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# Glass transition line for the system of charged hard spheres

M. Cardenas[a,*], M.P. Tosi[b]

[a]*Instituto de Fisica, Universidad Catolica de Valparaiso, Valparaiso, Chile*
[b]*NEST-INFM and Classe di Scienze, Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy*

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**Abstract**

We locate the glass transition line of the charged-hard-sphere system in the density–temperature plane, using a mean-field hypernetted chain approximation within the replica-symmetry-breaking scenario [S. Franz and G. Parisi, Phys. Rev. Lett. 79 (1997) 2486. [11]]. Our results demonstrate a dominant role of the steric factor and explain the ineffectiveness of purely Coulombic interactions in driving phase transitions.


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## 1. Introduction

The transition from a liquid to a glass presents in many materials a number of universal features in both thermodynamic and dynamic properties (for a review see Angell [1]). Supposing that the liquid has been supercooled fast enough to prevent crystallization, the behavior on further cooling can be described with reference to a first derivative of the free energy such as the density or the entropy, showing a rapid change of slope in a narrow temperature range, or to a transport coefficient such as the shear viscosity, which increases smoothly over many orders of magnitude. This behavior can be understood in terms of a slowing down and ultimate freezing of collective jumps between configurational minima in a rugged free-energy landscape (see e.g. Stillinger [2]). The disordered system behaves as a fluid as long as it visits many such minima during its evolution over a given observational time, and the glass transition can be said to occur when the time scale for such jumps becomes long relative to the experimentally accessible time scale.

In this Letter we evaluate the glass transition in a disordered assembly of charged hard spheres (CHS), which is the simplest model possessing some measure of realism for the liquid state of neutral and ionized matter. Let us briefly dwell on its opposite extreme limits, which are the system of neutral hard spheres (HS, see Alder and Wainwright [3]) and the one-component classical plasma (OCP, see Baus and Hansen [4]). Temperature plays no role in the HS system and the only control parameter is the reduced density $\rho^*=\rho\sigma^3$ or equivalently the packing fraction $\eta=\pi\rho^*/6$, with $\rho$ the particle number density and $\sigma$ the hard-sphere diameter. Computer studies by Hoover and Ree [5] have revealed a first-order equilibrium freezing transition occurring at $\eta=0.494$ and an equilibrium crystalline branch running from $\eta=0.545$ at melting up to the close-packed value $\eta=0.74$. Early work by Bernal [6] had shown that the maximum packing of an amorphous assembly of hard spheres is $\eta\approx0.64$, and indeed the equilibrium HS fluid branch has a metastable extension of amorphous states ending in a state of random close packing at $\eta=0.644$ [7].

* Corresponding author. Tel: +39 050 090 58; fax: +39 050 5635 13
*E-mail address:* m.cardenas@sns.it (M. Cardenas).

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At the opposite extreme the OCP is made of point-like charges embedded in a uniform neutralizing background. The control parameter is the coupling strength $\Gamma = Z^2e^2 = (ak_BT)$ where $Ze$ is the ionic charge, $T$ the temperature, and $a = (4\pi\rho = 3)^{-1/3}$ the Wigner–Seitz ion-sphere radius. A first-order equilibrium freezing transition into a BCC crystal occurs at $\Gamma = 180$ and studies of the supercooled fluid structure have suggested the possibility of amorphous states [8]. The location of the glass transition has been estimated from mean-field theory to lie at $\Gamma \approx 1500$ [9]. There is as yet no independent confirmation of this extremely large value of the Coulomb coupling that would be needed for the stability of a glassy state of the OCP: the relative inefficiency of purely Coulombic interactions in driving phase transitions is however well known. Consistency with evidence on molten salts and on colloidal dispersions was noted in Ref. [9].

The thermodynamic control parameters of the CHS system are both the density and the temperature, which are expressed in reduced units through the packing fraction $\eta$ and the Coulomb coupling strength $\Gamma$ as defined above. We evaluate its glass transition line in the $(\rho^*, \Gamma)$ plane, using a mean field approach stemming from the work of Mezard and Parisi [10]. In the implementation developed by Franz and Parisi [11–13] the transition is detected with the help of the replica method in statistical mechanics [14] by evaluating the structural correlations between the disordered system and a quenched replica exerting on it a short-range attraction. One searches for a self-consistent solution of the structural equations such that the system remains correlated with the quenched replica in the limit of vanishing attraction. This method emulates the freezing of collective jumps in the free-energy landscape.

The outline of the Letter is as follows. In Section 2 we recall the essence of the method and the structural relationship that exists between the strongly coupled OCP and the HS fluid. Our main results are reported in Section 3 and discussed in Section 4.

## 2. Theoretical approach and structural considerations

Our theoretical approach has already been described in Ref. [9] for the OCP and here we only need to summarize its main points. Following the work of Franz and Parisi [11,12], at given $\rho^*$ and $\Gamma$ we consider two replicas of the disordered CHS system with coordinates $x$ and $y$, such that the replica $y$ is quenched and acts on the other replica with a very short-ranged attraction described by the potential energy $-\varepsilon\phi(x-y)$ ($\varepsilon > 0$). The inter-replica correlations in different states of the system have the following features as functions of the coupling strength $\varepsilon$. In the equilibrium fluid states they show a high peak at $x = y$ if $\varepsilon$ is large and disappear in a continuous manner as $\varepsilon$ is made to vanish. In glassy states the correlations persist instead even in the limit $\varepsilon \to 0$, since the collective jumps between different minima in the free-energy landscape are frozen. Finally, in the supercooled fluid a discontinuous jump of the correlations occurs at a finite value of $\varepsilon$. The jump signals a first-order transition between two dynamically different states, from a state with substantial suppression of wanderings in the free-energy landscape to a state of essentially free configurational motions.

The degree of correlation between the two replicas is measured by their overlap $q(\varepsilon)$, which is defined by

$$q(\varepsilon) = (\rho^2/N)\int dx dy \phi(x-y) g_{12}(x-y) \tag{1}$$

Here $-\phi(x-y)$ is constructed as a sum of two-body square wells of unit depth and range $d \ll a$ centered on the particles of the quenched replica, and $g_{12}(x-y)$ is the inter-replica pair distribution function. The overlap $q(\varepsilon)$ thus plays the role of an order parameter for revealing the glass transition: it takes large values in frozen states of the system and attains its lowest allowed value $q_0 = (d/a)^3$ in fluid states. In the following we choose $d = 0.2a$.

In the above viewpoint the problem has been reduced to evaluating the structure of a special case of a quenched-annealed mixture. The Ornstein–Zernike relations between the direct correlation functions and the pair distribution functions in such a mixture have been derived with the replica method by Given and Stell [15]. In the calculations that we report below we combine these structural relations with the hypernetted-chain closure (HNC). For an explicit exposition of these sets of equations the reader may refer, for instance, to our previous work on a quenched-annealed mixture of particles interacting via square-well potentials [16].

In order to understand the results that we shall display in 3 from the solution of these equations, it is important at this point to discuss the relationship between the fluid structure of the strongly coupled OCP and that of the CHS system. With increasing $\Gamma$ the OCP develops a Coulomb hole around each of its particles, and it was first shown by Gillan [17] that the shape of the Coulomb hole at strong coupling is reminiscent of the excluded-volume region in the HS fluid except that the OCP pair distribution function $g(r)$ vanishes smoothly rather than with a discontinuous jump at contact. The case of present interest refers to the OCP at $\Gamma \approx 1500$, where $g(r)$ vanishes at $r \approx 1.5a$ and has its main peak at $r \approx 1.76a$. Evidently, this OCP function will also give the pair structure of the CHS fluid at the same $\Gamma$ for $\sigma < 1.5a$. Fig. 1(a) reports a comparison between the OCP $g(r)$ and that of the CHS fluid with $\sigma = 1{:}63a$, showing that the pair correlations are still rather similar in these two fluids. The subsequent evolution of the pair structure with increasing hard-sphere diameter towards the HS fluid is illustrated in Fig. 1(b) for selected values of the system parameters on the glass transition line.

## 3. Results on glass transition and phase diagram

Fig. 2 illustrates the behavior of the inter-replica overlap $q(\varepsilon)$ as a function of the strength $\varepsilon$ of the attractive