Jamming phase diagram of colloidal dispersions by molecular dynamics simulations

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We report a three-dimensional jamming phase diagram of a model colloidal system obtained from molecular dynamics simulations where the inter-colloidal forces are represented by the Derjaguin–Landau–Verwey–Overbeek potential. The jamming threshold is uniquely defined in terms of the critical volume fraction, the critical temperature, and the critical yield stress. The simulation results indicate that near the jamming transition the shear viscosity diverges following a critical-like scaling law as observed for realistic colloids. These results offer a convincing proof for unifying different nonequilibrium transitions in colloids under the concepts of jamming.

Under a wide variety of conditions, colloids and other soft-matter systems solidify without the formation of a crystalline order for reasons that appear quite unrelated to each other. Phrases such as gelation, coagulation, kinetic arrest, dynamic slowdown, and ergodic-nonergodic transition have been used to loosely describe the solidification phenomena. The resulted long-lived, but nonequilibrium fragile materials are of profound practical importance, being relevant to paint, pharmaceutical, food, and numerous other industries. The formation of amorphous materials rather than crystalline solids is sometimes undesirable, especially during the crystallization of the proteins in solution or in the fabrication of ordered nano-structures by self-assembly. However, prediction of the experimental conditions leading to desired ordered/disordered structures has been very difficult due to the lack of a clear understanding of the control parameters. Unifying a framework to describe the phase behavior of various nonequilibrium states could be of immense importance.

The off-equilibrium solidifications in colloids are characterized by the sudden arrest of the dynamics of the constituent particles. In addition, all these transitions show kinetic heterogeneities near the onset of solidification where the particle mobilities become heterogeneous in space and intermittent in time. These general observations led Liu and Nagel to conjecture that different transitions due to the attractive van der Waals interaction in our system is modeled by the (1/r^6) potential, but in real colloidal systems the attraction is much shorter ranged and sharply diminishing. Second, the repulsive interaction is not essential to maintain the stability of the model system. In other words, the van der Waals attraction alone as shown in Eq. (1) is insufficient to cause colloidal aggregations. Because of these differences, a quantitative agreement between simulation and experiments is not anticipated. However, we expect that the jamming transitions in the model system should be qualitatively similar to those corresponding to experimental observations. Different from the potential models used in other simulation studies, the potential given by Eq. (1) has a long-ranged repulsion which suppresses a complete phase separa-
tion when the system is quenched into the coexistence region resulting in a nonequilibrium state. A potential that is purely attractive at long range, such as in the Lennard-Jones potential, has no mechanism to suppress the long-range fluctuations leading to the complete phase separation. Moreover, we believe that a long-ranged repulsive potential plays an important role in the slowing down dynamics of colloidal systems, especially at low volume fractions. In the jammed state, where the particles are kinetically trapped and the relative motion of colloidal particles and the suspending fluid are minimal, hydrodynamic interactions will not be of importance and can be safely ignored.

Microcanonical ensemble molecular dynamics simulations were performed for a system of 512 particles at different volume fractions and temperatures. The equations of motion were integrated using the velocity Verlet algorithm. Periodic boundary conditions were imposed in all three dimensions. Equilibration of the system was tested by monitoring the total energy and other quantities like the mean-squared displacement (MSD). When the total energy is a constant, and the MSD curves show no dependence on the initial time, the system is claimed equilibrium and the dynamic properties are then calculated. The central quantity of our study is the shear viscosity calculated using the Green–Kubo relation

$$\eta = \frac{1}{k_B T V} \int_0^\infty dt \langle J_v(0) J_v(t) \rangle,$$

where $k_B$ is the Boltzmann constant and $J_v$ is the momentum flux related to the particle momentum $p$, mass $m$, and inter-particle force $F_{ij}$

$$J_v = \sum_j \frac{p_j^x p_j^y}{m} + \sum_{i>j} r_{ij}^x F_{ij}^y.$$

In Eq. (3) $i$ and $j$ are the particle indices and $x$ and $y$ stand for the $x$ and $y$ components of momentum and force.

Figure 1(a) shows the shear viscosity plotted against $1/T$ at different volume fractions of colloidal particles. The shear viscosity diverges as the transition temperature is approached and it follows a power-law behavior of the form

$$\eta = \eta_s (1/T_c - 1/T)^{-\nu_\eta}.$$

We found that the exponent $\nu_\eta = 0.155$ by best fitting of the simulations results. For jamming phase diagram of polystyrene dispersions, Trappe et al. reported $\nu_\eta = 0.13$ which agrees well with the simulation results. Using the value of $T_c$ obtained by fitting the simulation results to Eq. (4) at different
ent volume fractions, we were able to get the jamming phase diagram at zero applied stress as shown in Fig. 1(b).

The third dimension of the jamming phase diagram is defined by the applied stress, which affects the formation of the solid network spanning the system. An increase in the applied stress causes the jammed systems to yield and flow and thereby shift the value of \( \phi_c \) toward higher values and \( T_c \) toward lower values. In order to find the dependence of \( \phi_c \) and \( T_c \) on the applied stress, we carried out NPTensemble molecular dynamics simulations where the number of particles (\( N \)), pressure (\( P \)), and temperature (\( T \)) are fixed. A shear stress is applied by introducing nonzero off-diagonal elements in the pressure tensor. The behavior of shear viscosity is monitored at different applied stresses. This enabled us to calculate the yield stress at different volume fractions and also at different temperatures. The dependence of the yield stress, \( \sigma_y \), on volume fraction, \( \phi \), and temperature, \( T \), are also well described by critical-like behavior

\[
\sigma_y = \sigma_0 (\phi - \phi_c)^{\mu_\phi},
\]

\[
\sigma_y = \sigma_T (1/T - 1/T_c)^{\mu_T}.
\]

By fitting the simulation results as shown in Figs. 2(a) and 2(b), we obtained the values of the exponents \( \mu_\phi = 0.66 \) and \( \mu_T = 0.93 \). These exponents are different from those reported by Trappe et al. (\( \mu_\phi = 3.4 \) and \( \mu_T = 2.4 \)).

Figure 3 shows the full three-dimensional jamming phase diagram. The overall shape and behavior is similar to that obtained in the experiments. The simulation results support the concept of jamming and the existence of a jamming phase diagram in the case of attractive colloids. As observed in experiments, the shape of the surface separating the jammed and unjammed states is concave everywhere in contrast to the original proposal of jamming phase diagram by Liu and Nagel.14

To summarize, the results from molecular dynamic simulations confirm the existence of a jamming phase diagram in colloidal systems. The dynamical properties follow a critical-type behavior during the jamming transition.

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