P H Y S I C A L   R E V I E W   L E T T E R S

Numerical Investigation of Glassy Dynamics in Low-Density Systems

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Vitrification in colloidal systems typically occurs at high densities driven by sharply varying, short-ranged interactions. The possibility of glassy behavior arising from smoothly varying, long-ranged particle interactions has received relatively little attention. Here we investigate the behavior of screened charged particles, and explicitly demonstrate that these systems exhibit glassy properties in the regime of low temperature and low density. Properties close to this low-density (Wigner) glass transition share many features with their hard-sphere counterparts, but differ in quantitative aspects that may be accounted for via microscopic theoretical considerations.

The origins of the precipitous slowing down of dynamics in supercooled liquids are still unclear even after many decades of intense scrutiny. Model systems often form the basis for detailed investigations that include the core features known to give rise to generic glassy behavior. Perhaps the most prominent example of such a model system is the hard-sphere suspension, which has served as the basis for numerous experimental, theoretical and computational studies of the glass transition [1–3]. Many of the most interesting properties of supercooled liquids and glasses, including two-step relaxation, stretched exponential decay of density correlations and dynamic heterogeneities occur in hard-sphere systems [4–6].

While the glass transition of hard spheres has become a paradigm for vitrification at *high densities*, serving as a reference point for conceptual attempts to connect the behavior of physically diverse classes of disordered arrested states of matter, another physically important limit of glassy systems has received much less systematic scrutiny. This limit is that of a dilute assembly of particles interacting via long-ranged, soft repulsive forces such as those arising in charged systems. Over 20 years ago Chaikin and co-workers [7,8] investigated the phase behavior of dilute suspensions of charged colloids. Low-density glasses stabilized by Coulomb repulsion were called "Wigner glasses"[7]. At that time a detailed investigation of the structure and dynamics of these suspensions was not carried out. Hints of glassy behavior in one-component plasmas have also been noted [9], and the notion of a Wigner glass has been revived in colloidal systems [10–13] due to recent activity focusing on physical gelation in charged systems [14–18]. Indeed, the study of glassy properties of dilute Coulomb systems has consequences that reach beyond classical systems and may shed light on routes to the formation of glasses in electronic systems [19,20], where glassy effects might persist even in the limit of weak to vanishing quenched disorder [21]. Such self-induced glassiness results from electron-electron interactions, an effect analogous to classical Wigner glass formation in colloidal systems.

Similar to the experimental situation, few theoretical investigations of the emergence of glassy dynamics in low-density Coulomb systems have been carried out [22]. The most detailed investigations have been performed by Bosse and Wilke [23,24], who have used idealized mode-coupling theory (MCT) [25,26] to predict the dynamical behavior of a low-density charged system in a neutralizing background as it approaches the putative Wigner glass transition. These authors predict that glassy behavior in this dilute regime shares many properties with the high-density hard-sphere system, but some unique behavior also emerges. Indeed, Wigner glasses are stable even in the extreme dilute limit where the static structure factor shows no modulation due to molecular shell structure. Furthermore, when the electrostatic repulsion is complemented by an excluded volume interaction, the MCT glass line is predicted to show a reentrant behavior due to the (density dependent) competition between the hard-core and the soft long-ranged repulsion [23,27].

There are two main goals for the work presented here. First, we show that it is possible to generate Wigner glasses in simulations of dilute binary long-ranged (screened) Coulomb systems with a judicious choice of the interaction potential parameters and of the studied state point. Indeed, no previous theoretical work has addressed the stability of the Wigner glass with respect to the competing facility of crystallization [28–31]. This first result has important implications for the modeling and interpretation of dynamics in charged colloidal suspensions [32,33]. Our second goal is to systematically study the glassy behavior of dilute Coulomb systems and to test some aspects of the MCT predictions for dynamics as the Wigner glass state is approached.

Our choice of interparticle potential is dictated by a reasonable compromise between simplicity and realism. In particular, our simulations employ the standard Yukawa

form. Because of the rapid crystallization of one-component Yukawa systems, we have investigated 50%–50% binary mixtures of point particles that may serve as models for dilute Wigner glasses. It should be noted that we have not included an additional short-range hard-sphere term in the potential. The advantage of this (unrealistic) simplification is that it allows us to study the effects of soft, long-ranged interactions in isolation of hard-core contributions. A disadvantage of this choice is that the notion of volume fraction is ill defined; hence, we will discuss our results in terms of number density $n = N/L^3$ where L is the simulation box length and N is the number of particles. The issue of reentrance, crucially depending on the existence of disparate length scales, may only be investigated if the hard-core repulsion is included and will be the subject of future work.

The interaction potential between species i and j is

$$V_{ij}(r) = A_{ij} \frac{\exp(-r/\xi_{ij})}{r/\xi_{ij}}. \qquad (1)$$

The amplitude of the repulsion differs for the two species as $A_{11} = 0.2\epsilon$, $A_{22} = 3.5\epsilon$, and $A_{12} = 0.837\epsilon$, with ϵ being the unit of energy, while the screening lengths are all identical and taken to be $\xi_{ij} = \xi = 1$. Lengths are measured in units of ξ. Such mixture corresponds to a model of two dilute colloidal species with different surface charges [34]. We perform molecular dynamics simulations of point particles of unitary mass m for two system sizes, i.e., $N = 10^3$ and $N = 10^4$, at a fixed number density $n = 0.002\,984$, while the temperature T (measured in units of k_B, which we set equal to 1) is varied. In the following we always use the reduced temperature $T^* = T/10^{-5}$. The time step is 0.5 in units of $\xi/(m\epsilon)^{1/2}$. Since the potential is long-ranged, we choose a cutoff distance equal to 25ξ, which ensures that all repulsive contributions at sufficiently long distances are accounted for. For all studied state points with $T^* \geq 1.7$ data have been collected in the *NVE* ensemble following a sufficiently long equilibration period, controlling that no aging phenomena are detectable. Simulations for $T^* \lesssim 1.7$ show aging even after extremely long equilibrations, confirming the approach to a nonergodic state.

In Fig. 1 we show results for the partial radial distribution functions $g_{ij}(r)$ and for the partial static structure factors $S_{ij}(q)$ in the supercooled regime. A progressive structuring, as well as a shift towards larger distances, of the peaks of all partial radial distribution functions is observed upon decreasing T. Standard signatures of supercooled liquid structure, such as a split in the second peak, are evident. Type-1 particles are significantly closer on average than type-2 ones, due to the weaker repulsion. No sign of crystallization is noted during the whole duration of the runs. Focusing on the partial structure factors, we notice that the amplitude of all S_{ij} is small as compared to the canonical glass formers. Moreover, $S_{11}(q)$ shows a
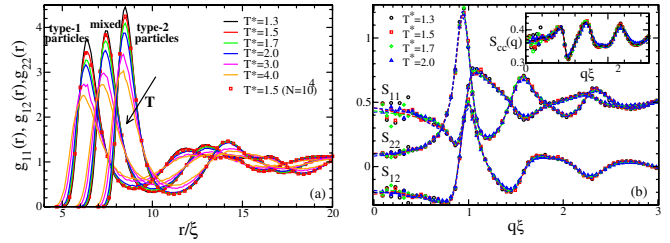

FIG. 1 (color online). Evolution in the supercooled regime, upon decreasing T, of: (a) partial radial distribution functions $g_{11}(r)$, $g_{12}(r)$ and $g_{22}(r)$. The perfect agreement between two different simulation sizes, i.e., $N = 10^3$ (lines) and $N = 10^4$ (symbols), provides evidence that results are equilibrated, reproducible and not phase separating; (b) partial static structure factors $S_{ij}(q)$, as well as $S_{cc}(q)$ [35] which rules out the presence of a demixing transition. Symbols are results for simulations with $N = 10^4$ particles, lines are splined curves.

consistent upturn at low q, again a manifestation of the smaller repulsion experienced by the type-1 particles with respect to the type-2 particles. Indeed, such feature is less evident for S_{12} while it is absent for S_{22}. To rule out the possibility that a phase separation process interferes with the dynamical slowing down, we have monitored the time dependence of $S_{11}(q)$ and visually inspected the configurations, both observations providing evidence against this putative process. Moreover, upon further decrease of T, the low-q amplitude of $S_{11}(q)$ saturates to a constant value. The concentration-concentration structure factor $S_{cc}(q)$ [35], [shown in the inset of Fig. 1(b)] does not display any increase at low q, ruling out the possibility of a demixing transition. Results for the structural properties $g_{ij}(r)$ and $S_{ij}(q)$ for the larger system size, also shown in Fig. 1, are identical to those of the smaller system.

Having demonstrated that our system shows stable structural behavior, we next turn to investigate the dynamical behavior. In Fig. 2(a) we show the decay of the self autocorrelation function of the density of type-1 particles, $\phi_1^s(q, t)$ close to the first peak of the structure factor. Strikingly, the behavior observed is qualitatively similar to that seen in the familiar *dense* systems containing a harsh repulsive core. In particular, the dynamics slows down by several orders of magnitude, giving rise to a typical two-step decay, in which the final relaxation is of stretched exponential form. Hence, the formation of a wide, soft cage around each particle arises, due to the *long-range* repulsive interactions of different strengths.

In Fig. 2(b) we test time-temperature superposition (TTS) via rescaling $\phi_1^s(q, t)$ by the (T-dependent) α-relaxation time. For all $\phi_1^s(q, t)$ showing a two-step decay TTS holds down to $T^* = 1.7$. For $T^* \lesssim 1.7$ the plateau height changes significantly, leading to a clear breakdown of TTS. In the same T range, aging effects can be observed, namely, extremely slow drifts of the energy as well as dependence of the dynamical variables of the initial observation times.
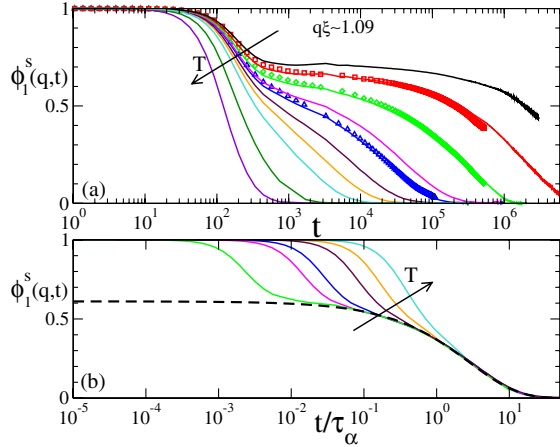
FIG. 2 (color online). Self autocorrelation function for the density of type-1 particles $\phi_1^s(q, t)$ at $q\xi \simeq 1.09$: (a) T dependence (from left to right: $T^* = 10, 5, 3, 2.5, 2.25, 2, 1.9, 1.7, 1.5, 1.3$) and (b) TTS scaling only in the temperature range $1.7 \lesssim T^* \lesssim 3$. The dashed line is a stretched exponential fit of the master curve with stretching exponent $\beta \sim 0.65$. In (a) data for the larger simulation size (symbols) are also reported. Below $T_c^* = 1.7$ the system shows a clear aging behavior, as well as a breakdown of TTS due to the increase in the plateau height. For type-2 particles, a similar, albeit slower dynamics (due to the larger repulsion amplitude), occurs.

We also study the mean squared displacement $\langle r_1^2(t) \rangle$ as a function of T^*. It shows the typical development of a long intermediate plateau, indicative of a dynamical slowing down (see Fig. 3). The magnitude of the plateau is quite high, larger than ξ. The extracted diffusion coefficient D, evaluated from the long time limit of the MSD, is reported in the inset. Power-law fits to $D \sim |T^* - T_c^*|^{\gamma_D}$ provide a method to estimate an effective "mode-coupling temperature" of $T_c^* = 1.7$, although the extracted exponent $\gamma_D = 1.45$ is smaller than the lowest limit set by MCT [25].

Below T_c^*, we observe clear deviations from the power-law behavior suggesting that hopping processes are particularly relevant due the softness of the repulsive cages. A further evidence of a change in the dynamics around T_c^* is the fact that the plateau height, which can be operatively defined as the inflection point of log(MSD) vs log(t), significantly decreases for $T^* < 1.7$.

An interesting aspect of the MCT predictions [23] is that the two-step relaxation is maintained even as structural correlations induced by Coulomb repulsion are diminished due to dilution effects. In particular, the Debye-Waller factors, $f_q^j = \lim_{t\to\infty} \phi^{jj}(q, t)/S_{jj}(q)$ [where $\phi^{ij}(q, t)$ is the collective intermediate scattering function] for both species are expected to show weak oscillations as a function of q that become still weaker for lower density, until oscillations are not observable [23]. While we could not access this ultra-low-density limit, the Debye-Waller factors extracted from our simulations displayed in Fig. 4 show the precursor of this behavior. Indeed, the simulation data show weaker oscillations in f_q^j, as compared to that seen at T_c^* for the standard Kob-Andersen Lennard-Jones (KA) mixture [36,37]. Two other features are noteworthy in the context of this comparison. First, the range of wave vectors over which caging is present is much smaller than in standard high-density systems such as the KA mixture. The small q values are reflective of caging at long length scales induced by the soft long-ranged potential. Second, $f_q^j \to 1$ for $q \to 0$. This behavior is in contrast to that seen for the majority species in the KA mixture [37], and might result from the relatively large compressibility of the system on these length scales [13]. It should be noted that both features are found in other soft materials such as colloidal gels [38].
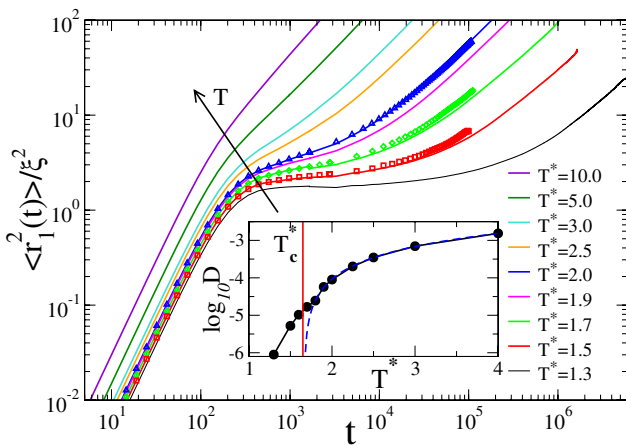

FIG. 3 (color online). $\langle r_1^2(t) \rangle$ for type-1 particles with decreasing T^*. Lines and symbols refer, respectively, to simulations with $N = 10^3$ and $N = 10^4$ particles. Inset: Power-law fit to the diffusion coefficient D, with exponent $\gamma_D = 1.45$ and $T_c^* \simeq 1.67$.
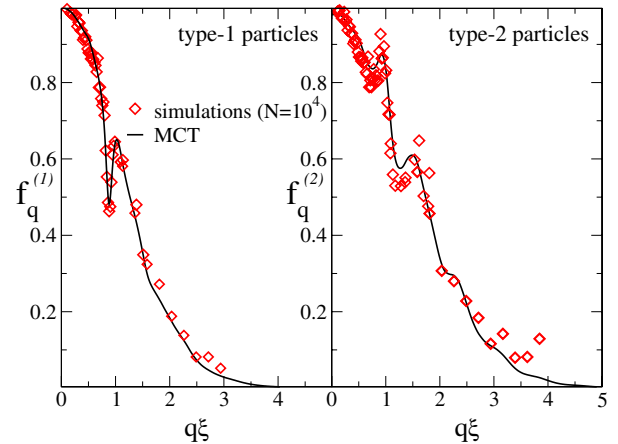

FIG. 4 (color online). Debye-Waller factors from simulations extracted from stretched exponential fits (symbols) and from MCT calculations (lines) for type-1 (left) and type-2 (right) particles, respectively. The simulation temperature is $T^* = 2.0$, while for MCT calculations we report results at the critical temperature $T_{MCT}^* = 2.81$.

We also calculated f_q^j directly from MCT using the numerical structure factors from Fig. 1. Critical MCT Debye-Waller factors are also reported in Fig. 4 and they are compared to the ones calculated from fitting the numerical correlators for $T^* \geq T_c^*$. The agreement is remarkable, quantitatively matching all of the notable features exposed via direct MD simulation.

Data presented in the previous figures show that a MCT description of the dynamics can be applied for $T^* > T_c^*$ and that the qualitative relaxation behavior is of the usual ''type-B'' variety [25], in agreement with the predictions of Bosse and Wilke [23,24]. While we postpone a detailed exposition for a future publication, it should be noted that features such the violation of the Stokes-Einstein relation, the growth of the non-Gaussian parameter and multipoint dynamical susceptibilities also occur in our simulated system. These features become prominent close to T_c^* and behave in a manner similar to that found in standard glass-forming systems.

In conclusion, we have clearly demonstrated the existence of a stable classical Wigner glass state in a model of low-density charged particles, which is independent of competing processes such as crystallization or phase separation. The low-density soft glass studied here exhibits significant differences from the high-density hard-sphere glass. Most dramatically, we recall a much larger localization length, which manifests itself both in the MSD plateau as well as in the width of the Debye-Waller factors. Despite these differences, several important aspects of the dynamics can be successfully described by MCT. On the other hand, deviations from hard-sphere behavior and from MCT predictions, in particular, a small value of the power-law exponent for the diffusion constant as well as clear indications of activated processes, facilitated by the softness of the potential, are also observed. The possibility of reentrant relaxation emanating from an interplay of hard-core and long-ranged repulsion has not been explored in this work, and will be the subject of future investigation.

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