Scaling of dynamics with the range of interaction in short-range attractive colloids

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We numerically study the dependence of the dynamics on the range of interaction \( \Delta \) for the short-range square well potential. We find that, for small \( \Delta \), dynamics scale exactly in the same way as thermodynamics, both for Newtonian and Brownian microscopic dynamics. For interaction ranges from a few percent down to the Baxter limit, the relative location of the attractive glass line and the liquid-gas line does not depend on \( \Delta \). This proves that in this class of potentials, disordered arrested states (gels) can be generated only as a result of a kinetically arrested phase separation.

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Colloidal dispersions form gels, disordered arrested states of matter at low packing fraction \( \phi \), if the colloidal-harsh-sphere repulsion is complemented by a short-range attraction \( \Delta \) \cite{ref1}. The nature of the gel transition in short-range attractive colloidal systems has received significant attention in recent years \cite{ref2}. Several routes to the gel state have been proposed and critically examined. In particular, it has been speculated that the gel-line constitutes the extension to low \( \phi \) of the attractive-glass line, an idea which would provide an unifying interpretation of the gel and glass arrest state of matter \cite{ref3}. An alternative interpretation suggests that colloidal gel results from an interrupted liquid-gas phase separation, interrupted by the glass transition which takes place in the dense regions created during the spinodal decomposition kinetics \cite{ref4}. The two scenarios, which differ only by the relative location of the glass line(s) with respect to the phase separation line, are sketched in Fig. 1. In case (i), the attractive glass line pre-empt the meta-stable liquid-gas-separation and the glass line can be approached from equilibrium conditions \cite{ref5}. In case (ii), the class meets the phase separation line on the high \( \phi \) branch, and the morphology of the low \( \phi \) arrested state is dictated by the phase separation kinetic \cite{ref6}. The thermodynamic phase diagram of simple models for short-range attraction has been evaluated theoretically \cite{ref7} and successfully compared with experimental data \cite{ref8,ref9,ref10}. When the attraction range is a few percent of the particle size, the equilibrium phase diagram is composed only by a fluid-phase and a crystalline phase. The liquid-gas coexistence locus is hidden within the region of fluid-crystal coexistence. For small range of attractions, the liquid-gas coexistence curve for different models can be scaled onto each other by comparing different systems at the same value of the second virial coefficient \cite{ref11}, providing an effective characterization of the dependence of the liquid-gas coexistence line on the range of attraction.

The dependence of dynamic properties on the range of attraction has been studied at large \( \phi \) within the mode-
this question, by examining the dependence of the dynamics on the attraction range, both for Brownian (BD) and Newtonian (ND) dynamics. We show that, for interaction ranges from a few percent down to the Baxter limit and for packing fraction smaller than 0.40, (the packing fraction range where gels are observed in experiments), dynamics and thermodynamics loci scale with the range of interaction in the same way, ruling out case (i) as route to the gel formation in short-range attractive colloids.

We investigate a system that has been extensively studied earlier, a binary square well (SW) mixture 23, 24. The binary system is a 50%-50% mixture of N = 2000 particles. The two species (labeled A and B) are characterized by a diameter ratio \( \sigma_A / \sigma_B = 1.2 \). Masses are chosen to be equal and unitary. The attraction is modeled by a SW interaction defined according to:

\[
V^{\alpha,\beta}(r) = \begin{cases} 
\infty & r < \sigma_{\alpha,\beta} \\
-u_0 & \sigma_{\alpha,\beta} < r < \sigma_{\alpha,\beta} + \Delta_{\alpha,\beta} \\
0 & r > \sigma_{\alpha,\beta} + \Delta_{\alpha,\beta}
\end{cases}
\]  

(1)

where \( \sigma_{\alpha,\beta} = (\sigma_\alpha + \sigma_\beta) / 2 \), \( \alpha, \beta = A, B \) and \( \Delta_{\alpha,\beta} \) is the range of the attraction. We fix \( \sigma_{\alpha,\beta} \) and vary the relative well-width \( \epsilon = \Delta_{\alpha,\beta} / \sigma_{\alpha,\beta} \), where \( \sigma_\alpha \) is the diameter of the small specie is chosen as unity of length, i.e. \( \sigma_B = 1 \). Density is expressed in term of packing fraction \( \rho = (N_A + N_B) / L^3 \)

\[
\text{ND} = \frac{2}{3} \pi \frac{\sigma^3}{L^3}
\]  

(3)

For the equivalent 50-50 hard-sphere binary mixture, \( B_2 \) is

\[
B_2^{HS} = \frac{2}{3} \pi \left( \frac{\sigma^3_{AA} + \sigma^3_{BB} + 2 \sigma^3_{AB}}{4} \right)
\]

(4)

An adimensional second virial coefficient can be defined as \( B_2^* = B_2 / B_2^{HS} \). This quantity helps in comparing between different models and different samples. At small \( \epsilon \), \( B_2^* \) becomes essentially function of the variable \( \epsilon \delta u_0 \approx \Delta \). In the same limit, state points at the same \( B_2^* \) and \( \phi \) are characterized, to a very good approximation, by same thermodynamic properties, i.e. same bonding pattern, same energy, same structure. In the limit \( \epsilon \rightarrow 0 \) the system behaves similarly to the Baxter model 23 at the same \( B_2^* \) state point. The Baxter potential \( V_B(r) \) is best defined via

\[
e^{-\beta V_B(r)} = \theta(r - \sigma) + \frac{\sigma}{12 \tau} \delta(r - \sigma)
\]  

(5)

where \( \tau \) is the adhesiveness parameter, which plays the role of effective temperature, \( \theta \) and \( \delta \) are respectively the Heaviside and Dirac functions. This model has been extensively used in the interpretation of experimental data 31 despite its known pathologies 31, 32. For the Baxter potential, \( B_2^* = 1 - 1 / 4 \tau \) and the location of the liquid-gas critical point, recently determined with great accuracy, is \( \phi_c = 0.266 \) and \( B_2^* = -1.2 \).

Fig. 2 shows the spinodal line for the SW model with \( \epsilon = 0.01 \), estimated by bracketing it with the lowest \( T \) stable point and the first phase separating state point along each isochore. It also show the data from Miller and Frenkel 33 for the Baxter potential. The agreement between the two set of data, notwithstanding the different system (binary mixture vs. one component, SW vs. Baxter) confirms that the Baxter limit is already reached when \( \epsilon = 0.01 \). Fig. 2 also shows the ND isodiffusivity lines 34, defined as the locus where the normalized diffusion coefficient \( D / D_0 \) is constant. For ND, the normalization factor \( D_0 = \sqrt{3k_B T / \pi m} v_{th} \sigma_B \) accounts for differences in the microscopic time due to different thermal velocity \( v_{th} \). The large values of \( D / D_0 \), even for \( \phi \approx \phi_c \), confirms that, as in previously studied \( \epsilon = 0.03 \) case 3, no arrested states can be approached in equilibrium for \( \phi < \phi_c \).

We next address the question of the dependence of the dynamics on \( \epsilon \). We focus on two specific values of \( \phi \), respectively on the left (\( \phi = 0.2 \)) and on the right (\( \phi = 0.4 \)) of the critical point. For each \( \phi \), we select several pairs of \( \epsilon - T \) values such that \( B_2^* = -0.405 \). The average energy per particle are respectively of \(-2 \) and \(-4 \). Within our numerical precision, simulations for different width can be scaled by using as scaling variable the value of the second virial coefficient \( B_2 \).
\( \epsilon - T \) values converge to the same average potential energy and same structure, supporting the hypothesis that for these small \( \epsilon \) values equality in \( B_2^* \) implies equal thermodynamic properties.

We focus on two dynamic quantities, the tagged-particle mean square displacement \( <r^2(t)> \) and the bond autocorrelation function \( C(t) \), defined by:

\[
C(t) = \frac{\sum_{i<j}^N c_{ij}(0)c_{ij}(t)}{\sum_{i<j}^N c_{ij}^2(0)}
\]

where the \( N \times N \) matrix \( c_{ij}(t) \) defines the bonds at time \( t \) according to:

\[
c_{ij}(t) = \begin{cases} 
1 & \text{if } i \text{ and } j \text{ particles are bonded} \\
0 & \text{else}
\end{cases}
\]

Two particles are considered bonded if their relative distance is in the attractive well.

Fig. 2 shows \( <r^2(t)> \) for both ND and BD. Data are reported as a function of \( tD_0 \) to account for the trivial differences in \( v_{th} \) for ND and in the bare self-diffusion coefficient \( D_0 \) for BD. For both \( \phi \) and both microscopic dynamics, \( <r^2(t)> \) is independent on the range of the attractive potential, when the comparison is done at constant \( B_2^* \). In other words, the only difference in the dynamics is accounted by the trivial microscopic \( D_0 \) scaling factor. This implies that the isodiffusivity curves calculated for the \( \epsilon = 0.01 \) case, when reported in a \( B_2^* - \phi \) plane, describe the entire class of SW potentials with range shorter than \( \epsilon = 0.01 \).

Fig. 3 shows \( C(t) \) as a function of \( tD_0 \) for different pairs \((\epsilon,T)\) at fixed \( B_2^* \). Since \( B_2^* \) is constant by construction, the average number of bonds in the system is the same for all investigated \((\epsilon,T)\) pairs. In agreement with the data shown in Fig. 2, all \( C(t) \) collapse onto the same curve both for ND and BD. This suggests that, in \( tD_0 \) units, the probability of breaking a bond does not change along constant \( B_2^* \) paths. It is worth stressing that, while the collapse is observed for both type of microscopic dynamics, the shape of the ND and BD correlation functions differs. In ND, \( C(t) \) is to a good approximation exponential while in BD it is stretched, with a stretching exponent \( \approx 0.5 \). The same considerations hold for \( \phi = 0.40 \) (Fig. 4b). The fact that the decay of \( C(t) \) is still strongly affected by the microscopic dynamics, implies that MCT can not be applied at these \( \phi \).

In general, assuming that bond breaking is an activated process, the bond breaking probability can be expressed as a product of a frequency of bond breaking attempts \( \omega \) times \( e^{-\beta u_0} \), which express the probability of overcoming the barrier. In the case of ND, \( \omega^{-1} \) is proportional to the time requested to travel a distance of the order of \( \Delta \), and \( \omega^{-1} \sim \Delta / v_{th} \). Hence, the bond lifetime, apart from the thermal contribution \( v_{th} \) absorbed in \( D_0 \), is controlled by the product \( \Delta e^{-\beta u_0} \), the same quantity controlling the value of \( B_2^* \) at small \( \epsilon \) and \( T \).

Results presented in Figs. 2-4 suggest that, for small \( \epsilon \), the value of \( B_2^* \) characterizes not only thermodynamics, but also dynamics. In other words, at a given value of \( B_2^* \)
it corresponds a family of systems with different $T$ and $\epsilon$, including the limiting case of Baxter, that posses the same static and dynamic properties. According to the present results, the apparent long bond lifetime characteristic of the Baxter model is only induced by the extremely small thermal velocity associated to the vanishing of $T$ implicit in the limit $\epsilon \to 0$ at fixed $B_2^\star$. The similar scaling of dynamics and thermodynamics has important consequences for understanding gel formation in short-range attractive colloidal dispersions. The isodiffusivity lines reported in Fig 4 describe not only the case $\epsilon = 0.01$ for which they have been calculated but also the dynamics of all shorter ranged potentials, down to the Baxter limit, at least up to the tested $\phi = 0.4$ value. This has a profound consequence for the two scenarios discussed in Fig 1, since it proves that in short-ranged potentials the glass line always meet the liquid-gas line on its right side. In this class of potentials, disordered arrested states at low $\phi$ can only be created under out of equilibrium conditions, requiring a preliminary separation into colloid rich (liquid) and colloid poor (gas) phases followed by an attractive-glass dynamic arrest in the denser regions.

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FIG. 4: Bond correlation function $C(t)$ as a function of $tD_0$ for different relative well width $\epsilon$ and $T$ but all at $B_2^\star = -0.405$. Data for both ND and BD are reported. (a) $\phi = 0.20$; (b) $\phi = 0.40$. The insets show, for the case of ND, $C(t)$ vs $t$. 

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