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Competition between crystallization and glassification for particles with short-ranged attraction. Possible applications to protein crystallization

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Abstract

We discuss the phase behaviour of spherical hard-core particles, with an attractive potential, as described by a hard-core Yukawa model. The ratio of the range of the attraction to the diameter of the particles is an important control parameter of the problem. Upon decreasing the range of the attraction, the phase diagram changes quite significantly, with the liquid–gas transition becoming metastable, and the crystal being in equilibrium with the fluid, with no intervening liquid. We also study the glass transition lines and, crucially, find that the situation, being very simple for pure repulsive potentials, becomes much richer in competition between glass and crystal phases for short-range attractions. Also a transition between attractive and repulsive glass appears somewhat in analogy with the isostructural equilibrium transition between two crystals.

Keywords: Colloidal systems; Glass transition; Phase equilibrium; Metastability

1. Introduction

One of the most interesting challenges in modern colloidal, soft matter and nanoparticle science is to understand the fundamental principles by which macroscopic

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materials can be prepared with either an amorphous or a crystalline nature. For various optoelectronic purposes, such as photonic crystals, it is important to have crystalline order with optical wavelengths. However, such arrangements are necessarily quite fragile, and special strategies must be devised to fabricate them as stronger entities. On the other hand, if we decide to make disordered states, these can have many interesting mechanical properties, leading us to sensible strategies for soft materials. Interestingly, despite the profound importance of these questions, there have been few attempts to understand the fundamental scientific issues involved. Furthermore, in systems such as globular protein solutions, there are related issues, and there we seek to make good crystals in order to be able to carry out X-ray crystallography [1]. Again, the challenge is to understand how to optimize the potential to form a crystal. All these systems share the important feature of having a repulsive core in the potential that is considerably larger than the range of the attractions [2]. If, as we expect, there are unifying ideas, and generic features to be understood, it would be of interest to solve these questions in the simplest possible model.

There are some features to consider that may be important in determining why, in practice, crystal do, or do not form. Firstly, the nucleation rate itself must be sufficiently large for this to occur, which in itself requires sufficiently large numbers of critical nucleii. However, given a small nucleation rate there is still no intrinsic reason that good crystals may not form, unless a dynamical arrest, or glassification intervenes. In the case of ideal monodisperse spherical particles, even with a short-ranged potential, crystals generally form before any other effects are exhibited [3], possibly indicating a high nucleation rate. However, it is commonly observed in the attractive colloidal systems and globular proteins that, for most conditions, crystallization is essentially impossible to arrange. The reason, we believe, is that the crystallization process is interrupted by glassification. We study this effect in this paper.

We present the study of the phase diagram, combined with the lines of dynamical arrest, i.e. glass transition lines, for a simple model of attractive colloidal spheres, interacting with a hard-core Yukawa potential. A key parameter of such a model is the range of the attractive well. Upon varying this, the phase diagram changes significantly, as well as the behaviour of the glass transition curves, leading to interesting interplay between the equilibrium and glassy states.

The hard-core Yukawa model can be studied very effectively by means of the Self-consistent-Ornstein-Zernike-approximation (SCOZA) [4–6]. This approximation is able to predict the fluid properties of the system, and its results for the gas–liquid phase separation, and critical points, have been found in very good agreement with Monte Carlo simulations, at least for not too small values of the range of the potential. For studying the equilibrium properties of the solid phase, we have used a second-order perturbation theory for the free energy. This has also already been shown to be quite accurate compared to simulations [7–9] for short-ranged potentials.

The Mode Coupling Theory (MCT) [10] is used to determine the region in the phase diagram where the system undergoes a dynamical transition to a non-ergodic state, i.e., the glass state. However, the theory must be considered to be subject to the constraint that crystals do not form. In fact, equilibrium MCT describes a dynamics that obeys the fluctuation dissipation theorem of type two [11], with the input of the liquid static structure factor of the system, thereby crystallization cannot occur.

2. Model and theory

We have chosen to study the hard-core Yukawa fluid, with inter-particle potential given by

$$v(r) = \begin{cases} \infty, & r < \sigma\,, \\ -\sigma\varepsilon \dfrac{e^{-b(r-\sigma)}}{r}, & r \geqslant \sigma\,. \end{cases} \tag{1}$$

Here, the screening parameter b controls the range of the attraction, while ε defines the energy scale and σ is the particle diameter. In the present calculation $\varepsilon = 1$ and $\sigma = 1$. The equilibrium properties of the fluid for this model can be calculated with SCOZA. This approximation provides a closure relation for the OZ equation [12], which, as the name suggests, is thermodynamically consistent by construction. In fact, it gives an expression for the direct correlation function $c(r)$ in terms of the potential and some parameters, which can then be determined by imposing the appropriate condition of consistency for the virial and energy routes to calculate the thermodynamic quantities. Thus, $c(r)$, and consequently the static structure factor $S(q)$, as well as free energy, pressure and chemical potential can be calculated. A more detailed explanation of SCOZA can be found in Refs. [4–6].

To calculate the solid free energy, we have adopted the perturbative approach, previously used for the phase diagram of a colloidal solution with depletion interactions in Ref. [7]. This is based on the separation of the interaction potential into the sum of two terms, i.e. the hard-core contribution, which is considered as a reference for the perturbation, and the attractive part, which is the perturbation itself. Thus, the solid free energy is calculated carrying the perturbative expansion up to second order within the Barker and Henderson approximation [13], around the hard sphere crystal free energy. Also, for the Helmholtz free energy and radial distribution function of the hard sphere system, we use the equation of state introduced by Hall [14], and perform an integration starting from a known thermodynamic configuration [6].

To construct the phase boundaries between two phases (gas–liquid, fluid–solid, etc.), we have imposed, along an isotherm, the standard conditions:

$$\mu^{(1)} = \mu^{(2)}, \quad P^{(1)} = P^{(2)}\,, \tag{2}$$

where μ is the chemical potential, i.e. the Gibbs free energy per particle, $\mu = G/N$ and P is the pressure.

For $b \leqslant 9$, where SCOZA and perturbation theory predictions have been checked with simulations, the equilibrium phase diagram is highly accurate [5,9,6]. Simulations have not been carried out beyond $b = 9$ as yet and some degradation is likely to occur as b becomes quite large. However, the results reported here should be amongst the most accurate of those currently available for this system.

We now turn our attention to the study of the glass transition, for which we have used the ideal MCT [10], that is able to give predictions in particularly good agreement with experimental results on purely repulsive colloidal systems [15]. Recently, the focus of many studies [16–21] has been a new type of arrested state, usually referred as the 'attractive' glass, as it is generated by the presence of strong, very short-ranged attractive interactions, and it is profoundly different [20] from the usual hard-sphere type of glass, where the dominant mechanism of arrest is only packing.

MCT describes the non-ergodicity transition by a nonlinear integro-differential system of equations for the normalized time correlation functions of density fluctuations $\Phi(q,t)$. Apart from parameters entering from the microscopic motion, the only input to the MCT equations is the equilibrium wavevector-dependent structure factor of the system, S_q. As explained above, in the present scheme, this is calculated within SCOZA. The glass transition lines are identified by determining the long time limit of the density correlators, known as the non-ergodicity parameter $f_q = \lim_{t\to\infty} \Phi(q,t)$. An ergodic state is characterized by $f_q = 0$, and this value is always a solution of the MCT long-time limit equations [10]. Thus, the glass transition appears as an ergodic to non-ergodic transition for the system, where $f_q \neq 0$ solutions arise as bifurcations singularities of the MCT equations. Thus, these points are commonly identified as A_n MCT singularities, with n being the order of the singularity, and, depending on the number of control parameters of the model, they can be of increasingly higher order, producing interesting features of the arrested states diagrams both for static and dynamics. It has been already shown for a square well model [19] that upon varying the range of the attractions, A_3 and A_4 singularities appear. In particular, these signal the presence of a glass–glass transition line between attractive and repulsive glasses. It is of interest to understand if this prediction is general, or if it depends on the particular choice of the potential model, which, in the case of the square well, presents a discontinuous behaviour.

3. Results

We report here some results of the method explained above for the phase diagram and glass transition line for some representatives values of the screening parameter b, plotting the temperature in units of the well depth ($k_B T/\varepsilon$) against the volume fraction $\phi = \pi\sigma^3\rho/6$, where $\rho = N/V$ is the number density of the system.

Thus, in Fig. 1, we show results for the value $b = b^* = 6.05$. This corresponds to a particular value of the interaction range, for which, as indicated in the picture, the triple point and the critical point of the gas–liquid phase separation coincide. Thus, for smaller values than b^*, corresponding to a longer ranged potential somewhat more common in molecular systems, one finds a typical phase diagram, with ordinary triple point and gas–liquid binodal (see for example in Ref. [6]), while for larger values this transition becomes metastable with respect to the fluid–crystal one. Our estimate of b^* is found to be the same (within numerical errors) as the one obtained by Gibbs ensemble Monte Carlo (GEMC) simulations [9]. We note here that the hard sphere packing fractions for solidification and melting, i.e. respectively $\phi \simeq 0.49$ and 0.55, are correctly found. Also, the glass line is reported in the figure. It is evident that it is

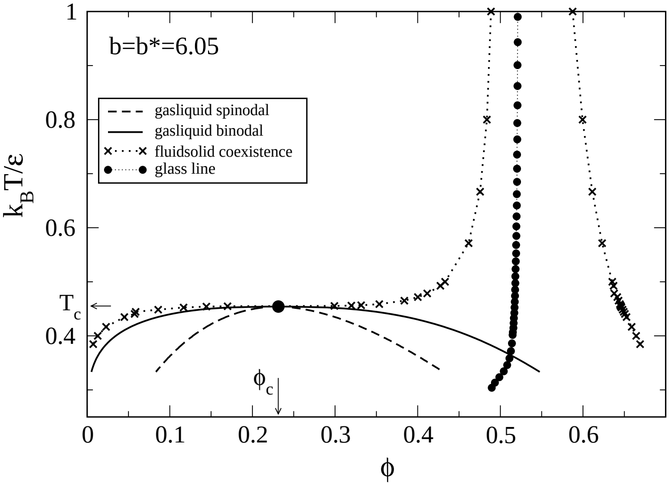

Fig. 1. Phase diagram for the Yukawa fluid with screening parameter $b = 6.05$. The crosses represent fluid–solid phase transition, the continuous line is the gas–liquid binodal and the dashed one is the spinodal. The filled circle marks the critical point, for which the critical values T_c and ϕ_c are also presented. The glass transition line, as evaluated from MCT, is also displayed (open circles). For this value of the range of the potential, the critical point and the triple point are the same, while the glass line is almost vertical around the hard-sphere glass transition packing fraction, predicted by MCT, of about 0.52. Redrawn from Ref. [6].

almost entirely vertical at the packing fraction $\phi \simeq 0.52$ for which MCT predicts the hard-sphere glass transition.

In Fig. 2 we present the case $b = 30$, which corresponds to a much smaller potential range. Here, we clearly see that the gas–liquid phase transition is, indeed, well inside the fluid–solid region, i.e. highly metastable. We also notice that the glass line is shifted towards much lower densities, and in particular, it passes very closely to the gas–liquid critical point. It is interesting to point out that this is a typical feature of MCT [16,20], that has been already related to what is commonly observed in experiments [22], as regards the respective positions of gel and binodal lines. This fact is currently under investigation via accurate simulations of short-ranged potential model, to establish the true nature of the arrested transition with respect to the equilibrium phase separation [3]. Also, it can be noticed that the beginning of a shoulder on the crystal side of the fluid–solid transition, which is a precursor of an isostructural solid–solid transition that will be found for narrower ranges.

It is this choice of b that is probably more typical of the experimental situations we have discussed above, such as globular proteins. Thus, in this case, the system is dominated by the glass or arrested phase and this is the reason why crystals are not easy to form, instead leading to the 'gel-like' states reported in the protein literature [1,23]. In fact, there are cases where we can enter the super-cooled regime, and potentially form crystals without meeting the arrested state. To make this clear we have divided the phase diagram for $b = 30$ into three regions: I, II, and III. These are meant to be the

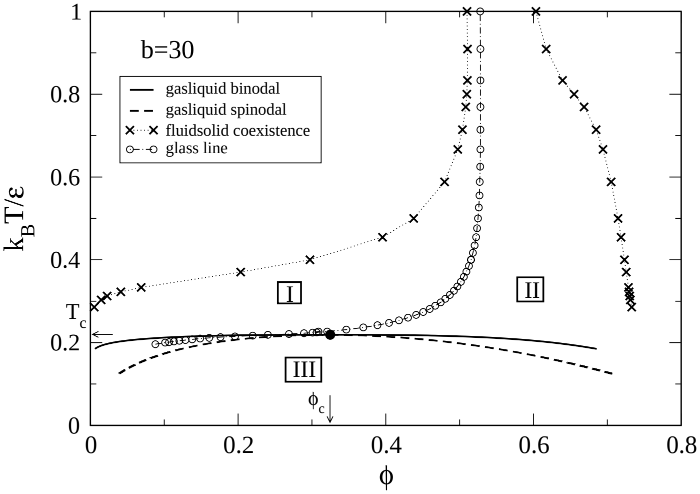

Fig. 2. Phase diagram for the Yukawa fluid with screening parameter $b=30$. The gas–liquid transition is now metastable with respect to the fluid–crystal one. Also, the glass transition line turns towards low densities, passing very close to the critical point of the gas–liquid transition, and, at lower densities, it crosses the binodal line. Redrawn from Ref. [6].

theoretical phase-diagram expression of the regions marked in Ref. [23, Fig. 12]. Thus, only in region I we can safely super-cool below the disperse phase-crystal boundary, and not form an arrested state. Nucleation rates are likely to be very small, but once the crystal nucleii reach a critical size, the crystal can grow at its normal rate, thereby avoiding the intermediate regime that would involve regions II and III.

We now present the case of extremely narrow wells, with a screening parameter $b=100$ in Fig. 3. We note that, for this value, the results produced by SCOZA have not been tested by simulations. However, very interesting new features appear in this case. Firstly, there is a solid–solid (equilibrium) transition between two crystals with the same lattice structure but different lattice spacing, and so different density. This phenomenon was previously found in simulations of other systems [24,8], as well as theoretically predicted for short-ranged potential models [25], and it is due to the competition of attractive and repulsive interactions in the system. We note that this phenomenon is also present for larger ranges of the Yukawa, such as $b=60$ [6]. A completely new result is the presence also of a glass–glass transition line for the Yukawa potential, although partial evidence of it for the Yukawa model, based on observations of a discontinuity of the shear modulus at the transition, was presented in Ref. [26]. This phenomenon was previously found and extensively discussed for a square well potential [19,20]. Thus, as explained in detail there, we have a transition between two different types of glasses, dominated, respectively, by the attractive well and the repulsive hard core. The transition line ends with an end-point singularity A_3, which in MCT is signalled by the exponent parameter λ [10] being equal to 1. In our case, the last point reported on

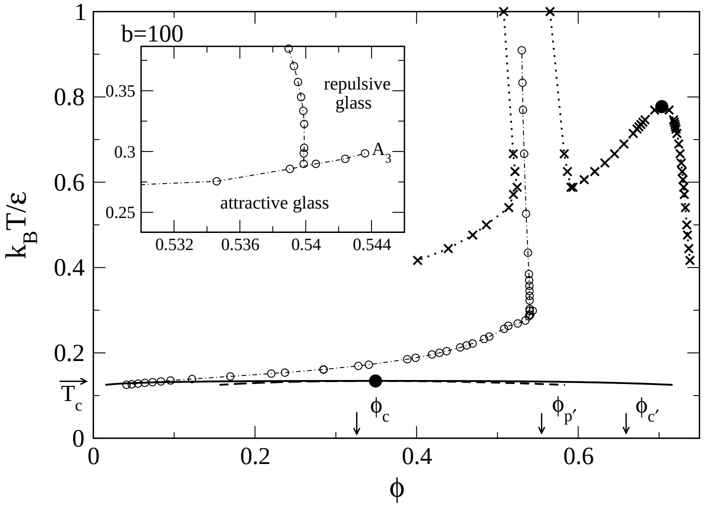

Fig. 3. Phase diagram for the Yukawa fluid with screening parameter $b = 100$. A solid–solid transition is observed as well as a glass–glass one, also enlarged in the inset, terminating in the end-point singularity A_3.

the glass–glass line, represented in the figure, corresponds to $\lambda \simeq 0.991$.[1] Thus, it is interesting to note that the mechanism of competition between the two different parts of the potential originates both equilibrium and dynamic solid–solid transitions, for very narrow attractive interactions. Immediately, the similarity of such a phase diagram to the one presented in Ref. [6] for a square well potential, with an attractive well equal to 3% of the particle diameter, can be seen. Thus, the presence of two distinct types of glasses, and crystals, seems to be typical of any type of very short-ranged potential model, independent of its shape.

4. Conclusions

We have presented here a study of the hard-core Yukawa potential model via an hybrid method, consisting of the combination of quite accurate liquid and solid-state theories, i.e. SCOZA and second-order perturbation theory, with the MCT for determining the dynamical arrest, and so the glass transition.

We have shown that when the range of the potential becomes short in comparison to the core size, the phase diagram is deeply affected. Practically speaking, by choosing the appropriate range parameter, both theoretically and experimentally (for example by

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[1] We note that the location of these points strongly depends on the accuracy within which one has calculated the equilibrium structure factor, and thus solved SCOZA. Since SCOZA requires an integration over a grid in the parameter space (ϕ, T), the more defined the grid, the more accurate the description of the system will be. For the glass–glass line we have used a grid of 100 points in packing fraction, after we checked that the resulting structure factor is in good agreement with the same as calculated on a grid of 1000 points.

changing the coating on the colloidal particles), one can reproduce most of the usual, and particularly unusual, scenarios. Thus, the gas–liquid transition can be stable or metastable, or one could have a typical gas–liquid–solid triple point, while an unusual fluid–solid–solid could in principle also be found in some cases. Also, the study of the glass lines has evidenced for the first time in a smooth potential the presence of an attractive–repulsive glass transition within MCT.

The possibility of changing the phase diagram can be useful in many ways. By elucidating those issues that determine where crystals and glasses form [6], we may begin to understand why it is difficult to crystallize proteins, and then to develop new approaches to make this possible. Also, we may begin to be able to develop control of the mechanical properties of glasses, leading to soft materials.

Another issue to be clarified is the relation of what is commonly observed experimentally, and identified as gellation process, with the MCT glass transition, especially at low densities where the curves seem quite reasonable, though the theoretical underpinnings of the MCT theory itself are less clear [20]. On the other hand, at higher volume fractions, near the $A_3 - A_4$ scenario, we expect the theory to be reasonably satisfactory. Further work in experiments or simulations should be directed at identifying those signals of the re-entrant behaviour of the glass line and of the glass–glass transition for very short-ranged attractions, that appears to be a general prediction of MCT, independent both on the potential shape and on the liquid-state theory used for the static structure factor. The first simulations that seem to establish these results are now becoming available [3,27].

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