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LETTER TO THE EDITOR

Glass transition and effective potential in the hypernetted chain approximation

Miguel Cardenas†‖, Silvio Franz‡¶ and Giorgio Parisi§+

† Scuola Normale di Pisa, Piazza de Cavalieri 7, 56126 Pisa, Italy

‡ Abdus Salam International Center for Theoretical Physics, Strada Costiera 11, PO Box 563, 34100 Trieste, Italy

§ Università di Roma 'La Sapienza', Piazzale A. Moro 2, 00185 Rome, Italy

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Abstract. We study the glassy transition for simple liquids in the hypernetted chain (HNC) approximation by means of an effective potential recently introduced. Integrating the HNC equations for hard spheres, we find a transition scenario analogous to that of the long-range disordered systems with 'one-step replica symmetry breaking'. Our results agree qualitatively with Monte Carlo simulations of three-dimensional hard spheres.

The hypernetted chain (HNC) approximation is one of the most widely used approaches to describe the density–density correlation function $g(x)$ for liquids at equilibrium [1]. It consists of a self-consistent integral equation that can be derived by a partial resummation of the Mayer expansion, and corresponds to the variational equation for a suitable free-energy functional [2, 3]. The simple HNC approach does not by itself allow us to detect freezing [4]. The simple inspection of the pair correlation function certainly does not allow us to do so, being qualitatively similar in the liquid and glass. Freezing, although present, can be hidden if one concentrates on simple equilibrium quantities [5].

It has recently [3] been stressed that the freezing transition can be detected by combining the HNC approximation with the replica method by studying the correlation functions among different replicas of the same system in the presence of a potential which couples them. At low temperatures (or at high density) one finds a self-consistent solution where different replicas remain correlated also in the limit of zero coupling. This phenomenon corresponds to freezing and it goes under the technical name of replica symmetry breaking.

In this letter we pursue this idea of studying the glass transition in the HCN approximation. We are not concerned about the behaviour in the glassy phase. Our aim is to use an effective potential recently introduced by two of us [6, 7], to study the glass transition of HNC hard spheres in three dimensions. We compare the results with Monte Carlo simulations of real hard spheres. The conceptual advantage of this approach is that all the subtle points of the usual approach related to replica symmetry breaking are not needed in order to expose the transition.

‖ E-mail address: cardenas@SABSNS.sns.it

¶ E-mail address: franz@ictp.trieste.it

+ E-mail address: giorgio.parisi@roma1.infn.it

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The effective potential is constructed as follows. For a system described by the coordinates of all the particles $x = (x_1, \ldots, x_N)$ and with potential energy $H(x) = \sum_{i<j}^{1,N} \phi(x_i - x_j)$.

Let us consider a reference configuration y chosen with probability $\exp(-\beta' H(y))/Z(\beta')$, where $\beta' = 1/T'$ is some arbitrary inverse temperature. Let us define a distance among configuration as $d(x, y) = 1 - q(x, y)$, with the 'overlap' $q(x, y)$ defined as $q(x, y) = \frac{1}{N} \sum_{i,j}^{1,N} w(|x_i - y_j|)$. w is an attractive potential which we choose as $w(r) = \theta(r_0 - r)$ with r_0 a fraction (e.g. equal to 0.3) of the radius of the particles. To very different configurations it corresponds to large distance and small overlap, to similar configurations small distance and large overlap. We define a constrained Boltzmann–Gibbs measure at temperature T as

$$\mu(x|y) = \frac{1}{Z(\beta, q, y)} \mathrm{e}^{-\beta H(x)} \delta(q(x, y) - q) \tag{1}$$

where $Z(\beta, q, y)$ is the integral over x of the numerator. This conditional measure allows us to probe regions of the configuration space having vanishingly small probability, and as we will see, it will help us to reveal the glassy structure hidden in the simple equilibrium approach.

Introducing a Lagrange multiplier conjugated to q to enforce the delta function and integrating over it by saddle point, one sees that the free energy associated to (1), $V(q) = -T \log Z(\beta, q, y)$, can be computed as the Legendre transform of $F(\epsilon) = -T \log Z(\beta, \epsilon, y)$ with $Z(\beta, \epsilon, y) = \int \mathrm{d}x \, \mathrm{e}^{-\beta(H(x) - \epsilon q(x, y))}$. If the coupling ϵ is positive there is an attraction to the reference configuration y. Of special interest will be the cases $\epsilon \to 0^+$, while q will go to a non-trivial value. The free energy $F(\epsilon)$ and the potential $V(q)$ should be self-averaging with respect to the distribution of y, and therefore be just functions of their argument and the temperatures β and β'. Hereafter, we will limit ourselves to the case $\beta = \beta'$ which will be enough to detect freezing in the system. It is conceptually important, however, to consider the more general case if one would like to describe a system which, after crossing the freezing temperature, remains confined in the vicinity of the configuration where it was last able to thermalize.

In order to compute $F(\epsilon)$ in any physical system we need to average $Z(\beta, \epsilon, y)$ over the distribution of y. This can be done in a convenient way by using the replica method, where one writes $\overline{\log Z} = \lim_{r \to 0} \frac{\overline{Z^r} - 1}{r}$, and computes the limit from an analytic continuation from integer r. In principle the replica method can be avoided but it is quite useful to make all the computations quite straightforward. Explicitly:

$$\overline{Z^r} = \int \mathrm{d}x_0 \, \mathrm{d}x_1 \ldots \mathrm{d}x_r \, \mathrm{e}^{-\beta \sum_{a=0}^{r} H(x_a) + \beta\epsilon \sum_{a=1}^{r} q(x_0, x_a)} \tag{2}$$

we have written $x_0 = y$. The problem is reduced to that of an equilibrium mixture of $r + 1$ species (with $r \to 0$), and is formally similar to the one developed by Given, Stell and collaborators to study liquids in random matrices [8]. The use of the formalism is, however, different. In [8] the replica method was used to deal with the quenched disorder represented by the medium, while for us the potential is a tool to probe regions of configuration space of small Boltzmann probability and we do not have quenched disorder. The HNC equation can be derived from the following free-energy functional [2, 3]

$$\begin{aligned} -2\beta F(\epsilon) = \int \mathrm{d}^d x \sum_{a,b=0}^{r} \rho^2 g_{ab}(x) [\log g_{ab}(x) - 1 + \beta \phi(x) \delta_{ab}] \\ + 2\beta\epsilon \sum_{a=1}^{r} \rho^2 g_{0a}(x) w(x) + \mathrm{Tr}\, \boldsymbol{L}(\rho h) \end{aligned} \tag{3}$$

with $\boldsymbol{L}(u) = u - u^2/2 - \log(1+u)$, $h_{ab} = g_{ab} - 1$, the trace of $\boldsymbol{L}$ is intended both on replica indices and in the operator sense in space. The equations, and the relative value of the free energy are obtained extremizing (3) over all the replica correlation functions g_{ab}'s, and extracting the terms of order r.

In order to continue analytically F we use the ansatz $g_{ab} = g_{00}$ for $a = b = 0$, $g_{ab} = g_{10}$ for $a = 0$ or $b = 0$ and $a \neq b$ and $g_{ab} = g^*_{ab}$ for both a and b different from 0. In this letter we will only consider the replica-symmetric ansatz $g^*_{ab} = g_{11}\delta_{ab} + g_{12}(1 - \delta_{ab})$. We warn the reader that this ansatz should give the correct value of the potential $V(q)$ for high and low values of q in the liquid phase, replica symmetry breaking effects are to be expected in an intermediate regime [9] even in the liquid phase. The physical meaning of the various elements of g_{ab} within this ansatz is immediate. 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 $r \to 0$ and coincides with the usual HNC equation for a single-component system. 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 of the Edwards–Anderson order parameter in disordered systems [10], and represents the long time limit of the time-dependent autocorrelation function at equilibrium [6].

In order to study q as a function of ϵ we have solved the HNC equations in three dimensions with the hard sphere potential $\phi(r) = \infty$ for $r < 1$, $\phi(r) = 0$ for $r > 1$ for various values of the density (using a space resolution equal to 0.01 and a large distance cut-off equal to 10). The density ρ is the control parameter of the freezing transition in this problem where there is no temperature. We have rescaled $\beta\epsilon \to \epsilon$, and chosen $r_0 = 0.3$ in the definition of the overlap. We have reconstructed the curves $q(\epsilon)$ and $V(q)$ following the solution of the HNC equations starting from high and low values of ϵ and respectively decreasing or increasing it slowly. In figures 1 and 2 we see that for low enough density q is a single-valued function and the potential is convex, with the minimum corresponding to $g_{01}(x) = 1$ for all x. This is a fair description of the liquid phase. Above a critical density $\rho^* \approx 1.14$ the potential loses convexity, and a coupling can induce a transition between a high and low q phase [7]. For $\rho = \rho_c \approx 1.17$ a second minimum at high q appears, deepening and deepening as the density is increased. The presence of this second minimum shows that above ρ_c the system is in the glassy phase. If, by means of a large ϵ we prepare the system in the vicinity of y and we then let $\epsilon \to 0$, the system remains confined. It should be noted that while the shape of $V(q)$ depends on the particular definition of the overlap, the properties of the minima of the potential do not, as they correspond to vanishing coupling.

As discussed in [6, 7], the two-minima structure is associated to a Gibbs–Di Marzio glass transition scenario. At ρ_c the ergodicity is broken and an extensively large number of metastable states $\mathcal{N} = \mathrm{e}^{N\Sigma}$ contribute to the partition function. The relative height of the two minima is exactly equal to the 'configurational entropy' Σ, and as we can see in figure 3, as ρ is increased Σ decreases, until it vanishes at $\rho = \rho_s \approx 1.203$. (The values of ρ_c and ρ_s are compatible with those found in [3], indeed the potential method reproduces the results of replica symmetry breaking approach for the static and dynamic critical densities.) The shape of the potential is the characteristic one of a system undergoing a first-order phase transition. We can use Maxwell construction to locate the transition line in the plane $\epsilon - \rho$, which is shown in figure 4. The computation as it stands is not consistent for $\rho > \rho_s$; it gives a negative configurational entropy in that region. To describe consistently the behaviour there, the replica symmetry breaking formalism of [3] is needed.

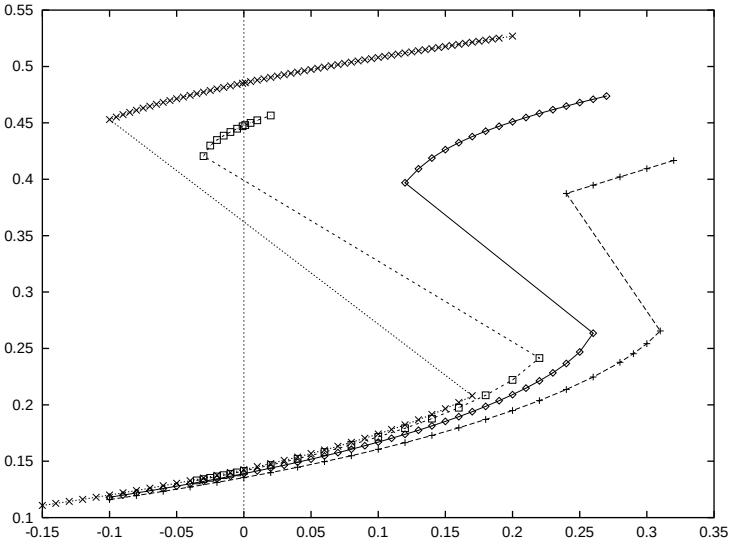

Figure 1. The behaviour of q as a function of ϵ for HNC hard spheres for $\rho = 1.14, 1.17, 1.19, 1.20$. For high enough density q is a multivalued function of ϵ. We have shown only a portion of the curve in the region where it is multivalued. For graphical transparency in this and the next figure we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

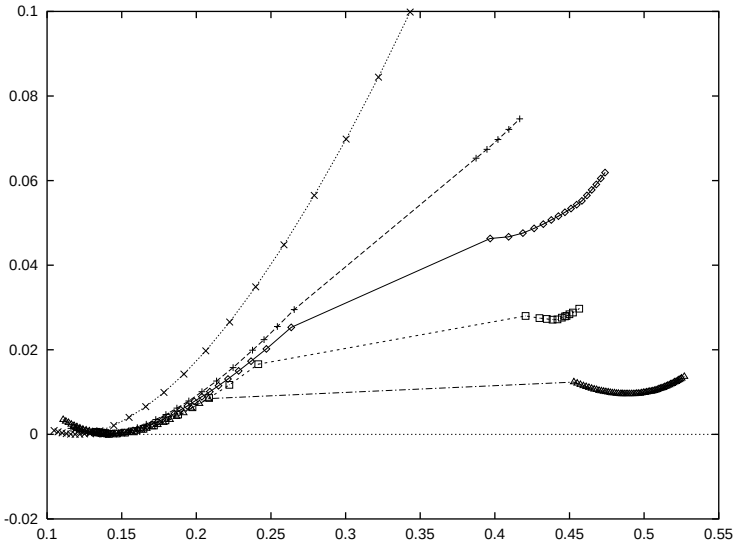

Figure 2. The effective potential for HNC hard spheres. From top to bottom $\rho = 1.0, 1.14, 1.17, 1.19, 1.20$. For low density, high up in the liquid phase the potential is convex. In the glass phase two minima are present.

Although we did not try to compare quantitatively the values of the freezing density we obtained with the one previously found in numerical simulations [11], we have performed our own Monte Carlo simulations to test in a qualitative way the prediction of a first-order transition in the presence of a coupling with a fixed configuration.

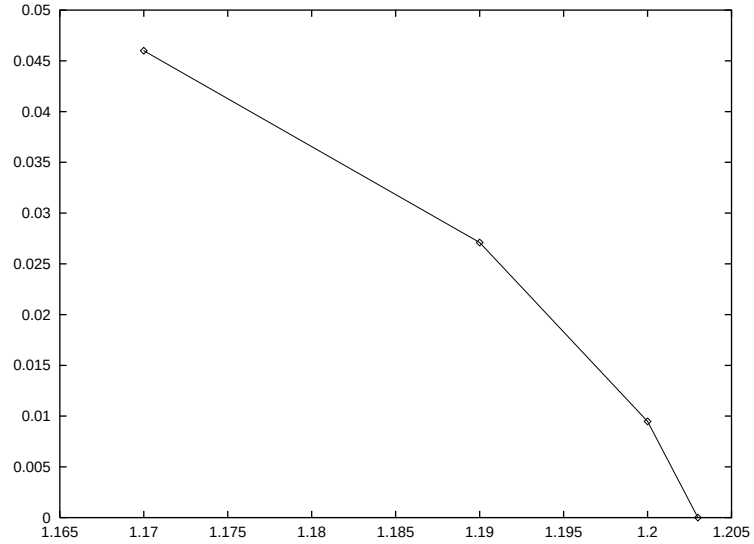

Figure 3. The configurational entropy Σ as a function of ρ.

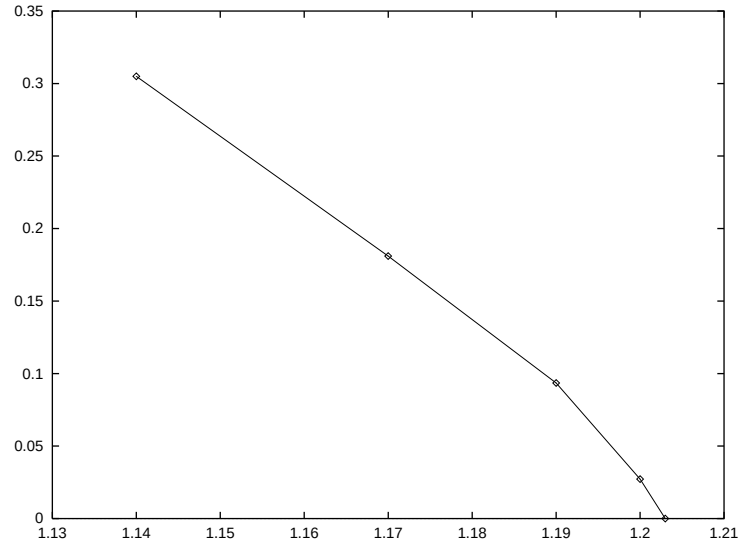

Figure 4. Phase diagram in the plane $\epsilon - \rho$. A first-order transition line terminating in a critical point separates a low q from a high q phase.

To generate configurations at fixed density we start with N particles of zero radius in a three-dimensional box with periodic boundary conditions, and we let the radii grow until two particles become in contact. At this point we make a Monte Carlo sweep and iterate the procedure until the desired density is reached. The volume and radius (r) are at the point rescaled in order to have $r = 1$. We thermalize the system for 4000 Monte Carlo sweeps and use the configuration y reached as 'external field' for our coupled replicas experiments. The relatively short thermalization is chosen in order to avoid crystallization. Having generated the configuration y we let a coupled system x evolve. For various densities, we start the

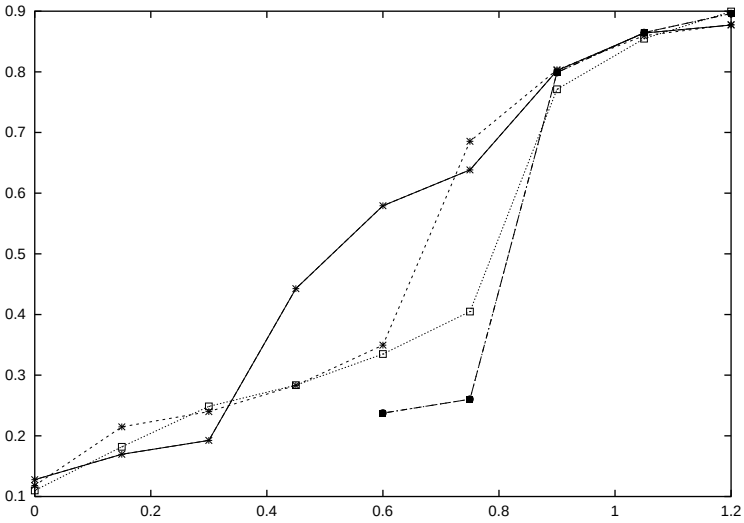

Figure 5. The behaviour of q as a function of ϵ for a system of 258 particles and $\rho = 1.04$. The different curves correspond to different thermalization times 2^k for each value of ϵ. From top to bottom $k = 17, 19, 21, 23$. For larger thermalization times the system seems to develop a first-order jump in q.

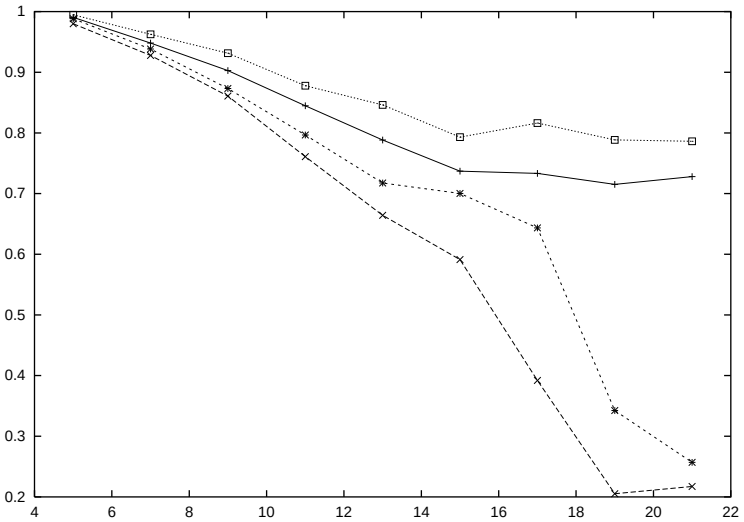

Figure 6. The overlap as a function of time in a logarithmic scale (the horizontal axis is $\ln_2(t)$) starting from y at time 0 and evolving for fixed ϵ. In this figure $\rho = 1.04$ and from top to bottom $\epsilon = 0.8, 0.7, 0.6, 0.5$, the number of particles is 1024.

evolution from the configuration y with an 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 figure 5 we plot q as a function of ϵ for different values of k. We see that, as it should be 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. We have presented here results for $\rho = 1.04$. Other simulations (which we do not display here) show that at lower density, the discontinuity occurs at higher

ϵ, while it is pushed towards smaller ϵ for higher density. From the quantitative point of view there is about a 20% agreement on the value of the density at which a transition is present in the ϵ–q plane; however the qualitative prediction of a first-order transition at values of ϵ of order 1 is clearly satisfied.

A different numerical experiment is presented in figure 6. Here we let the system evolve at fixed ϵ starting at time zero from $x = y$ and we plot the overlap as a function of time. Again we observe a behaviour compatible with a discontinuity of q as a function of ϵ.

We see that the HNC approach predicts a glass transition scenario very close to the one found in systems with 'one-step replica symmetry breaking' with a non-convex [6] effective potential and Gibbs–Di Marzio entropy crisis [12]. The HNC is in this respect a genuine mean-field theory, giving infinite life metastable states. In real systems metastable states have a finite lifetime and the potential has to be a convex function of q for any densities. As it has been discussed many times in the application of the theory to real systems [13], the picture should be corrected to take that into account. The density ρ_c, representing the point where the relaxation time diverges in mean field, becomes a crossover value where the dynamics is dominated by barrier jumping processes [4]. Elucidation of the dynamical processes responsible for restoration of ergodicity beyond mean field is one of the currently open issue in glass physics.

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References

[1] Hansen J P and McDonald I R 1976 *Theory of Simple Liquids* (London: Academic)
[2] Morita T 1960 *Prog. Theor. Phys.* **23** 829
Morita T and Hiroike K 1961 *Prog. Theor. Phys.* **25** 537
[3] Mezard M and Parisi G 1996 *J. Phys. A: Math. Gen.* **29** 6515
[4] For review see, Gotze W 1989 *Liquid, Freezing and the Glass Transition (Proc. Les Houches* ed J P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland)
Angell C A 1995 *Science* **267** 1924
[5] Monasson R 1995 *Phys. Rev. Lett.* **75** 2847
[6] Franz S and Parisi G 1995 *J. Physique* I **5** 1401
[7] Franz S and Parisi G 1997 *Phys. Rev. Lett.* **79** 2486
Franz S and Parisi G 1997 *Preprint* cond-mat/9711215
[8] Given J A and Stell G 1993 *Condensed Matter Theories* vol 8, ed L Blum and F B Malik (New York: Plenum)
Given J A 1992 *Phys. Rev.* A **45** 816
Lomba E, Given J A, Stell G, Weis J J and Levesque D 1993 *Phys. Rev.* E **48** 223
[9] Barrat A, Franz S and Parisi G 1997 *J. Phys. A: Math. Gen.* **30** 5593
[10] Mézard M, Parisi G and Virasoro M A 1987 *Spin Glass Theory and Beyond* (Singapore: World Scientific)
[11] Bernu B, Hansen J-P, Hitawari Y and Pastore G 1987 *Phys. Rev.* A **36** 4891
Barrat J-L, Roux J-N and Hansen J-P 1990 *Chem. Phys.* **149** 197
Hansen J-P and Yip S 1995 *Transp. Theory Stat. Phys.* **24** 1149
[12] Kirkpatrick T R and Thirumalai D 1987 *Phys. Rev.* B **36** 5388
Kirkpatrick T R and Wolynes P G 1987 *Phys. Rev.* B **36** 8552
A review of the results of these authors and further references can be found in Kirkpatrick T R and Thirumalai D 1995 *Transp. Theory Stat. Phys.* **24** 927
[13] Parisi G 1995 *Phil. Mag.* B **71** 471
Lindstrom U (ed) 1995 *Proc. Symp. 'The Oskar Klein Centenary'* (Singapore: World Scientific)