to use is not suitable for the description of the glassy phase and leads to incorrect results for the thermodynamic transition. For the time being we do not exclude that a more accurate numerical study of the thermodynamic transition might yield different results (see Table I in Sec. IV and consider that the grid used in [12] had only  $N=128$  points). However, in this paper we limit our attention to the first transition, commonly known as “dynamical” glass transition.

We first review the basic equations derived in [12]; then, we perform a careful study of the hard-sphere system, in order to test the accuracy of the method and to estimate the numerical uncertainty of our results. Finally, we investigate the effects of a short-range interaction and compare our results with MCT predictions. We anticipate that, although the transition line we find is rather similar to those of MCT clearly showing the predicted reentrant behavior, we have no evidence in favor of a glass-glass transition, within the adopted approximations.

## II. REPLICA METHOD FOR STRUCTURAL GLASSES

According to the previous discussion, in order to implement the replica symmetry breaking scheme for a model of fluid, we need a formal expression for the free energy functional of a mixture of  $n$  identical copies (replicas) of the original system. In the following, the indices  $a$  and  $b$  identify different replicas. Such a generalized free energy functional  $F$  depends on the two-body interactions among particles  $U_{ab}(r)$  (both intrareplica and interreplica) and on the two-point correlation functions  $g_{ab}(r)=h_{ab}(r)+1$ , whose entries are labeled by replica indices: ordinary (intrareplica) two-point functions on the diagonal and interreplica correlation functions as off-diagonal elements. The original physical system can be recovered by setting  $n=1$ . The key property of

the functional  $F$  is to attain its global minimum when the pair correlations  $g_{ab}(r)$  assume the physical value corresponding to the given interaction  $U_{ab}(r)$ . RSB occurs when a nontrivial minimum (i.e., a solution with finite correlations among different replicas) is present in the physical limit of uncoupled replicas  $U_{ab}(r)=U(r)\delta_{ab}$ . For a homogeneous system, the general structure of the free energy density functional is

$$F[U, g] = \sum_{a,b} \frac{\rho_a \rho_b}{2} \int d^3 \mathbf{x} g_{ab}(x) U_{ab}(x) - TS[g]. \quad (1)$$

The internal energy contribution is exactly given by the first term of Eq. (1) while the entropy density  $S$  is known to be a functional of the pair correlation functions alone, which can be written [13] as a sum of  $p$ -particle contributions:  $S = \sum_p s_p$ . By use of the Gibbs-Bogoliubov inequality [14] it is easy to prove that the functional  $F$  defined in Eq. (1) satisfies the requirements previously mentioned. Unfortunately, a closed expression for the entropic contribution  $S$  is not available and we have to resort to some approximation. Following Ref. [12] we keep the exact two-body term of the excess entropy  $s_2$ ,

$$s_2 = -k_B \sum_{a,b} \frac{\rho_a \rho_b}{2} \int d^3 \mathbf{x} [g_{ab}(x) \ln g_{ab}(x) - h_{ab}(x)], \quad (2)$$

while approximating the residual contribution  $\Delta S = S - s_2$  in terms of the pair distribution function:

$$\Delta S = -k_B \frac{1}{2} \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \text{Tr} L(\rho \mathbf{h}(q)), \quad (3)$$

where the function  $L(y)$  is defined as

$$L(y) = -\ln(1+y) + y - \frac{y^2}{2}$$

and  $\mathbf{h}(q)$  represents the  $n \times n$  matrix whose elements are the Fourier transforms of the correlation functions  $h_{ab}(r)$ . This form follows the resummation of the infinite class of non-crossing diagrams in the formal expansion of the entropy as a functional of  $h(r)$ . Collecting all terms together we find the final expression for the free energy functional:

$$2\beta F = \rho^2 \int d^3 \mathbf{x} \sum_{a,b} \{g_{ab}(x) [\ln g_{ab}(x) + \beta U_{ab}(x)] - h_{ab}(x)\} + \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \text{Tr} L(\rho \mathbf{h}(q)). \quad (4)$$

In the case of a single component ( $n=1$ ), the minimization of the free energy functional (4) leads to the usual hypernetted chain (HNC) integral equation for the pair correlation:

$$\begin{aligned} \ln g(x) &= -\beta U(x) + W(x), \\ W(x) &= \int \frac{d^3 \mathbf{p}}{(2\pi)^3} e^{-i\mathbf{p}\cdot\mathbf{x}} \frac{\rho h^2(p)}{1 + \rho h(p)}. \end{aligned} \quad (5)$$

Yet by keeping  $n$  unspecified, a second equation is obtained: the appearance of multiple solutions for this new equation

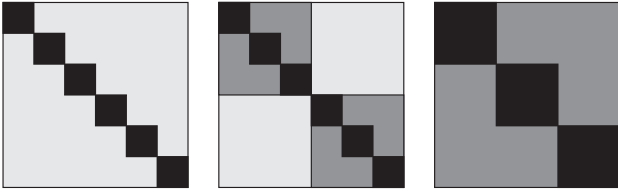


FIG. 1. Replica symmetric (left) and one-step replica symmetry breaking (center) form of the correlation matrix for a replicated system. The black squares represent single elements ( $g_*$ ), while the dimension of the  $n \times n$  matrix (light gray for  $g_0$ ) and of the  $m \times m$  blocks (dark gray for  $g_1$ ) is, in general, not fixed. In the figure,  $n = 6$  and  $m = 3$ . Since in the physical case of zero replica coupling the correlators corresponding to the light-gray area vanish, the numerical computations can be simplified by considering only one of the blocks (right).

signals a phase transition. Given the replicated free energy, the fundamental ansatz is a one-step RSB. As we said, in general, a RSB directly mirrors a change in the “effective topology” of the configuration space which takes on a multivalley structure, with “disconnected” single-valley domains. By choosing a one-step RSB we impose only two possible patterns for the functional form of the correlations between replicas: either two replicas are in the same minimum of the free energy or they are in different minima; in the latter case we *assume* that the correlation of every pair of replicas is the same, no matter what the two minima are. In particular, for a structurally disordered material, we expect that any spatial correlation between two replicas in different minima should vanish: this conjecture follows from the observation that the correlation between different disordered configurations, despite possible local similarities, should vanish in the thermodynamic limit, when averaged over the infinite volume of the system. A formal argument for the relevance of the one-step RSB in structural glasses and a physical interpretation of  $m$  (defined below) in terms of effective temperature is presented in [15]. In terms of correlation matrices, the standard procedure is to group the  $n$  replicas into  $n/m$  sets with  $m$  replicas each. Ideally, the  $m$  replicas within a block are in the same minimum of  $F$ . The “topological” structure of the matrix of correlation functions  $g_{ab}$  is pictorially depicted in Fig. 1: The black squares represent the ordinary two-point correlation functions for a fluid ( $g_*$ ); the correlation functions in the light-gray blocks ( $g_0$ ) are assumed to be unity (different minima are unrelated) and the correlation functions in the dark-gray blocks ( $g_1$ ) may be nontrivial (replicas in the same minimum). The interaction potential  $U_{ab}$  has the same structure:  $U_*$  terms on the diagonal, representing the physical interaction between particles,  $U_1$  for the off-diagonal terms of the blocks on the diagonal, to enforce a coupling between replicas in the same group, and  $U_0 \equiv 0$  for the off-diagonal blocks [19].  $U_0 = 0$  implies  $h_0 = 0$ , and because of such a block-diagonal form of the correlations, the free energy *per replica* turns out to be independent of  $n$  and the problem reduces to the study of any of the  $n/m$  blocks of dimension  $m \times m$  ([16] [Fig. II(c)]). Expressing  $F$  in terms of  $g_*$  and  $g_1$ ,

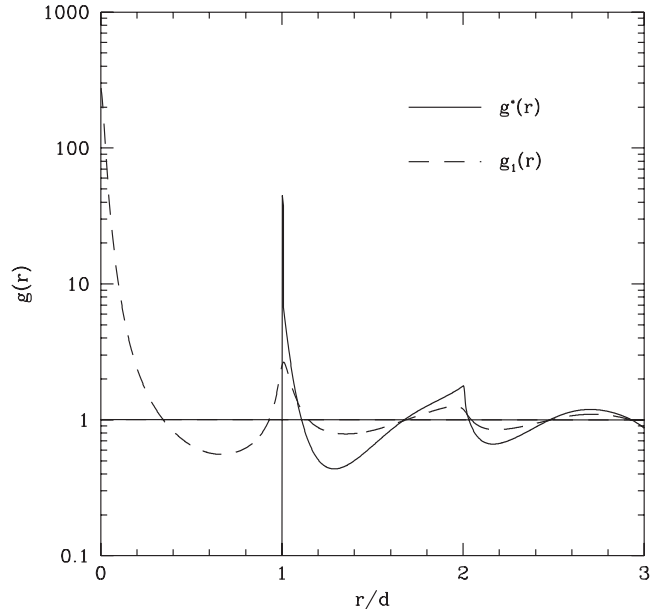


FIG. 2. An example of correlation functions for sticky spheres close to the dynamical glass transition. The thermodynamic state is  $\rho = 1.1878$  and  $T = 0.6$ , and the data refer to the system with  $\Delta = 1/64$ .

$$\begin{aligned} \frac{2\beta F}{n\rho^2} = & \int d^3\mathbf{x} (g_*(x) [\ln g_*(x) + \beta U_*(x)] - h_*(x) - (1-m) \\ & \times \{g_1(x) [\ln g_1(x) + \beta U_1(x)] - h_1(x)\}) \\ & - \int \frac{d^3\mathbf{q}}{(2\pi)^3} \left( \frac{1}{m\rho^2} \ln[1 + \rho h_*(q) - (1-m)\rho h_1(q)] \right. \\ & - \frac{h_*(q)}{\rho} + \frac{h_*^2(q)}{2} - \frac{1-m}{m\rho^2} \ln[1 + \rho h_*(q) - \rho h_1(q)] \\ & \left. - (1-m) \frac{h_1^2(q)}{2} \right). \end{aligned} \quad (6)$$

The stationary condition with respect to  $g_*$  is the usual HNC equation (5) with  $U(x)$  substituted by  $U_*(x)$ , while, due to a simplification of factors  $(1-m)$ , the extremal equation for the interreplica correlation function  $g_1$  is nontrivial also in the “physical” case  $m \rightarrow 1$ :

$$\begin{aligned} \ln g_1(x) = & -\beta U_1(x) + W_1(x), \\ W_1(q) = & \frac{\rho h_*^2(q)}{1 + \rho h_*(q)} - \frac{\rho [h_*(q) - h_1(q)]^2}{1 + \rho [h_*(q) - h_1(q)]}. \end{aligned} \quad (7)$$

Because of the nonlinear structure of Eq. (7), we can now hope to obtain nontrivial solutions  $g_1(x)$  which would otherwise be ruled out by the replica symmetry of the partition function. Indeed, we will show that the extremal equations for the free energy (6) admit nontrivial correlations between replicas [i.e., a nontrivial  $h_1(x)$ ], even for *vanishing* interreplica coupling. The typical behavior of such a solution is shown in Fig. 2.

TABLE I. Glass transition density  $\rho_t$  for different choices of the discretization parameters: total number of mesh points,  $N$ , and number of points inside the hard-sphere diameter,  $N_d$ .

|          | $N$   | 128    | 256    | 512    | 1024   | 2048   | 4096   | 8192   |
|----------|-------|--------|--------|--------|--------|--------|--------|--------|
| $\alpha$ | $N_d$ |        |        |        |        |        |        |        |
| 5        | 32    | 1.1124 | 1.1031 | 1.1026 | 1.1026 | 1.1026 | 1.1026 | 1.1026 |
| 6        | 64    | 1.1364 | 1.1518 | 1.1391 | 1.1396 | 1.1396 | 1.1396 | 1.1396 |
| 7        | 128   |        | 1.1497 | 1.1681 | 1.1552 | 1.1560 | 1.1559 | 1.1560 |
| 8        | 256   |        |        | 1.1553 | 1.1753 | 1.1627 | 1.1636 | 1.1636 |
| 9        | 512   |        |        |        | 1.1578 | 1.1787 | 1.1663 | 1.1672 |
| 10       | 1024  |        |        |        |        | 1.1590 | 1.1804 | 1.1680 |
| 11       | 2048  |        |        |        |        |        | 1.1595 | 1.1812 |
| 12       | 4096  |        |        |        |        |        |        | 1.1598 |

To summarize, starting with a one-component model of fluid, by introducing  $m$  identical copies and taking the limit  $m \rightarrow 1$  after simple algebraic manipulations of the approximate free energy functional (4), we obtain the usual HNC equation for the two-point function *and* one additional equation which describes correlations between different replicas. Since for  $m=1$  an interreplica correlation has apparently no meaning, we could naively interpret  $h_1(x)$  as an infinite-time limit of some sort of self-correlation function. Unfortunately, although carrying information about the breaking of ergodicity, it seems that  $h_1(q)$  is not directly related to the usual nonergodicity factor (i.e., the infinite-time limit of the intermediate scattering function).

### III. SOLUTION OF THE EQUATIONS

For any density,  $h_1(x) \equiv 0$  is a solution of Eq. (7). By linearizing Eq. (7) around  $h_1(x) \equiv 0$  it can be shown that, if another solution exists, it does not bifurcate from the trivial one. However, if we introduce a strong enough [17] coupling between replicas, the linearized equation does not forbid a continuous bifurcation of solutions and a second solution has indeed been found. When the coupling is eventually turned off, one of these solutions converges to  $h_1(x) \equiv 0$  (“liquid” solution), while the other one maintains a spatial structure (“glassy” solution). This signals a multiminimum free energy, which we interpret as a nonergodic phase. In fact, the free energy is now a functional of  $g_*$  and  $g_1$ : the occurrence of a second minimum with  $g_1 \neq 0$  mirrors the appearance of many minima in  $F[\langle \rho(x) \rangle]$  [18]. The glassy solution of Eq. (7) does not exist for all values of the control parameters but only in a region of the density-temperature plane, and the boundary between the one-solution and two-solution domains in the phase diagram marks the glass transition.

The two-point functions  $h_*(x)$  and  $h_1(x)$  are computed by the numerical solution of Eq. (7). We first introduce a mesh in the radial coordinate, thereby reducing the unknown function  $h_1(x)$  to a set of  $N$  discrete values  $[h_1(x) \mapsto h_1(x_i), i = 1, \dots, N]$ . Then we use the iterative Newton-Raphson method for solving the resulting set of nonlinear equations. In order to find a nontrivial result, we proceed as follows:

starting from the “liquid” solution at low density ( $\rho < \rho_t$ ), we introduce a finite attractive coupling  $U_1$  among replicas [19] and *subsequently* increase gradually the density until a continuous bifurcation takes place. We then follow the glassy solution and finally reduce to 0 the coupling between replicas, obtaining a nontrivial correlation function  $h_1(x)$  even for vanishing interreplica coupling. The transition density  $\rho_t$  can then be pinpointed by decreasing (at zero interreplica coupling) the density until the glassy minimum of the free energy disappears. The values we report in the following for the transition densities are the first ones for which our algorithm does not find the glassy solution. Theoretically, the introduction of a coupling among replicas provides a way to discover multiple degenerate states; in this case it is motivated only by the computational convenience to obtain a *continuous* bifurcation of the new minimum of the free energy from the known one.

### IV. HARD-SPHERE FLUID

The glass transition in the hard-sphere fluid has already been studied by the replica method in Refs. [12,17]. Here we consider the dependence of the critical density on the choice of the discretization parameters used in the numerical solution and we provide an estimate of the transition density  $\rho_t$ .

Given the number of points  $N$  for the discretization of the correlation functions, the only arbitrary choice is the mesh size  $a = 1/N_d$  (where  $N_d$  is the number of points used to describe a hard-sphere diameter). It then follows that we can describe a correlation function  $h(r)$  only for  $r \in [0, N/N_d]$ . The physical limit should require both  $a \rightarrow 0$  and  $N/N_d \rightarrow \infty$ .

After choosing a value for  $N_d$ , we proceed by calculating the transition density for grids with more and more points  $N$  while keeping  $N_d$  fixed: for  $N$  large enough, the value of the transition density becomes independent of  $N$  and we can label it as  $\rho_t(N_d)$ . Repeating the procedure for larger and larger  $N_d$ 's the sequence of values we obtain converges to a finite value. Our results for the hard sphere fluid are summarized in Table I.

It is clear that only when  $N/N_d \geq 4$  are the values  $\rho_t(N_d)$  almost independent of  $N$ . If we now consider the values obtained for the 8192-point grid, by *arbitrarily* interpolating



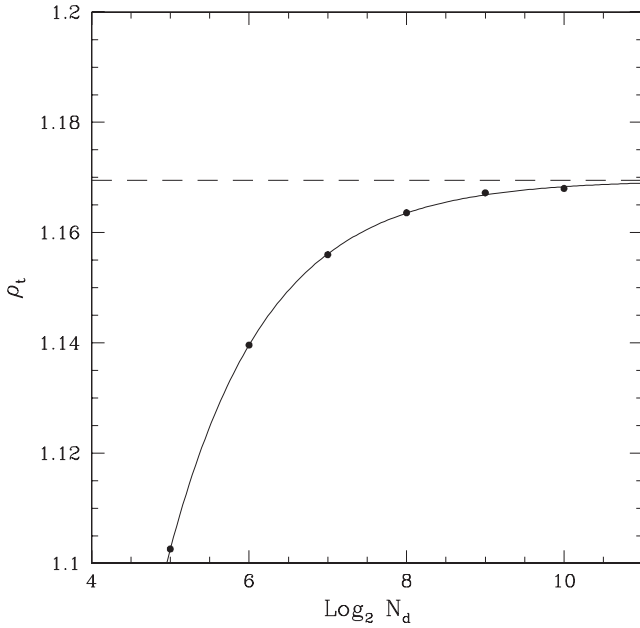


FIG. 3. Dependence of the critical density on the grid: the dots represent the data in the last column of the table; the dashed line is the best fit using Eq. (8).

the values  $\rho_t(N_d)$  with a function of the form

$$\rho_t(N_d \equiv 2^\alpha) = \rho_t - A \exp(-k\alpha), \quad (8)$$

we can extrapolate a limiting value  $\rho_t$  (see Fig. 3).

Depending on the inclusion of the first five or six points in the interpolation ( $\alpha=5, \dots, 9$  or  $\alpha=5, \dots, 10$  respectively, the boldface entries in the table), we obtain  $\rho_t=1.1699$  or  $\rho_t=1.1695$  (corresponding to a packing fraction  $\eta_t \approx 0.612$ ); this should be considered the final prediction for the transition density of a hard-sphere fluid in the HNC approximation. This result is rather close to the random close-packing limit ( $\eta_{rcp} \sim 0.64$ ) and is considerably higher than the prediction of MCT ( $\eta_t \sim 0.516$ ) [5]. We note that recent experiments suggest that, in the absence of gravity, the glass transition in “hard-sphere colloids” is in fact remarkably close to  $\eta_{rcp}$  [20].

For the sake of completeness we obtained a similar table for the thermodynamic glass transition also (up to a 4096-point grid): the extrapolation of the asymptotic density yields  $\rho_g \approx 1.189$ , which is equivalent to a packing fraction  $\eta_g \approx 0.623$ .

## V. SQUARE-WELL FLUID

In order to model a colloidal suspension, we now investigate the effects of the presence of a short-range attraction by adding an attractive square well to the repulsive hard core. The interaction potential is thus

$$U(r) = \begin{cases} \infty, & r \leq d, \\ -w_0, & d < r \leq d + \Delta, \\ 0, & d + \Delta < r. \end{cases} \quad (9)$$

As usual, we take  $d$  as the unit of lengths. The application of the replica method is straightforward, but the phenomenol-

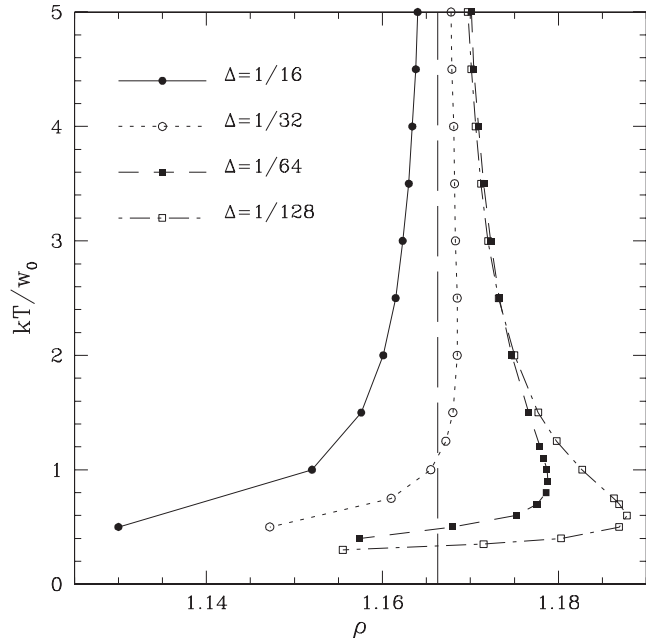


FIG. 4. Phase diagram for the square well fluid for different well widths  $\Delta$ . The dashed line represents the hard sphere transition density computed with the same discretization parameters.

ogy is now potentially richer, since both the density and temperature are meaningful thermodynamic parameters. By inserting the potential (9) into Eq. (5) and applying the procedure described in Sec. III for different temperatures, we determine a whole transition line  $\rho_t(T)$  in the  $\rho$ - $T$  plane.

In Fig. 4 we summarize the numerical study of the short-range limit of the square-well fluid. The results agree with the qualitative picture following from the above considerations: at high temperatures the glass transition line in the  $\rho$ - $T$  plane is almost vertical and, as for the hard-sphere fluid, the glass transition is governed by excluded volume effects. At low temperatures, the transition line displays a strong dependence on the temperature and only a slight dependence on the density: the dynamical arrest is driven mainly by the stickiness of the spheres. The replica method correctly captures both regimes, extending the transition line to densities well below  $\rho_t$ . Moreover, in a region of the phase diagram, the “competition” between energy and entropy stabilizes the liquid phase at densities *larger* than  $\rho_t$ . This phenomenon, commonly referred to as “reentrant behavior,” is also reproduced.

The computations were performed on a 4096-point grid (512 points for a hard-sphere diameter). Because of the very short range of the attraction, few points were available to describe the narrowest wells. Due to the nonlinearity of the integral equations, an estimate of the errors introduced by our discretization is quite difficult; yet, the *qualitative* behavior of the transition line seems to be well established. As an empirical test of the reliability of our results for wells described with very few (two or four) points on the grid, we repeated the computations for part of the phase diagram in Fig. 4 using a looser grid (2048-point grid, 256 points for a hard-sphere diameter and a corresponding rescaling by a fac-

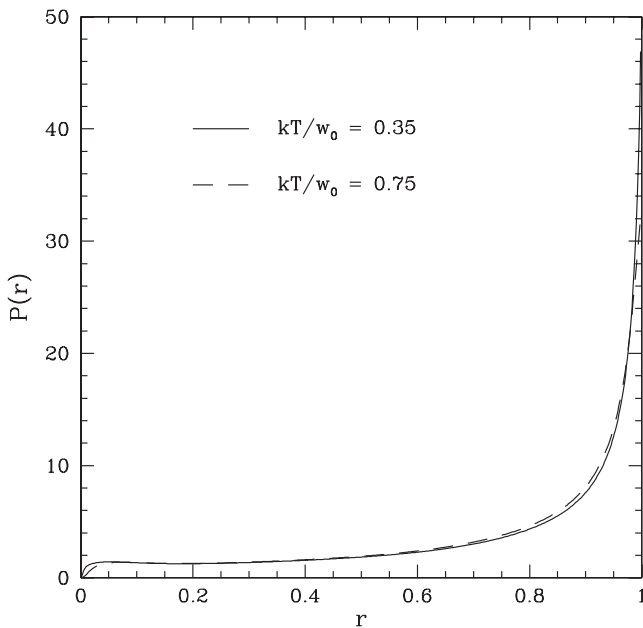


FIG. 5.  $P(r)$  for the same density ( $\rho=1.19$ ) and  $\Delta=1/128$  but different temperatures.

tor of 2 for the attractive wells). The numerical results agreed within 0.2%.

The convergence of our algorithm becomes rather delicate as we follow the liquid-glass transition line to low temperatures and low densities, and we defer to future studies the behavior of the transition line in such a limit. An intrinsic limitation of our approach comes from the equilibrium character of the replica method, which cannot be applied below the spinodal decomposition line.

As already found in the pure hard-sphere fluid, the transition densities are significantly higher ( $\sim 15\%$ ) than those obtained by MCT [5] and the corresponding critical temperatures are lower, roughly by a factor of 2. The reentrant behavior of the glass transition, found by MCT, is confirmed by RSB method when  $\Delta$  is sufficiently small: while in MCT the reentrance appears for  $\Delta \lesssim 5\%$ , in our calculations a similar shape is found only for  $\Delta \lesssim 1.5\%$ . However, it is known that the agreement between MCT and experimental or simulation results is usually only qualitative and the predicted phase diagrams are often arbitrarily translated and rescaled in order to fit actual data. Numerical simulations usually resort to fluid mixtures with different hard-core radii to avoid crystallization; when compared with one of such phase diagrams inferred by MD simulation [21] our results (obtained for a *monodisperse* fluid) show that the replica approach locates reasonably well the liquid-glass transition line. Yet the replica method requires well widths narrower approximately by a factor of 2 in order to reproduce the same characteristic reentrant behavior. As a general remark, we also emphasize that the quantitative results obtained from the description of extremely dense fluids through the HNC approximation on which our computations are based are usually not completely satisfactory.

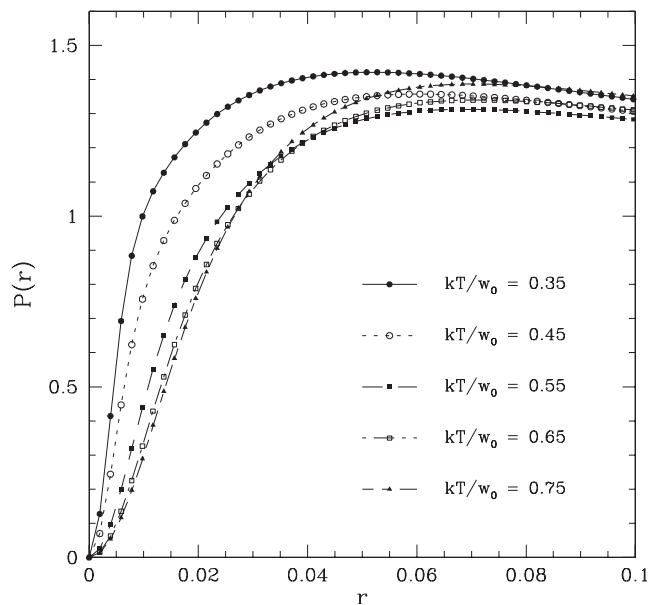


FIG. 6. Detailed structure of  $P(r)$  at short distance for the data of Fig. 5. As the temperature decreases at constant density  $\rho = 1.19$  no singular behavior of  $P(r)$  is observed.

## VI. GLASS-GLASS TRANSITION

An interesting phenomenon that might be within the scope of the replica approach is the glass-glass transition predicted by MCT and confirmed by simulations [21]. In particular, in a dynamical theory, the localization length of a particle can be defined:  $\sigma = \lim_{t \rightarrow \infty} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ . In a solid or in a glass,  $\sigma$  attains a finite value, while it diverges in the fluid phases. It has been shown [5] that  $\sigma$  undergoes a discontinuous change across the glass-glass transition line, decreasing from its value in the repulsive glass to a smaller value comparable to the attractive well width, in the attraction-induced glass.

In our formalism, this information is not directly accessible. However, a hint at the local structure of the glassy state could be obtained by defining the quantity  $P(r) = 4\pi r^2 g_1(r)$  which represents the probability (per unit length) that two particles belonging to different replicas lie at distance  $r$  from one another. In Fig. 5 we plot such a probability for values of the control parameters which, according to the MCT, should identify distinct glassy phases. In all cases, the probability distribution is uniformly spread over a region of the order of a hard-sphere volume (see Fig. 6). Even considering other observables such as the position of the local maximum of  $P(r)$  for  $r \approx 0.05$  (see Fig. 5), comparable to MCT localization length  $\sigma$ , its position varies *smoothly* with the control parameters and its value is always close to the one obtained for the pure hard-sphere system. We cannot exclude that a different choice for the replica symmetry breaking scheme (e.g., a two-step RSB) might lead to a well-defined glass-glass transition: the two-step RSB would then represent the splitting of the free energy minima revealed with the one-step RSB into subminima representing a further trapping of

the caged particles within the range of the attractive wells. This possibility is currently under investigation.

## VII. CONCLUSIONS

In this paper we first investigated the occurrence of RSB in a model of hard spheres, providing an accurate finite-size scaling for the transition density. The mean-field replica approach implies a sharp (dynamical) glass transition; the asymptotic result we obtained for hard spheres, at a packing fraction of  $\eta_{\text{repl}} \approx 0.612$ , should be compared with the MCT value  $\eta_{\text{MCT}} \sim 0.52$  and the commonly accepted value  $\eta \approx 0.58$  for the slowing down of the dynamics of colloidal suspension and simulated hard-sphere systems (even though experiments conducted in microgravity conditions [20] have recently raised this value, significantly closer to the random close-packing limit  $\eta_{\text{rcp}} \sim 0.64$ ). By introducing attractive interactions we obtained a glass transition line in the density-temperature plane. The expected reentrant behavior related to

the change between “repulsive” and “attractive” glasses is reproduced within the RSB approach. Quantitative discrepancies with respect to MCT and numerical simulations are found for the square-well fluid and analogously for the hard-sphere case. Moreover, contrary to MCT, the attractive and repulsive glassy regimes are smoothly connected with no sign of a sharp transition. These results have been obtained within a simple approximation of the more general RSB method: we just considered the *one-step* RSB scheme and we evaluated the entropy functional by a HNC-like expression. It is clearly desirable to go beyond these limitations in order to check the qualitative and quantitative stability of the results obtained in this work.

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