A thermodynamic description of colloidal glasses

Mauro Sellitto¹ and Francesco Zamponi²

¹ Dipartimento di Ingegneria Industriale e dell’Informazione, Seconda Università di Napoli
Real Casa dell’Annunziata, I-81031 Aversa (CE), Italy, EU
² Laboratoire de Physique Théorique, Ecole Normale Supérieure, UMR 8549 CNRS - 24 Rue Lhomond,
F-75005 Paris, France, EU

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Abstract – The phase behavior of hard-sphere particles interacting with a short-ranged potential is studied in the limit of infinite space dimensionality via the Franz-Parisi approach and the replica method of disordered systems. For an attractive square-well potential, the phase diagram exhibits reentrance of the liquid-glass transition, multiple glass states and glass-glass transition. For a repulsive square-shoulder potential no such special features are observed. Our results show that the Franz-Parisi approach can be consistently extended to deal with higher-order glass singularities and that interparticle attraction is crucial for complex glassy behavior in large enough dimensions, at least for monodisperse systems.

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Introduction. – Interacting hard spheres (with weak long-range attraction) have been used since van der Waals to describe the gas-liquid phase transition. More recently, they have been much studied in relation with colloidal suspensions [1]. The interest has been especially motivated by the possibility of introducing a (depletion-induced) attraction between colloidal particles by adding a suitable amount of non-adsorbing polymers to the suspension [2]. In doing so, the intensity and the range of attraction can be tuned by changing the polymer concentration and the polymer coil radius, respectively. One can thus explore a wide range of static and dynamic behaviors which are not accessible in a single liquid system. When the range of attraction is microscopic (i.e. of the order of a small fraction of the sphere diameter), some fascinating large-scale macroscopic properties emerge in such systems. They include the reversible freezing-by-heating of the liquid phase and, at higher packing density, structurally distinct types of dynamically arrested states [3–10]. Such features have been generally ascribed to structural changes of the cage that confines particle motion. For weak attraction and high packing density, the glass formation is mainly driven by the usual excluded-volume effects, while for strong attraction the tight clustering of particles leads to an amorphous state with a rigid gel-like structure which can exist even at very low packing. The passage from one glass state to the other can occur either smoothly or discontinuously (in the latter case the Debye-Waller factor undergoes an extra jump). Interestingly, similar complex glassy features have been also identified in systems with no attractive interaction [11–14], where distinct glass states with different packing properties arise solely from the competition between crowding effects on different microscopic length scales.

In this paper we investigate the statistical mechanics of interacting hard spheres in the case in which the space dimensionality is infinitely large. In statistical physics high-dimensional spaces are, in fact, a blessing. They make some computations more feasible [15,16] and, most importantly, provide a limiting case in which the various mean-field approximations become exact [16,17]. For this reason, the mean-field replica approach we use is exact [18,19] and this allows for a comparison with the results obtained by alternative methods, such as the Mode-Coupling Theory (MCT) [20,21], numerical simulations [3,5,6], experiments [7,8], spin glass (or lattice glass) models [22–26], and the heterogeneous facilitation picture [14,27,28]. We generally find that for a short-range enough attraction, the phase diagram exhibits reentrance of the liquid-glass transition line, multiple glass states and glass-glass transition (much similar to those observed in colloid-polymer mixtures, numerical simulations and MCT), while for short-range repulsion no such special features are observed. Our results show that the
The model. -- We consider a system of $d$-dimensional hard spherical particles of unit diameter interacting with an attractive potential of constant strength $U_0$ over a distance $\hat{\sigma}/d$:

$$v(r) = \begin{cases} 
\infty, & \text{for } r < 1, \\
-U_0, & \text{for } 1 < r < 1 + \hat{\sigma}/d, \\
0, & \text{for } r > 1 + \hat{\sigma}/d,
\end{cases}$$

(1)

where $r$ is the inter-particle distance. Note that, in order to have a non-trivial limit for $d \to \infty$, the width of the attractive part has been rescaled by the dimension according to the cage size dependence on $d$ in the glass (i.e. proportionally to $1/d$), see [19] and eq. (2) below.

For a system of density $\rho$ in the thermodynamic limit, we define $\hat{\varphi} = 2^d \varphi/d$ where $\varphi = \rho^{d/2}/(1 + \sigma^2/2 \rho)$ is the packing fraction of the repulsive core. The motivation behind this scaling is that in the replica approach the glass transition occurs for values of $\hat{\varphi}$ that remain finite for $d \to \infty$ (e.g. in the pure hard-sphere case, the dynamical transition happens at $\hat{\varphi} = 4.8$ [19]). We observe that MCT gives a different scaling for the dynamical transition density, but numerical data seems to support the replica result [29]. Note, for comparison, that it can be proven that that sphere packings exist at least for $\hat{\varphi} \leq 6/e$ [30], hence a $\hat{\varphi}$ of order 1 is a quite natural scale for hard spheres in large dimensions (see [19,31] for a more detailed discussion).

Moreover, we fix $\beta U_0 = 1/\hat{T}$, where $\beta = 1/k_B T$. The control parameters are therefore rescaled density $\hat{\varphi}$, rescaled temperature $\hat{T}$ and the width of the attraction $\hat{\sigma}$. In the following we will also consider a “sticky” or “Baxter” limit in which $\hat{\sigma} \to 0$ while the intensity of the attraction diverges, hence $\hat{T} \to 0$, while $\mu = -1/\hat{T} - \log \hat{\sigma}$ is held constant.

Franz-Parisi potential. -- The basic idea of the replica approach to the glass transition is that the kinetic slowing-down on approaching the glass phase is due to the sudden appearance of a bunch of long-lived metastable states [32–34]. Under this assumption, the glass transition can be identified by looking at the free energy of a constrained equilibrium system. This is known as the Franz-Parisi potential [35–37], see also [34,38] for an alternative but very related approach. For particle systems, the best way of computing this potential explicitly is the following. One considers an equilibrium configuration $X = \{x_{i}^{\alpha}, \alpha = 1, \ldots, d, i = 1, \ldots, N\}$ of the liquid, and another configuration $Y = \{y_{i}^{\alpha}, \alpha = 1, \ldots, d, i = 1, \ldots, N\}$ that is constrained to be close to the first one, in such a way that the mean square displacement is bounded by a fixed constant $\hat{A}$:

$$\frac{1}{2dN} \sum_{\alpha=1}^{d} \sum_{i=1}^{N} (x_{i}^{\alpha} - y_{i}^{\alpha})^2 \leq \hat{A} \hat{\sigma}/d^2.$$

(2)

One computes the free energy of the system given for a $X$, and then averages it over the equilibrium distribution of $X$. The result is the average free energy $\mathcal{V}_F(\hat{A})$ of a system constrained to be at distance $\hat{A}$ from a typical liquid configuration. In the liquid phase, particles diffuse away from any reference configuration, and correspondingly $\mathcal{V}_F(\hat{A})$ has a unique minimum at $\hat{A} = \infty$. On the contrary, in the glass phase, particles are “caged” in a sphere of average radius $\sqrt{\hat{A}}$ around the reference configuration and consequently there is a local minimum of $\mathcal{V}_F(\hat{A})$ at finite $\hat{A}$. The dynamical glass transition $T_{\text{dyn}}(\varphi)$ is signaled by the appearance of an inflection point in $\mathcal{V}_F(\hat{A})$, and hence the secondary minimum appears discontinuously at a finite $\hat{A}$ below $T_{\text{dyn}}(\varphi)$, and therefore represents a generic fold singularity. From an analytic point of view, the computation of the Franz-Parisi potential requires the use of the replica method [19,37,39,40]. Since our method is a direct extension of previous works [19,41], we provide here only the final results of our computation.

The Franz-Parisi potential $\mathcal{V}_F$ can be obtained through the relation (more details of the derivation will be given in [42])

$$\mathcal{V}_F(\hat{A}) = -\frac{1}{\hat{A}} \left[ 1 - \hat{\varphi} \mathcal{F}_1(\hat{A}) \right],$$

(3)

where

$$\mathcal{F}_1(\hat{A}) = -\hat{A} \int_{-\infty}^{\infty} dy \, e^{\varphi y} \frac{\partial q(\hat{A} - \hat{\sigma}, y)}{\partial \hat{A}} \log q(\hat{A}, y)$$

(4)

and the function $q(\hat{A}, y)$ is

$$q(\hat{A}, y) = (1 - e^{\varphi y}) \Theta \left( y + \hat{A} - \hat{\sigma} - \frac{\sqrt{2 \hat{A}}}{\hat{\varphi} \hat{T}} \right) + e^{\varphi y} \Theta \left( y + \hat{A} + \frac{\sqrt{2 \hat{A}}}{\hat{\varphi} \hat{T}} \right).$$

(5)

The stationary points of $\mathcal{V}_F(\hat{A})$ are located at values of $\hat{A}$ which are the solutions of $1/\hat{\varphi} = \mathcal{F}_1(\hat{A})$. The values of $\hat{A}$ at the local minima represent the long-time mean square displacement (i.e. the Debye-Waller factor) in the glass. In this context the dynamical transition corresponds to the disappearance of all the local minima of $\mathcal{V}_F(\hat{A})$, which happens when $\hat{\varphi}^{-1} > \max_{\hat{A}} \mathcal{F}_1(\hat{A})$. Hence, the dynamic transition is located at

$$\frac{1}{\hat{\varphi} \hat{T}} = \max_{\hat{A}} \mathcal{F}_1(\hat{A}),$$

(6)

and its stability requires the local (up) convexity of $\mathcal{V}_F$. A phase diagram obtained in this static framework is therefore derived by studying the behavior of the functions $\mathcal{V}_F$ and $\mathcal{F}_1$. Let us now consider two specific cases.
Fig. 1: (Colour on-line) A section of the phase diagram in the rescaled variables, temperature $\tilde{T} = k_B T/U_0$ vs. packing fraction $\tilde{\varphi}$, for the attraction width $\tilde{\sigma}$. The vertical line is the packing fraction at the dynamic glass transition for the purely hard-sphere potential. In this case there is only one glass phase but the fluid-glass transition line is reentrant: the liquid freezes upon heating.

Square-well potential. – We first discuss the results obtained for the square-well attractive potential of width $\tilde{\sigma}$ and depth $U_0$. We find that when the attraction width is large enough (above $\tilde{\sigma} \approx 0.19$), the function $F_1$ has a single maximum for all densities and temperatures, and the resulting phase structure is easily determined: for each temperature, a single glass phase exists for densities larger than $\tilde{\varphi}_d$ defined by eq. (6).

In fig. 1 we show the phase diagram in the rescaled variables: reduced temperature, $\tilde{T} = k_B T/U_0$, and reduced packing fraction, $\tilde{\varphi}$. Interestingly, for packing fractions above the dynamic glass transition of the purely hard-sphere system, the liquid-glass transition line develops a reentrance: the liquid freezes upon heating. This reentrance effect is driven by the width of the square-well potential and is ultimately due to entropic reasons. The smaller the attraction width, the deeper the fluid phase enters into the glass region.

When the attraction width is below $\tilde{\sigma} \approx 0.19$, the function $F_1$ shows two maxima in a range of temperatures and densities, and the determination of the phase diagram requires some care because of the appearance of multiple glass phases. For simplicity we focus on a representative case, obtained by fixing $\tilde{\sigma} = 0.06$. The corresponding section of the phase diagram is shown in fig. 2. There are two lines, $A_3-C$ and $A_4-C$ separating the fluid phase from two distinct types of glass phase, named attractive glass (that with smaller $\tilde{\sigma}$) and repulsive glass (the one with larger $\tilde{\sigma}$). These lines, which correspond to the maxima of $F_1$, cross each other at the point C and terminate at the critical endpoints $A_3$ and $A_4$. The curve $A_3-A_4$ instead corresponds to the minima of $F_1$. The closed area delimited by the lines going through the points $A_3$, C and $A_3'$ represents the coexistence region of the two glass phases, while outside this region only one glass is present. It is important to observe that the $A_4$ point corresponds to a local quartic maximum of the Franz-Parisi potential: it is therefore dynamically unobservable as the repulsive glass will always be unstable around this singularity. On the contrary, the $A_3$ singularity corresponds to a local quartic minimum of the Franz-Parisi potential, and is therefore stable. The detailed shape of $\mathcal{V}_{FP}$ in the former case is shown in fig. 3 for densities located at the intersection of the transition lines with the horizontal segment $\tilde{T} = 0.47$. The dots denote the stationary points of the function $F_1(\tilde{A})$ and the corresponding ones in $\mathcal{V}_{FP}(\tilde{A})$. Notice that $F_1$ does not depend on density while $\mathcal{V}_{FP}$ does.

Fig. 2: (Colour on-line) Section of phase diagram at $\tilde{\sigma} = 0.06$. There are two distinct types of glass phases and fluid-glass transitions plus a glass-glass transition line. The two fluid-glass transition lines meet at a crossing point $C$ along with the glass-glass transition line. The two special points $A_3$ and $A_4'$ are cusp singularities whose stability is determined by the Franz-Parisi potential.

Fig. 3: (Colour on-line) Shape of the Franz-Parisi potential $\mathcal{V}_{FP}(\tilde{A})$ and the function $F_1(\tilde{A})$ in the region below $\tilde{T}_C$. The three $\mathcal{V}_{FP}(\tilde{A})$ curves correspond to the points at which the phase diagram transition lines intersect the horizontal segment at $\tilde{T} = 0.47$. The dots denote the stationary points of the function $F_1(\tilde{A})$ and the corresponding ones in $\mathcal{V}_{FP}(\tilde{A})$. Notice that $F_1$ does not depend on density while $\mathcal{V}_{FP}$ does.
potential correspond to dynamically stable solutions in MCT. This static approach can be therefore consistently extended to the determination of higher-order dynamic glass singularities.

For completeness we also show the related evolution of the cage radius $\sqrt{A}$ as a function of the packing density in fig. 4 at temperatures slightly above and below the C point. The double jump observed at $\hat{T} = 0.5$ represents the transition from the liquid to the repulsive glass followed, for increasing packing density, by the one from the repulsive glass to the attractive glass. As it happens with the usual first-order transition, hysteresis effects between the two glass phases should be observed. At $\hat{T} = 0.47$ there is only the liquid-to-attractive glass transition. In this latter case if by any chance the appearance of the attractive glass is delayed, the liquid could momentarily transform into a repulsive glass.

Figure 5 summarizes the global structure of the phase diagram in the two-glass region. Upon decreasing $\hat{\sigma}$ the glass-transition line shortens and eventually disappears at $\hat{\sigma} \approx 0.19$ where the A3 cusp merges into a singularity of type A4, also known as swallowtail bifurcation. From eq. (3) it is easy to see that at the stationary points of the potential, the vanishing of the $\ell$-th derivative of $F_1(\hat{A})$ leads to the vanishing of the $(\ell + 1)$-th derivative of $\nu_{FP}(\hat{A})$. The higher-order singularities, A3 and A4, are special singular points of the Franz-Parisi potential. Near these higher-order singularities peculiar slow logarithmic relaxation occurs, a behavior that has been explored in great detail in the MCT framework [3,4] and numerically [5,6,43,44]. Figure 5 also includes the Baxter (or sticky sphere) limit: $\hat{\sigma} \to 0$, $U_0 \to \infty$ (or equivalently $\hat{T} \to 0$) while $\mu = -\beta U_0 - \log(\hat{\sigma}) = -1/\hat{T} - \log(\hat{\sigma})$ is kept constant. In this limit the small-$\hat{A}$ maximum of $F_1(\hat{A})$, corresponding to the attractive glass, moves to $\hat{A} = 0$, meaning that particles are completely frozen. The height of this maximum can be computed explicitly and gives $\hat{\varphi}_d = 2e^\mu$. Hence in this case the cusp singularity A4 moves to infinite packing density. This implies that there is no smooth path in the phase diagram from the repulsive to the attractive glass. The resulting curve is reported in fig. 5 as a full line. Notice that in the limit $d \to \infty$ the Kauzmann transition is pushed at infinite packing density and is therefore outside the range of physical relevance. Very similar phase diagrams have been first obtained by MCT [3,4], and later confirmed by numerical simulations [5,6] and experiments [7,8]. In a previous attempt to use the replica method for this problem, based on the replicated hypernetted chain approximation and in $d = 3$, no glass-glass transition was found [45], arguably due to the rather poor accuracy of the replicated hypernetted chain approximation in the phase region where the “cage size” is very small [19].

**Square-shoulder potential.** – The analysis carried out above for the square-well potential can be immediately extended to the square-shoulder potential by exchanging $U_0 \to -U_0$. This case is interesting because it provides the first finite-dimensional ($d = 3$) instance in which multiple glasses are observed with only a purely repulsive potential [11]. Similar features have been recently obtained also in some binary mixtures [12] and in the heterogeneous facilitation approach [14]. The phase diagram for the square-shoulder potential in infinite dimension is reported in fig. 6. Perhaps surprisingly, we find no trace of distinct glasses but only the obvious widening of the glass phase when the repulsion gets stronger (or the temperature is lowered) and the interaction range increases.

This negative result suggests that the contribution of “ring diagrams”, which vanish in the limit of high dimensionality [19,46], is relevant for the appearance of multiple glasses in purely repulsive potential in finite dimension $d$. Indeed, in ref. [11] it is argued that the complex phase
The liquid phase, one has dimensions where all ring diagrams vanish: in this case, in effect, that is clearly observed in fig. 3 and the associated discussion in ref. [11]). This effect, that is, is responsible for the complex phase diagram of the square-shoulder potential is intimately connected to the competition between the amplitudes of the jumps of the pair correlation function of the square-shoulder potential for several values of the width $\sigma$. This leads us to conclude that, while the complex phase diagram of the square-well attractive potential requires the inclusion of many-body effects) which are absent in infinite dimensions.

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Fig. 6: (Colour on-line) Phase diagram for the square-shoulder repulsive potential for several values of the width $\sigma$. That the phase diagram will remain qualitatively the same, at least for the square-well attractive potential. For the square-shoulter potential, we expect that including properly the finite-dimensional contributions should allow one to recover the complex phenomenology discovered in [11]. Unfortunately, constructing a good approximation scheme for the dynamical transition in low dimensions within the small cage expansion scheme is a non-trivial task, but there is hope to achieve it and work is in progress in this direction. Moreover, one could compute within this framework the equation of state of the two glasses, the jump of specific heat at the glass transition, and address the role of the Kauzmann transition.

Conclusion. – The main result of this paper is that a static replica picture based on the Franz-Parisi potential allows to re-derive many of the results that have been previously obtained using the MCT for attractive colloids [3,4,9], namely the reentrance of the glass transition line and two distinct glass phases for very short-range attractions. Here we limited ourselves to the $d \to \infty$ limit where computations are easier and the replica theory is exact [18], at least according to the standards of theoretical physics. For soft-matter applications, one would like of course to extend this calculation in $d = 3$ [19]. We expect
