Partial clustering prevents global crystallization in a binary 2D colloidal glass former

F. Ebert, G. Maret, and P. Keim
Fachbereich für Physik, Universität Konstanz, D-78457 Konstanz, Germany

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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 the flat interface of a hanging water droplet. The particles are observed by video microscopy and the dipolar interaction strength is controlled via an external magnetic field. The system is a model system to study the glass transition in 2D, and it exhibits partial clustering of the small particles (N. Hoffmann et al., Phys. Rev. Lett. 97, 078301 (2006)). This clustering is strongly dependent on the relative concentration $\xi$ of big and small particles. However, changing the interaction strength $\Gamma$ reveals that the clustering does not depend on the interaction strength. The partial clustering scenario is quantified using Minkowski functionals and partial structure factors. Evidence that partial clustering prevents global crystallization is discussed.

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1 Influence of dimensionality on frustration

It is well known that the macroscopic behavior of crystallizing systems sensitively depends on dimensionality, as demonstrated by two examples: In 2D an intermediate phase exists between fluid and crystal, the hexatic phase, where the system has no translational order while the orientational correlation is still long range [1–3]. Such a two-step melting scenario is not known in 3D. The Ising model for ferromagnetics shows a phase transition for 2D and 3D but not for 1D [4]. For amorphous systems, however, it was found in experiments [5], simulations [6], and theory [7] that the glass transition phenomenology is very similar in 2D and 3D systems, both in dynamics and structure [5,8].

A subtle difference, the local density optimization in 2D and 3D, is the following: in 3D the local density optimized structure of four spheres is obviously a tetrahedron. However, it is not possible to completely cover space in 3D with tetrahedra, because the angle between two planes of a tetrahedron is not a submultiple of 360° [9]. The density optimized state with long-range order is realized by the hexagonal closed-packed structure or other variants of the f.c.c. stacking with packing fraction $\phi = \pi/\sqrt{18} \approx 74\%$. The dynamical arrest in 3D is expected to be enhanced by this geometrical frustration, because the system has to rearrange its local-density optimized structure to reach long-range order. The local geometrical frustration scenario is different in 2D. There, the local-density optimized structure and densest long-range–ordered structure are identical, namely hexagonal. For the glass transition in 2D it is therefore expected that an increase of complexity is necessary to reach dynamical arrest without crystallization: in simulations an isotropic one-component 2D system has been observed undergoing dynamical arrest for an inter-particle potential that exhibits two length scales, a Lennard-Jones-Gauss potential with two minima [14]. Other simulations showed that systems of identical particles in 2D can vitrify if the mentioned local geometric frustration is created artificially via an anisotropic five-fold interaction potential [15]. Alternatively, the necessary complexity can be created by polydispersity as found in simulations [16].

A bi-disperse system in general is simple enough to crystallize as, e.g., seen from the rich variety of binary crystal structures in an oppositely charged 3D Coulomb mixture [17]. In the system at hand, partial clustering prevents the homogenous distribution of particles and the system crystallizes locally into that crystal structure which is closest in relative concentration [8,18,19]. In this way the system effectively lowers its energy with a compromise between minimization of particle transport and minimization of potential energy. However, that means that the resulting structure is not in equilibrium, but in a frustrated glassy state. This competition of local stable

\[\text{e-mail: peter.keim@uni-konstanz.de}\]

\[\text{1 It is found in 3D hard-sphere systems that this geometrical frustration alone is not sufficient to reach a glassy state as it cannot sufficiently suppress crystallization [10–12], and additionally polydispersity is needed [13].}\]
crystal structures prevents the relaxation into an energetically equilibrated state, i.e. a large mono-crystal.

It was found that a binary mixture of magnetic dipoles is a good model system of a 2D glass former [5] as the dynamics and structure show characteristic glassy behavior: when the interaction strength $\Gamma$ is increased, the system viscosity increases over several orders of magnitude while the global structure remains amorphous.

For all measured interaction strengths the system shows no long-range order as probed by bond order correlation functions [8]. However, on a local scale it reveals non-trivial ordering phenomena: partial clustering and local crystallinity.

Partial clustering [20,21] means that the small particles tend to form loose clusters while the big particles are homogeneously distributed. The heterogeneous concentration of small and big particles leads to a variety of local crystal structures when the system is supercooled making up the globally amorphous structure. This local crystallinity obviously plays a key role for the glass transition in this 2D colloidal system as it dominates the glassy structure [8]. Therefore, the phenomenon of partial clustering is indirectly responsible for the frustration towards the glassy state. In sect. 4 the details of the clustering scenario are explained. The dependence on the parameters accessible in experiment and the relation to local crystallinity [8] are discussed in sect. 5.

Firstly, the experimental setup is introduced. After a brief discussion about origin of partial clustering, a morphological analysis using Minkowski measures is presented to characterize and quantify the effect. Finally, the dependence on relevant parameters like the average relative concentration $\xi$ and the interaction strength $\Gamma$ will be discussed using Euler characteristics and the partial static structure factors.

2 Experimental setup

The detailed experimental setup is explained in [22]. It 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 $\chi_A = 7.4 \cdot 10^{-11}$ A m$^2$/T, density $\rho_A = 1.5 g/cm^3$ and species $B$: $d_B = 2.8 \mu m$, $\chi_B = 6.6 \cdot 10^{-12}$ A m$^2$/T, $\rho_B = 1.3 g/cm^3$) 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 fig. 1. A magnetic field $H$ is applied perpendicular to the water/air interface inducing a magnetic moment $M = \chi H$ in each particle leading to a repulsive dipole-dipole pair 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

$$\Gamma = \frac{E_{magn}}{k_B T} = \frac{1}{T_{sys}} = \frac{\mu_0}{4\pi} \frac{H^2 \cdot (r \rho)^{3/2}}{k_B T} (\xi \cdot \chi_B + (1 - \xi) \chi_A)^2. \tag{1}$$

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 $l_B = 1/\sqrt{\rho_B}$. 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 $1170 \times 870 \mu m^2$ containing typically $3 \cdot 10^5$ particles, whereas the whole sample contains about up to $10^5$ 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. The inclination is controlled actively by micro-stages with a resolution of $\alpha \approx 1 \mu rad$. After several weeks of adjusting and equilibration, this provides best equilibrium conditions for long-time stability. Trajectories for all particles in the field of view can be recorded over several days providing the whole phase space information.

3 Origin of partial clustering

The origin of the clustering phenomenon lies in the negative nonadditivity of the binary dipolar pair potential [20, 21]. It is not expected in positive nonadditive mixtures like colloid-polymer mixtures or additive mixtures like hard spheres. In binary mixtures with additive hard potentials in 2D, phase separation was found using Monte Carlo simulations [23]. In addition to the negative nonadditivity, the relation $v_{BB} < v_{AB} < v_{AA}$ of the pair potentials has to be fulfilled [20,21]. Why this leads to partial clustering can be understood as follows: The negative nonadditivity prevents macro-phase separation as the negativity of the nonadditivity parameter $\Delta = 2\sigma_{AB} - (\sigma_{AA} + \sigma_{BB})$ means that particles are effectively smaller in a mixed state ($\sigma_{ij} = \int_0^\infty dr \{1 - \exp(-v_{ij}(r)/k_B T)\}$ are the Barker-Henderson effective hard-core diameters). Thus, a mixed configuration is preferred this way. Additionally, the inequality $v_{AB} < v_{AA}$ energetically favors direct neighbor connections between different species instead of big particles being neighbors. In competition to this, the inequality $v_{BB} < v_{AB}$ favors the neighboring of small particles. The