Local crystalline order in a 2D colloidal glass former

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Abstract. A mixture of two types of super-paramagnetic colloidal particles with long-range dipolar interaction is confined by gravity to a flat interface of a hanging water droplet. The particles are observed by video microscopy and the dipolar interaction strength is controlled by an external magnetic field. The local structure as obtained by pair correlation functions and bond order statistics is investigated as a function of system temperature and relative concentration. Although the system has no long-range order and exhibits glassy dynamics, different types of stable crystallites coexist. The local order of the globally disordered structure is explained by a small set of specific crystal structures. The statistics of crystal unit cells show a continuous increase of local order with decreasing system temperature as well as a dependence on sample history and local composition.

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1 Introduction

Many systems show a dynamic arrest as revealed by a drastic increase of viscosity. This phenomenon of kinetic vitrification may take place even when a phase transition into a long-range ordered state is possible and eventually may occur under appropriate conditions; examples are monodisperse hard spheres [1], semicrystalline stacks of lamellar crystals in polymers [2] or binary mixtures in metal alloys [3].

It appears obvious that disordered structure and dynamics are related. One example for a close formal connection between structure and dynamics of a glass-forming system is provided by Mode Coupling Theory (MCT), since the only input into the MCT equations is the static structure factor [4, 5]. Nevertheless, the microscopic connection between structure and dynamics is still under strong debate [6–8], especially the question how crystallization is connected to vitrification and dynamical heterogeneity [9, 10]. Simulations [10] suggest that crystallization plays a key role for the glass transition. The authors propose that “liquids tend to order into the equilibrium crystal, but frustration effects of locally favored short-range ordering on long-range crystalline ordering prevent crystallization and help vitrification”.

It was found in experiments [11], simulations [12], and theory [13] that glassy systems in 2D exhibit the full range of glass phenomenology known in three-dimensional glass formers, both in dynamics and structure. However, in experiments, glassy behavior in two dimensions is only possible by introducing polydispersity [13]. The simplest form of polydispersity is that of a binary system, which may of course also turn into binary crystal structures.

In experiments, colloidal glasses have the advantage over atomic systems that, besides statistical averaged information about the local structure, “quasi-atomic” resolution is provided by microscopy [6, 11].

The binary colloidal 2D system investigated here consists of a mixture of particles with two different magnetic moments. It exhibits all typical phenomenological features of a glass former, e.g. drastic increase of relaxation times for increasing interaction strength, no long-range order, and dynamic heterogeneities [11]. The dynamics of the system was compared with MCT and good agreement was found [13]. Partial clustering of small particles was observed [14, 15] due to the nonadditivity of the dipolar binary potential. This leads to a heterogeneous distribution of particle composition, which results locally in a coexisting variety of small areas with different underlying crystal structures. Thus, heterogenous distribution of small particles suppresses long-range order. Extended stable crystal structures for 2D binary dipoles were found in $T = 0$ lattice sum calculations [16, 17]. Especially all locally ordered structures discussed in this paper were predicted to be stable.

The idea that the disordered structure of this system is made up from particular substructures (triangular structures) was originally discussed in [18]. However, in this paper we suggest that the local ordered structure originates from the tendency of the binary mixture towards crystallization.
Crystallization may be geometrically possible, provided the relative concentration matches a certain crystal structure. However, crystallization is not at odds with a glass transition in a binary system. A decrease in temperature can force a system into a dynamically arrested state due to strong increase of viscosity before crystallization can establish long-range order. Since the small particles cannot reorganize fast enough, much disorder is “frozen” in. As a consequence different competing crystalline structures appear, while the global structure remains amorphous.

2 Experimental setup

Our experimental setup consists of a mixture of two different kinds of spherical and super-paramagnetic colloidal particles (species A: diameter \( d_A = 4.5 \mu m \), susceptibility \( \chi_A = 6.22 \cdot 10^{-11} \text{Am}^2/\text{T} \), density \( \rho_A = 1.5 \text{g/cm}^3 \) and species B: \( d_B = 2.8 \mu m \), \( \chi_B = 6.6 \cdot 10^{-12} \text{Am}^2/\text{T} \), \( \rho_B = 1.3 \text{g/cm}^3 \)) which are confined by gravity to a water/air interface. This interface is formed by a water drop suspended by surface tension in a top sealed cylindrical hole (6 mm diameter, 1 mm depth) of a glass plate as sketched in Figure 1. A magnetic field \( \mathbf{H} \) is applied perpendicular to the water/air interface inducing a magnetic moment \( \mathbf{m} = \chi \mathbf{H} \) in each particle leading to a repulsive dipole-dipole interaction. Counterpart of the potential energy is thermal energy which generates Brownian motion. Thus the dimensionless interaction strength \( \Gamma \) is defined by the ratio of the potential versus thermal energy:

\[
\Gamma = \frac{E_{\text{magn}}}{k_B T} \propto \frac{1}{T_{\text{sys}}}
\]

\[
= \frac{\mu_0}{4\pi} \frac{\mathbf{H}^2 \cdot (\pi \rho)^{3/2}}{k_B T} (\xi \cdot \chi_B + (1 - \xi) \chi_A)^2. \quad (1)
\]

Here, \( \xi = N_B/(N_A + N_B) \) is the relative concentration of small species with \( N_A \) big and \( N_B \) small particles and \( \rho \) is the area density of all particles. The average distance of neighboring big particles is given by \( l = 1/\sqrt{\rho_{bg}} \). The interaction strength can be externally controlled by means of the magnetic field \( H \). \( \Gamma \) can be interpreted as an inverse temperature and controls the behavior of the system.

The ensemble of particles is visualized with video microscopy from below and the signal of a CCD 8-Bit grayscale camera is analyzed on a computer. The field of view has a size of \( 1158 \times 865 \mu m^2 \) containing typically \( 3 \cdot 10^9 \) particles, whereas the whole sample contains about up to \( 10^9 \) particles. Standard image processing is performed to get size, number and positions of the colloids. A computer controlled syringe driven by a micro-stage controls the volume of the droplet to get a completely flat surface. In this way fluctuations around the set-point of particle density are suppressed below 0.1% and the biggest observed particle-density gradient in the horizontal plane is less than 1%. The latter is achieved by a variation of the inclination of the whole experimental setup. This inclination is also controlled actively by micro-stages with a resolution of \( \approx 1 \mu \text{rad} \). After several weeks of adjusting and equilibration this provides best equilibrium conditions for long-time stability. During data acquisition the images are analyzed with a frame rate down to 250 ms. Trajectories for all particles in the field of view can be recorded over several days providing the whole phase space information. The thermal activated out-of-plane motion of the colloids is in the range of a few tenth of nm so the ensemble can be considered as ideally two-dimensional.

3 Local order

Adding small particles prevents global crystallization of the system. As the susceptibility of the small particles is roughly ten times smaller compared to that of the big ones the local structure is dominated by the latter. This is demonstrated in Figure 2 where the Voronoi cells of the big particles (small particles are ignored) are shown for two different interaction strengths \( \Gamma \). Increasing \( \Gamma \), the small particles are forced into the potential dips formed by the big particles. The Voronoi vertices of the big and the positions of the small particles are highly correlated. In Figure 3 the probability distribution of distances \( d \) of the small particle to its next Voronoi vertex are shown for various temperatures. One sees that for increasing interaction strength the small particles are progressively pinned to the potential minima between the big ones. The deviation from a Gaussian distribution at higher interaction