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Static and dynamical correlation functions behaviour in attractive colloidal systems from theory and simulation

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Abstract

We present comparisons of theoretical and simulation results for static and dynamical correlation functions for a very simple model of attractive colloidal systems, the short-ranged square-well potential. In the region of the phase diagram investigated, the system displays slow (glassy) dynamics. In particular, we compare the static structure factor calculated by Percus–Yevick closure versus the simulation results, both in the small- and large-wavevector ranges. For the same model, we also compare the non-ergodicity parameter, i.e. the long-time limit of the dynamical density correlators, as calculated by mode-coupling theory and by simulation, confirming the presence of two distinct glassy phases.

1. Introduction

Colloidal suspensions have been extensively studied because of their practical importance and their relevance in biophysics, food science, the cosmetics industry, as well as medical applications. Experimentally they are much more easily accessible than simple fluids, because of their bigger particle size, and, thus, light scattering can be used to measure the various correlation functions. Another important feature is that the interactions between particles can be significantly varied both in range and in strength, for example by different coatings of the particles and/or changing the composition of the solvent [1, 2]. This means that real colloidal systems are greatly adaptable to reproducing various interaction models, and this explains why they also are of great theoretical interest.

In the past few years the idea that colloidal particles can form glassy structures has been established in a number of very interesting experimental and theoretical works. Most attention has been focused on colloidal particle systems that are dominated by repulsive interactions, for which, at high packing fraction values, the glass represents an alternative packing to the thermodynamically more favourable crystal structure. These systems are well represented by a simple hard-sphere model [3]. Where repulsive interactions dominate, the loss of ergodicity is due to blocking of the movements of particles by the quite dense surrounding cages formed by their nearest neighbours. For hard-sphere colloidal systems, mode-coupling theory (MCT) [4, 5] has played a leading role, interpreting and rationalizing some of the observations, and achieving quite remarkable numerical agreement in comparison to experiments [6].

Recent works [7–15] introduced and studied in detail the influence of a narrow attractive part in the colloidal interaction potential for various models within MCT. One of these, on which we focus in this paper, is the short-ranged square-well (SW) model, for which extensive molecular dynamics simulations have also been carried out [16, 17].

The addition of an attractive well to a hard core produces a new type of glass, distinct from the well-known ‘repulsive’ glass described above. This has been called the ‘attractive’ glass to underline the fact that the loss of ergodicity is driven by strong short-ranged attractive interactions. In other words, the mutual ‘stickiness’ of the particles eventually dominates the thermal motions, and the system freezes. Thus, close packing is no longer necessary for a glass to be stable, and it transpires that such glasses can form at much lower densities. A crucial parameter for the emergence of new phenomena is the narrow well width of the attractive potential. Indeed, at high densities, the competition between packing and short-ranged attractions generates a peculiar re-entrant region in the phase diagram [7, 8, 10]. It turns out that at much higher densities than the one characteristic of the hard-sphere glass, a fluid phase exists. As a result, along an isochore, one can produce a glassy state by either lowering or raising the temperature (or varying the strength of the interactions). This surprising behaviour has been recently found in experiments [21, 22] and simulations [16, 17, 20]. It has also allowed us to understand some puzzling old results which have now obtained a clear theoretical meaning [23, 24].

MCT also predicts the existence of a glass–glass transition occurring between the two types of arrested state, which can be found for attractive well widths smaller than about 4% of the particle diameter [10]. The dynamical properties of the two glasses vary discontinuously across the transition, and become continuous at an end-point. Also, a characteristic logarithmic decay of the density correlators is predicted by the theory [19]. These phenomena are due to the occurrence of higher-order singularities in the MCT equations for this model, as explained in the next section.

These theoretical results, derived both for the short-ranged SW potential using different closures for the input static structure factors [10], as well as for the hard-core Yukawa potential [13, 14], have been confirmed by MD simulations of the SW model [16, 17], as well as of a depletion interaction model [20]. Experimental evidence of the logarithmic decay of the correlators has been reported for various types of system with short attractive interactions [21, 22, 25, 26].

The aim of this paper is to provide evidence that:

- (1) the Percus–Yevick (PY) solution of the Ornstein–Zernike (OZ) relation for the static structure factor of the one-component SW model, in the region of the re-entrance phenomenon, provides a very accurate description of the ‘exact’ static structure factor as calculated from MD simulations;
- (2) the long-time limits of the dynamical density correlator, i.e. the non-ergodicity parameter,

obtained by solving the MCT equations using PY static structure factor and from the simulations are in good agreement;

- (3) the attractive and repulsive glasses are characterized by very similar structure factors (i.e. very similar static properties) but by very different dynamical properties.

2. Theory and simulation

We consider a one-component system of colloidal particles, interacting via a SW potential, with very narrow attractive range, defined as

$$V(r) = \begin{cases} \infty & r < d \\ -\beta u_0 & d < r < d + \Delta \\ 0 & d + \Delta < r \end{cases} \quad (1)$$

where $\beta = (k_B T)^{-1}$, with k_B the Boltzmann constant. Δ is related to $\epsilon = \Delta/(d + \Delta)$, which is the relative well width parameter. There are three control parameters for the system, i.e. the temperature T , the packing fraction $\phi = \pi \rho d^3/6$, where $\rho = N/V$ is the number particle density, and the relative width ϵ of the attractive well with respect to the total range of interaction.

Following the standard literature [3], the static structure factor, $S_q = \langle |\rho_q|^2 \rangle / N$ with $\rho_q(t) = \sum_{j=1}^N e^{iq \cdot r_j(t)}$ being the density variables, is related to the Fourier transform of the pair distribution function of the system $g(r)$. The OZ relation constitutes an integral equation for $h(r) = g(r) - 1$ in terms of the direct correlation function $c(r)$. This can be solved numerically within the PY approximation $c(r) = g(r)[1 - \exp(V(r)/k_B T)]$ to yield S_q by Fourier transformation [10].

The only inputs needed to solve MCT equations [5] for the normalized dynamical density correlators, i.e. $\Phi_q(t) = \langle \rho_q^*(0) \rho_q(t) \rangle / (N S_q)$, are S_q and ρ . Thus, from only static information, the theory provides predictions for the dynamics of the system. In particular, one can solve the long-time-limit MCT equations for the non-ergodicity parameter $f_q = \lim_{t \rightarrow \infty} \Phi_q(t)$. It turns out that $f_q = 0$ always corresponds to a solution of the equations [5]. This corresponds to an ergodic state of the system in which the density correlations decay to zero if one waits a sufficiently long time. For some critical values of the control parameters there appear bifurcations of the solutions, producing $f_q > 0$ solutions. These correspond to non-ergodic states, and, given that there is no positional order in the system, they are identified as glasses. Higher-order bifurcations produce MCT higher-order singularities labelled as A_j [5, 18, 19], j being the order depending on the number of control parameters in the system.

In the SW model, where the control parameters space is three dimensional, one can find up to an A_4 -singularity in the MCT for the critical value of $\epsilon \sim 4.11\%$ [10]. In the following, we will consider only the case $\epsilon = 0.03$, which has been extensively studied within MCT [10, 11] and MD simulations [16]. For this well width value, a glass–glass transition line is present, which ends at an A_3 -singularity in the MCT. We also consider a binary mixture of particles interacting via the SW potential, with a 3% value of ϵ for interactions between like and unlike species. This binary system [17] refers to a 50%–50% mixture of 700 particles with diameter ratio equal to 1.2 (larger particles with label A), just sufficient to prevent crystallization, without affecting the dynamics too much. By means of these studies, the re-entrant shape of the glass transition curve and the presence of a higher-order singularity have been firmly established for such narrow attractive wells.

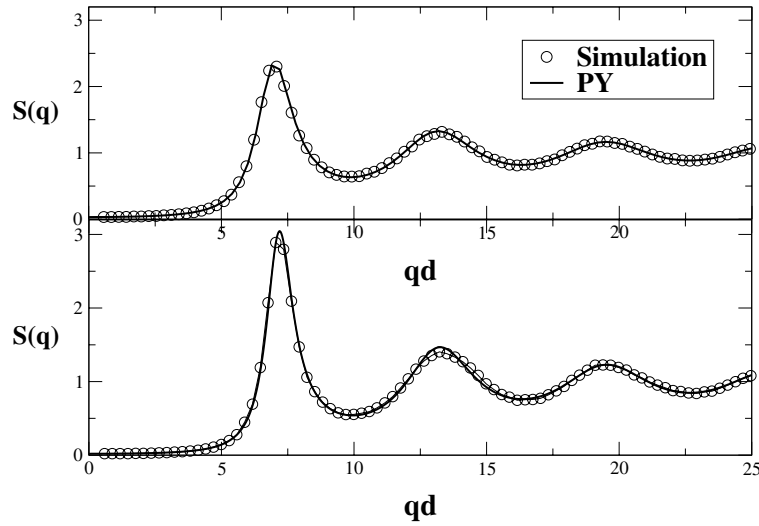


Figure 1. Comparison for the static structure factor at $T = 1.0$ and $\phi = 0.475$ (upper half) and 0.53 (lower half) for a one-component SW system with relative well width parameter $\epsilon = 0.03$, calculated via PY approximation and from MD simulation. The chosen values of (ϕ, T) refer to the system being in the fluid phase for the first case, and close to the A_3 -singularity for the second one (see the MCT-PY glass transition curves in [10, 11]).

3. Results

We start by comparing the theoretical results for the static structure factor S_q calculated from the PY approximation and the simulation results in figure 1. We show two cases in the high-density region: $\phi = 0.475$ in the upper box and $\phi = 0.53$ in the lower one, both at temperature $T = 1.0$. Thus, these can be considered as exemplary cases for the region of interest of these systems, i.e. where the most striking phenomena take place. Indeed, if one refers to the MCT glass transition lines in [10, 11], one can see that, for the PY solution, the second case represented is quite close to the A_3 -singularity. Clearly the numerical and theoretical solutions are in excellent agreement, at least in this region.

We here add a further comment. In figure 2, we plot the long-wavevector dependence of the static structure factor of the $\phi = 0.475$ case. What is interesting to note is the presence of ‘beats’ in the tail of S_q , i.e. finite oscillations which do not decay monotonically, despite becoming smaller and smaller. These are generated by the presence in the potential model of two characteristic length scales, the hard-core diameter and the well width. The competition between these two gives rise to this phenomenon, which is indeed not present in the hard-sphere case, as shown in the lower box of the figure. The numerical data reported in the upper panel, although quite noisy at these small amplitudes, confirm the phenomenon, which can now be considered to be truly characteristic of this model. Since the beats become more accentuated as the well width becomes smaller, this necessitates the choice of an appropriate cut-off q -vector for the convergence of the integrals in the MCT equations, as extensively discussed in [9].

Now we turn to examining the non-ergodicity factor for repulsive and attractive glasses. We compare results obtained by solving the MCT equations and by the MD simulations, with the procedures described below. In the lower half of figure 3 we show the non-ergodicity factor f_q obtained by solving MCT long-time-limit equations, for packing fraction $\phi = 0.54$ at two different temperatures. The input structure factor used in the equations was evaluated

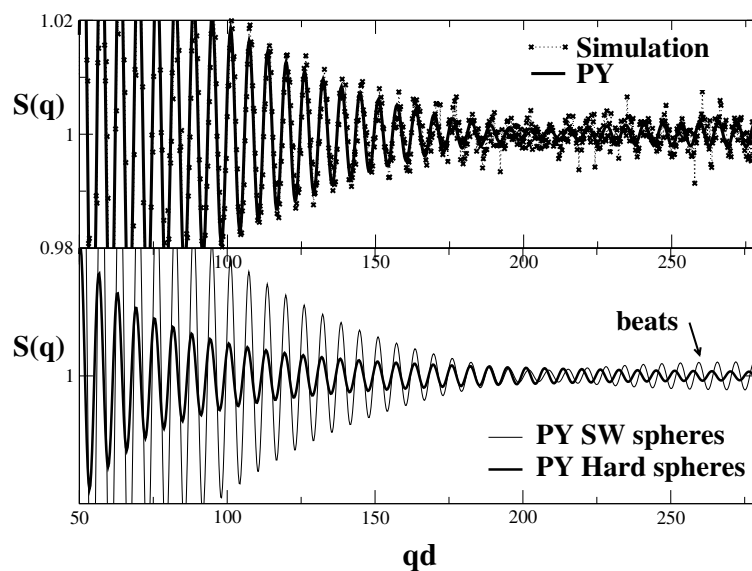


Figure 2. Upper half: comparison between PY and simulation results for the large- q tail of the static structure factor for the SW system with $\epsilon = 0.03$ at $T = 1.0$ and $\phi = 0.475$. Lower half: comparison between the PY solutions for the SW system with $\epsilon = 0.03$ at $T = 1.0$ and $\phi = 0.475$ and the hard-sphere system at the same packing fraction. The phenomenon of ‘beats’ typical of the SW model is thus established within theory and simulation.

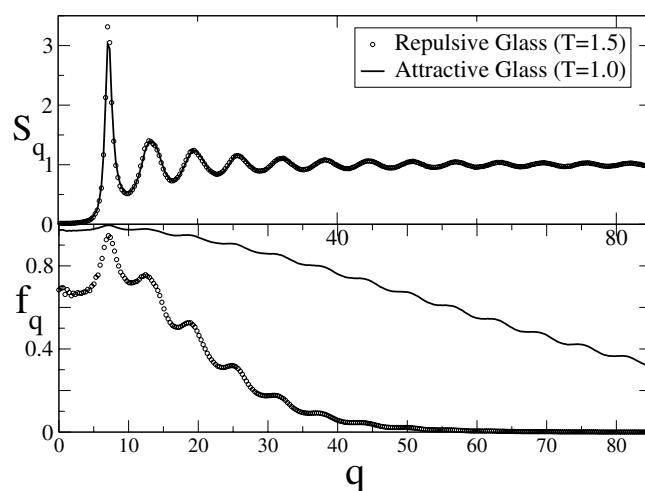


Figure 3. Upper half: static structure factors at $\phi = 0.54$ for temperatures $T = 1.5$ and 1.0 calculated by MD simulation. No significant change, except in the height of the first peak, is observed. Lower half: corresponding non-ergodicity parameters f_q calculated by solving MCT equations using the above S_q (for large wavevectors—i.e. $q > 90$ —the PY solution was used). The higher temperature clearly relates to a repulsive glass, while the lower one relates to attractive glass behaviour. Here $\epsilon = 0.03$.

from the simulation, and for completeness it is also reported in the upper half of the figure. For large wavevectors, i.e. $q > 90$, the PY solution was considered to avoid any artificial increase in the memory function due to the inevitably low signal-to-noise ratio in S_q at large

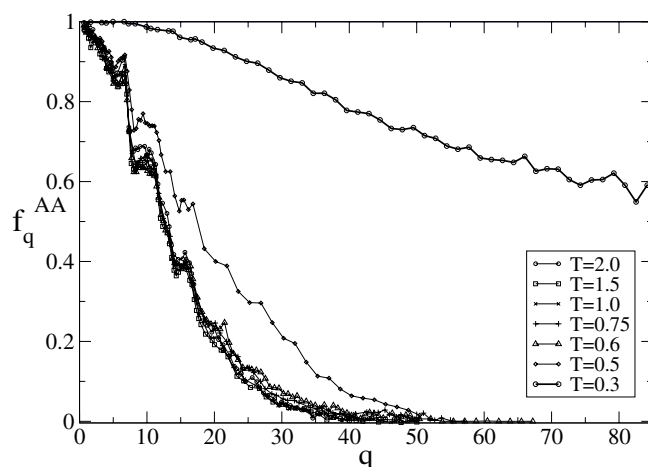


Figure 4. Non-ergodicity parameters for the larger particles f_q^{AA} along the lowest iso-normalized-diffusivity curve discussed in the text calculated from the simulation. This figure was redrawn from [17], where details of the calculation can also be found.

q -values. For the higher temperature, one finds the typical result already known for hard-sphere systems. However, when one enters the attractive glass region, the shape of f_q changes. It extends to much larger ranges of wavevectors and varies with temperature, since the strength of the attraction is now important for the classification. Significant changes in f_q (a dynamical quantity) are observed without significant changes in the structure, as shown by the minute changes (only relevant at the first peak) in S_q .

The results for the one-component system have been confirmed by simulations of binary mixtures of SW spheres [17]. The justification for the use of a binary system lies in the fact that it effectively avoids crystallization up to very large packing fractions, so the only limit to the simulation is given by the slowness of the dynamics with respect to processor speed, rather than by crystallization problems as in one-component systems [16]. To evaluate f_q from the simulation, we first calculated the density correlators for various wavenumbers by averaging over many configurations in time. Then we used asymptotic predictions to extract f_q as a fit parameter, as discussed at length in [17]. Figure 4 shows the non-ergodicity factor of the larger particles f_q^{AA} along the line of lowest diffusivity values reached within the simulation time. This line can be seen as the precursor of the ideal glass line. Thus, following it, from high to low temperatures, one should pass from repulsive to attractive glass behaviour. The plot confirms the existence of the two glasses, as well as the independence of temperature for the repulsive case. The similarity with figure 3 is strong, except for the behaviour at small q , i.e. below the first oscillation peak, where an increase arises in the binary case. This feature depends on the fact that we are looking at a partial quantity and its normalization, which in this case is the partial static structure factor. This agrees with what is expected from MCT applied to binary mixtures [27].

4. Conclusions

In this paper we aimed to get further insight into the already established correspondence between theory [10, 11] and simulation [16, 17] for the SW system. Thus, we showed by direct comparison the quality of the PY closure in yielding the static structure factor, at least

in the region of interest for these systems, i.e. in the high-density region where the re-entrant shape of the glass transition line is found. This acknowledges the validity of the input used in the use of MCT. Also, we further discussed the long-wavevector tail, where oscillations that are not monotonically damped, referred to as beats, take place due to the shape of the potential. Moreover, we remarked on the differences between the dynamical properties of the two distinct glasses that arise in these narrow-ranged attractive systems and we showed that results from theory and simulation also indicate the qualitative behaviours of the non-ergodicity factors of the two glasses to be the same.

The important conclusions to be drawn from this work are the following. Firstly, MCT relies on an input structure factor, which is calculated by using liquid-state theories, in our case the PY theory. Simulations have confirmed that in the glassy region also, the static structure of the glass is consistent with the liquid one. However, small changes in the structure produce drastic changes in the dynamical predictions of MCT, and this is also confirmed by simulations. Thus, the extensive MD simulations carried out in [16, 17] have allowed us to firmly establish and complete the information already available on this model from theoretical work.

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