Postponing the dynamical transition density using competing interactions

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Abstract
Systems of dense spheres interacting through very short-ranged attraction are known from theory, simulations and colloidal experiments to exhibit dynamical reentrance. Their liquid state can thus be fluidized at higher densities than possible in systems with pure repulsion or with long-ranged attraction. A recent mean-field, infinite-dimensional calculation predicts that the dynamical arrest of the fluid can be further delayed by adding a longer-ranged repulsive contribution to the short-ranged attraction. We examine this proposal by performing extensive numerical simulations in a three-dimensional system. We first find the short-ranged attraction parameters necessary to achieve the densest liquid state, and then explore the parameter space for an additional longer-ranged repulsion that could further enhance reentrance. In the family of systems studied, no significant (within numerical accuracy) delay of the dynamical arrest is observed beyond what is already achieved by the short-ranged attraction. Possible explanations are discussed.

Keywords Disorder systems · Glass · Dynamical transition · Square-well · Square-shoulder · Dynamical criticality

1 Introduction

Particles with short-ranged attractive and long-ranged repulsive (SALR) interactions can form fairly elaborate structures [1–9]. Despite the spherical symmetry of their pair interaction potential, at low temperatures these models assemble into exotic ordered and disordered mesophases, and their structural richness has clear dynamical consequences, even in the disordered phase at low and intermediate densities [10–12]. A recent theoretical proposal suggests that certain SALR models exhibit unusual dynamical features in the very dense fluid regime as well [13]. Maimbourg et al. [13]’s extension of a high-dimensional treatment of the glass transition [14–16] suggests that certain SALR models should display a very pronounced dynamical reentrance upon changing temperature. More precisely, their theoretical analysis suggests that a carefully chosen high-density SALR system that is glassy at low temperature should, upon heating, first melt and then become dynamically arrested once again, all while remaining completely disordered, i.e., without crystallizing.

On its own, such reentrance is not exceptional. The phase behavior of systems with square-well or with square shoulder interaction were first shown to exhibit multiple dynamically arrested phases leading to high-order singularities. These dynamical anomalies were proposed by mode-coupling theory [17–21], and verified by both experiments [21–26] and numerical simulations [27–34]. Dynamical quantities, such as the density-density correlator, then exhibit a logarithmic decay instead of a typical two-step relaxation, and the mean-squared displacement grows sub-diffusively instead of plateauing at intermediate times. A common physical interpretation of this effect is that introducing short-ranged attraction leads to an interplay between two localization mechanisms: caging from the hard-core repulsion and interparticle bonding. As a result liquids with a higher packing fraction than is possible from either mechanism can be stabilized [35]. The role of an additional longer-ranged repulsion is understood...
to effectively deepen the well created by the short-ranged attraction that leads to a slightly more efficient packing of neighboring spheres in the liquid state [13]. In the mean-field, $d \to \infty$ description, the nonergodicity transition to a glass phase is then pushed to densities about 3% higher [13].

If the scale of this enhancement persists in finite dimensional systems, it should be numerically distinguishable even if this mean-field transition is but a crossover away from the $d \to \infty$ limit [14].

In this article, we attempt to test this prediction in three dimensions via extensive numerical simulations. First, we tune the attraction range of a system of particles interacting via a hard core followed by a short-ranged square-well attraction (SW) to maximize the high-density extension of the liquid phase. We then optimize the interaction parameters of a system with an additional longer-ranged square-shoulder repulsion (SW + SS) in an attempt to push the dynamical arrest to even higher densities. The plan for the rest of this article is as follows. In Sect. 2 we describe the model, the simulation method and the observables of interest. In Sect. 3, we present the simulation results, and we briefly conclude in Sect. 4.

## 2 Models and simulation method

We study 50–50% binary (A–B) mixtures of $N = 1000$ spherical particles interacting via two potentials: (1) a simple square-well (SW) interaction, and (2) a SALR, square-well plus square-shoulder repulsion (SW + SS) interaction. In the dynamical regime considered the dynamical observables are found to be insensitive to the system size for $N \gtrsim 1000$. The hard core diameter ratio of the two particle types, $\sigma_A/\sigma_B = 1.2$, with an additive hard-core interaction, i.e., $\sigma_{ij} = (\sigma_i + \sigma_j)/2 \forall ij$, is chosen so as to strongly suppress crystallization. The interaction potential can then be generically expressed as

$$
V_{ij} = \begin{cases} 
\infty & r_{ij} \leq \sigma_{ij} \\
-U_0 & \sigma_{ij} < r_{ij} < \sigma_{ij} + \Delta_0^0 \\
U_1 & \sigma_{ij} + \Delta_0^0 < r_{ij} < \sigma_{ij} + \Delta_0^0 + x \Delta_1^1 \\
0 & \sigma_{ij} + \Delta_0^0 + x \Delta_1^1 < r_{ij}
\end{cases}
$$

where $\Delta_0^0 = \lambda_0 \sigma_{ij}$ and $U_0$ are the width and depth, respectively, of the square well, and $\Delta_1^1 = \lambda_1 \sigma_{ij}$ and $U_1$ are the corresponding parameters for the square shoulder. Model (1) has $x = 0$, while model (2) has $x = 1$, and in both cases temperature, $T$, is expressed in reduced units of $U_0$ with Boltzmann constant, $k_B$, set to unity. Hence, model (1) has a single tuning parameter, $\lambda_0$, while model (2) has three: $\lambda_0$, $\lambda_1$, and $U_1$. We consider the dynamics of these systems at constant $N$, volume $V$ and $T$ using a Monte Carlo dynamics that consists of attempting $N$ single-particle translations per unit time that are accepted with the standard Metropolis criterion. These translations are taken along a vector randomly drawn within a three-dimensional cube of side $\delta \epsilon$, chosen such that the relaxation time is minimum at a packing fraction close to the dynamical transition. The results of such Monte Carlo dynamics are known to be similar to those of other local dynamics in the dense fluid regime, of interest in this work [36–38].

Equilibration of the initial system is ensured by running Monte Carlo dynamics for at least ten structural relaxation times, $\tau_s$, defined from the characteristic decay, $Q(\tau_s) \equiv e^{-1}$, of the self-part of the particle-scale overlap function

$$Q(t) = \frac{1}{N} \sum_{i=0}^{N} \Theta(a - |r_i(t) - r_i(0)|),$$

where $\Theta$ is a step function and $a = 0.3 \sigma_B$ is a microscopic length chosen to be close to the typical particle cage size. This function therefore represents the fraction of particles having moved a distance smaller than $a$ by time $t$. In addition, we monitor structural quantities, including the pair correlation function and the structure factor, to ensure that the system has not crystallized or fractionated. As reference, note that the systems closest to the dynamical transition are simulated for about 170 CPU hours on a single CPU core.

The equilibrium $Q(t)$ for the liquid is averaged over the trajectory that begins after equilibration. Typical plots for the relaxation time as a function of the packing fraction are shown in Fig. 1 for different temperatures. At fixed $T$, $\tau_s(\rho; T)$ is used to estimate the (avoided) dynamical transition density, $\rho_d(T)$, by fitting to the critical scaling form, $\tau_s(\rho; T) = A(\rho_d(T) - \rho)^{-\gamma}$—see Fig. 1. Because of the presence of activated processes in finite dimensions, this power-law scaling persists for at most a couple of decades [14], but this range suffices to estimate $\rho_d$ with ±1% accuracy. The resulting $\rho_d(T)$ provides the dynamical diagram in the $T - \rho$ plane.

## 3 Results and discussion

We first tune the interaction range of the simple SW system in order to maximize the depth of the fluid pocket. To the best of our knowledge this optimization had not been previously attempted in simulations. Most previous studies only considered models with $\lambda_0 = 0.03$, following the MCT prediction for the existence of an anomalous glassy regime for that interaction range. The dynamical diagrams for different $\lambda_0$ around 0.03 are shown in Fig. 2; the dynamical reentrance of the liquid is clearly visible. The maximum accessible liquid density, $\rho_d^\ast$, is however, not attained with $\lambda_0 = 0.03$, but rather with $\lambda_0^\ast = 0.019(2)$. Although our result
Fig. 1 Relaxation time $\tau_\alpha$ as a function of the packing fraction $\varphi$ at different temperatures for the SW–SS model. Results here are given for a model with $\lambda_0 = 0.019$, $\lambda_1 = 2.5$, $U_1 = 0.10$. Inset: dynamical transition densities, $\varphi_d(T)$, estimated by fitting the structural relaxation times to a power-law $\tau_\alpha(\varphi;T) = A(\varphi_d(T) - \varphi)^{-\lambda}$. Deviations from the power-law as $\varphi \to \varphi_d$ are associated with activated processes. For visual clarity (inset), the vertical scale for $T = 0.800, 0.604, 0.524, 0.440$ and $0.368$ has been multiplied by $10^0, 10^1, 10^2, 10^3$, and $10^4$, respectively.

Fig. 2 Dynamical diagram, $\varphi(T)$, for spheres interacting via a square-well attraction of different well widths $\lambda_0$. Inset: maximum fluid packing fraction, $\varphi^*_d$, accessible from the liquid side for different $\lambda_0$. The value of $\varphi_d$ when $\lambda_0 = 0$ is taken from Ref. [39]. Lines are only guides for the eye.

for $\lambda_0^*$ is in the vicinity of the infinite-dimensional theoretical prediction of $\lambda_0^* = 0.029/d$ which for $d = 3$ gives $\lambda_0^* = 0.010$ [13], it is nonetheless significantly different from it. Because the intricate liquid structure of finite-dimensional systems is neglected in the mean-field study---$g(r)$ is then simply $= \exp(-\beta V_d(r))$---this discrepancy is not particularly surprising. In three-dimensional liquids, the nearest-neighbor shell structure is indeed much more pronounced than the above form suggests (see Fig. 3).

We next explore whether adding a suitably tuned repulsive force to the potential can further delay the dynamical arrest. In this case, three parameters are to be optimized: $\lambda_0$, $\lambda_1$, and $U_1$. We expect the three-dimensional parameter space $(\lambda_0, \lambda_1, U_1)$ for the SW + SS system to be simple with a single minimum (corresponding to the densest liquid configuration) connected to the minimum of the SW system ($U_1 = 0, \lambda_1 = 0$) through a path without large barriers. To nonetheless ensure that our optimization does not miss its target, we explore a wide range of parameter values. We search for an optimum over $\lambda_0 \in (0.010, 0.060)$, $\lambda_1 \in (0.5, 5.0)$, and $U_1 \in (0.0, 0.40)$ by gridding the parameter space, and compute $\varphi_d$ for a few temperatures around the reentrance regime in the dynamical diagram for each grid point to estimate $\varphi^*_d$. From this scheme we identified the set of parameters that pushes the dynamical transition furthest as $\lambda_0^* = 0.019(3), U_1^* \leq 0.10$, and $0.8 \leq \lambda_1^* \leq 3.0$. All directions away from this optimum lead to lower or comparable values of $\varphi^*_d$. The optimal parameters identified are in qualitative agreement with the theoretical prediction that the repulsion should be much weaker and longer ranged than the attraction and that the attraction range does not markedly broaden in going from a SW to a SW + SS model. In particular, our estimates of $\lambda_0^*$ and $\lambda_1^*$ are quite close to the infinite dimensional prediction---$\lambda_0^* = 0.0536/d (= 0.018$ for $d = 3$) and $\lambda_1^* = 2.29/d (= 0.76$ for $d = 3$) [13]. In our case, however, the attraction range barely changes from the SW case.

Fig. 3 Partial pair correlation function $g_{AA}(r)$. The liquid shell structure is much stronger in $d = 3$ than in the mean-field limit. Inset: the evolution of $\tau_\alpha$ with $\varphi$ is quite insensitive to the choice of $\lambda_1$. Very small deviations can nonetheless be seen for $\lambda_1 > 2.5$.
while the theoretical calculation predicts that $\lambda_0^*$ increases from 0.010 to 0.018. Here again, the tightness of the finite-dimensional neighbor shell likely explains the discrepancy.

A more significant difference is that while the dynamics (and thus $\varphi_0(T)$) is somewhat sensitive to the repulsion strength $U_1$, its dependence on the repulsion range $\lambda_1$ is much weaker over the parameter window considered. The dynamics of all models with $\lambda_1 \in [0.5, 2.5]$ indeed roughly coincides (see Fig. 3 inset). Once more, the pronounced shell structure of three-dimensional dense fluid is likely at play. While in the $d \to \infty$ limit self-solvation can be strongly impacted by the interaction potential in the absence of intricate structure, in three dimensions the influence of the hard core-repulsion is felt much more strongly (see Fig. 3). As a result, adding a weak repulsive contribution to the interaction potential has a much weaker structural impact. For a repulsion range that falls within the intershell depletion regime, no notable effect on the dynamics are thus observed.

Given the relative insensitivity of the optimization to $\lambda_1$, we can concentrate on the two-dimensional parameter space, $\lambda_0 - U_1$, for identifying $\varphi_0^*$. Figure 4 shows the maximum fluid packing fraction $\varphi_0^*$ in the space of $U_0$ and $\lambda_1$ where $\lambda_1 = 2.5$. Interestingly, the optimization landscape is relatively flat along $U_1$. The SW optimum is therefore connected by a fairly soft mode to the SW + SS optimum. Along $\lambda_0$, by contrast, $\varphi_0^*$ changes much more rapidly. This landscape projection is therefore consistent with the above discussion.

The resulting dynamical diagrams for the SW and the SW + SS optima are compared in Fig. 5. The results show that the corresponding $\varphi_0(T)$ values are not significantly different (within numerical uncertainty) from one another. If any enhancement of the reentrance pocket is present, it is therefore much smaller than the 3% predicted by the $d = \infty$ calculation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Maximal fluid packing fraction $\varphi_0^*$ for the SW + SS system in the parameter space of $U_1$ and $\lambda_0$ for $\lambda_1 = 2.5$. The line $U_1 = 0$ corresponds to the SW system. This plot reveals that longer-ranged repulsion does not significantly push $\varphi_0^*$ to higher densities in three dimensions, but nonetheless gives rise to a parameter pocket of enhanced reentrance around $\lambda_0 = 0.019(2)$, away from the $U_1 = 0$ axis.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Dynamical diagram for the SW system with $\lambda_0 = 0.019$ and the SW + SS system with optimized parameters ($\lambda_0 = 0.019$, $\lambda_1 = 2.5$, $U_1 = 0.10$). Adding longer-ranged repulsion does not significantly push $\varphi_0^*$ to higher densities in these models.}
\end{figure}

\section{4 Conclusion}

Motivated by a recent mean-field, ($d \to \infty$) prediction that the dynamically sluggish fluid regime for models with SALR interactions can be pushed to higher densities than for models with purely short-ranged attraction, we have performed extensive Monte Carlo simulations of a family of SW and SW + SS models. We first identified that SW models with an attraction range of about 1.9% exhibit a maximally extended reentrance pocket. Interestingly, this optimum may be verified experimentally using, for instance, PMMA particles with short-range attraction induced by a polymer coating of polystyrene whose size and concentration controls the range and depth of the interaction [35]. However, our exploration of parameters for the SW + SS model did not identify (within numerical uncertainty) any SALR model that pushes the dynamical transition significantly beyond the densest fluid achievable by short-ranged attraction alone. We did, however, identify a branch of parameters over which the optimum extends. This nontrivial feature could be a finite dimensional echo of the $d \to \infty$ prediction. The theoretical prediction that further tuning the interaction potential could engender additional (smaller) gains in $\varphi_0^*$ [13] is however, unlikely to have any detectable impact on three-dimensional systems.

Data associated with this work are available from the Duke Digital Repository at https://doi.org/10.7924/r4xd0wb95.

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Compliance with ethical standards

Conflict of interest We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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