Local particle rearrangements in a two-dimensional binary colloidal glass former

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Abstract. In a two-dimensional (2D) glass former composed of two kinds of different sized and repulsively interacting colloidal particles, the time-dependent particle positions were observed by video-microscopy. Analyzing the local particle arrangements by 3-point correlation functions, we find four different local density-optimized configurations of nearest neighboring particles, which we call elementary triangles (ET), one for each three-particle combination of small and big particles. These four ET form a random tiling in the 2D monolayer, which is not space filling. Therefore, a heterogeneous local particle packing does not have long-range order and shows structural frustrations. Furthermore, an analysis of structural relaxations, using triangles of nearest neighboring particles (TNNP) in the monolayer, suggests that hopping processes are the reason for the rearrangements of the particles. In the outlook, we propose a concept of local density-optimized crystallite-clusters to describe the glass transition as a percolation of stable local density-optimized triangles.

In supercooled liquids the particle dynamics of mean-square displacements can be classified in three time zones. For the short-time dynamics the particles diffuse like free ones. In the intermediate time region the particles are captured by their surrounded neighbors for a while, like in a cage, until in the long-time zone structural relaxations allow the particles to escape their vicinity. For decreasing temperatures, such cages become stronger and remain visible longer, as the system solidifies at the glass transition temperature due to the cage-effect becoming the stable state. Considering the short-range order in supercooled liquids by pair-distribution functions (PDF), the local packing becomes better structured for decreasing temperatures while at the glass transition temperature no discontinuous changes occur. This is why a glassy state can be considered as a supercooled melt, forming a solid with liquid-like structure and with frozen-in particle dynamics [1], [2], [3].

Up to now no theory is able to describe the properties of glass formers or to figure out the interconnection between the microscopic particle dynamics and the local particle configurations. But, undoubtedly, the cage-effect and structural relaxations are clearly related to the local microscopic structure. Therefore, in our opinion, the glass transition can only be understood if the interplay between the microscopic dynamics and the local particle configurations in the amorphous structure is recognized.

In this work, novel microscopic structural analyses are introduced which try to combine the local particle arrangements with the dynamics of the local structure. Therefore, in a binary 2D colloidal glass former of known time-dependent particle positions, the structure of triangles of nearest neighboring particles and their time-dependent changes have been analyzed simultaneously.

EXPERIMENT

Time-dependent particle positions of a 2D binary colloidal suspension of repulsively interacting paramagnetic PMMA colloids were directly observed by video-microscopy. The particles lay on a completely flat adjusted water-air interface of hanging droplet geometry, confined due to gravity. In the monolayer, the big (b) and small (s) colloids interacted with their induced magnetic moments, tunable by an external magnetic field B_{ext}.

During the measurements, the particle area density, ρ, the ratio, $\xi = n_s/(n_s + n_b)$, of the number n_s of s particles to the number of all colloids $n_s + n_b$, the room temperature, T, as well as the magnetic susceptibilities χ_b and χ_s of the b and s colloids remain constant. Therefore, the strength of the particle repulsion can be controlled via B_{ext}. Because of the experimental conditions, other in-plane particle interaction potentials can be neglected.

The 2D system is characterized by a dimensionless interaction parameter, $\Gamma(B_{ext})$, which is the magnetic energy E_{magn} divided by the thermal energy $k_B T$. Thus, Γ corresponds to an inverse effective system temperature, T_{sys}, tuneable by B_{ext}. The full form of Γ is given by:

$$\Gamma = \frac{E_{magn}}{k_B T} = \frac{\mu_0 \sqrt{\pi}}{4} \frac{B_{ext}^2 \rho^{3/2}}{k_B T} \left(\xi \chi_s + (1-\xi)\chi_b \right)^2 . \quad (1)$$

More details of the experiment are presented in this issue [4]. There it is also shown that the investigated 2D system behaves like a glass former. Additionally, we have to point out that Zahn and Maret have used the same 2D setup (but using monodisperse colloidal suspensions) as model system for studying the 2D melting scenario of Kosterlitz and Thouless [5].

MICROSCOPIC STRUCTURE

Up to now, microscopic amorphous 2D structures were mainly investigated by the Voronoi construction [1], which divides the area into cells around each particle, or by bond-order parameter methods [6], which characterize the orientational structure by an order parameter. In this work, a novel microscopic structure analysis is introduced: We investigate the structural and dynamical properties of our colloidal model system by analyzing triangles of nearest neighboring particles (TNNP) which are defined as the smallest area units of the local microscopic particle arrangements in the binary 2D sample. Such analysis is not common since we no longer consider properties of single particles or pair-distances, but triangles.

In the first step, we are interested in the local density-optimized packing of the particles investigating a highly supercooled 2D binary monolayer, i.e. of well-defined short-range order. Therefore we use 3-point correlation functions (3-PCF) and define the distances of the two fixed s or b particles in a narrow interval around the first peak of their corresponding partial PDF. This determination definitely guarantees pairs of nearest neighbors. All such pairs in the monolayer are transformed on the x-axis of a new coordinate system. Additionally, in the 3-PCF all s and b third particles are plotted on top of each other lying in a given region, which is aligned to the position of the two fixed particles in the monolayer (see Fig. 1).

In the 3-PCF, around both fixed particles there is first a zone with no particles followed by a ring of s (blue) and then of b colloids (red) with high particle probabilities (Fig. 1). The ring-radii correspond to the first maximum positions of the PDF of the corresponding pair-combination. At the point of intersection for the two rings of the same kind of colloids, an accumulation point is seen where particles are simultaneously nearest neighbors of both fixed particles. Hence, the local density-optimized packing of each of the four different 3-particle combinations of b and s colloids (bbb, bbs, bss, sss) can be read off from the isosceles triangles in Fig. 1. Thus, for each of the four 3-particle combinations of b and s particles exactly one local density-optimized triangular structure can be found. These triangles we call elementary triangles (ET). For the bbb and sss 3-particle combi-
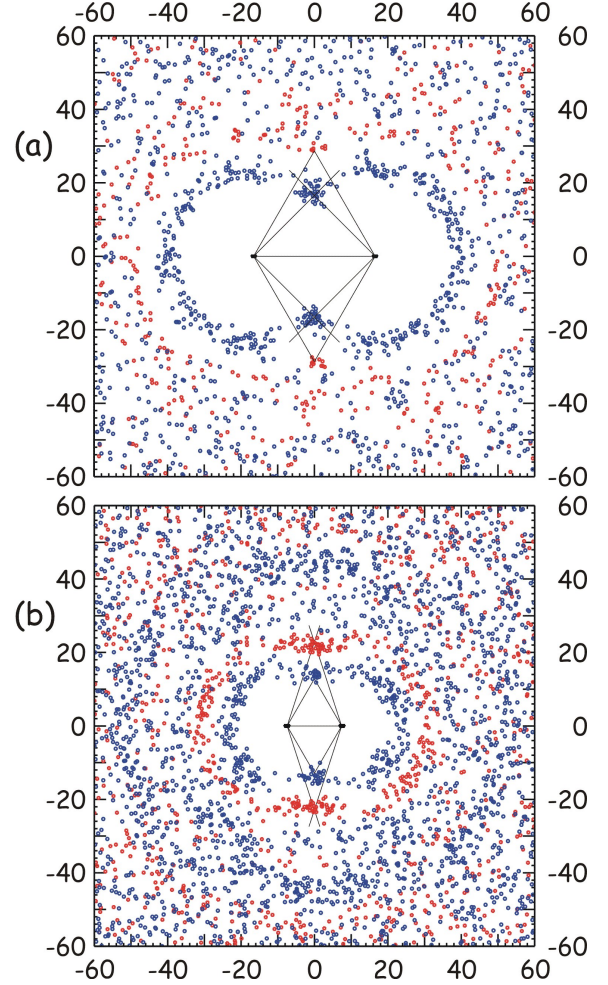

FIGURE 1. 3-point correlation functions for (a) two b or (b) two s colloids fixed at the first maximum of the corresponding partial PDF, sitting symmetrically around the origin on the x-axis. The units are μm. (a) The two fixed b colloids have distances in the interval $[32\mu m, 34\mu m]$. (b) The two fixed s colloids have distances in the interval $[14\mu m, 16\mu m]$. The elementary triangles are indicated by solid lines. Black: The two fixed particles; Red: b colloids; Blue: s colloids. $\Gamma = 411$, $\xi = 0.7$, $\rho = 2.34 \cdot 10^{-3} \mu m^{-2}$, $B_{ext} = 7mT$.

nations the ET are equilateral or hexagonal, the bbs ET are rectangular and the bss ET have a 36° angle near the b particle. Nevertheless, the particles undergo thermal fluctuations while in reality the TNNP of the monolayer deviate from the shape of the idealized ET, seen in Fig. 1. However, if the shape of a TNNP is comparable with that of the corresponding ET we call it ET-like TNNP.

Since in Fig. 1 neither orientational order nor any long-range order is seen, the 2D sample is amorphous although ET are present. By simple arguments the apparent contradiction of global disorder and local order can be solved as follows.
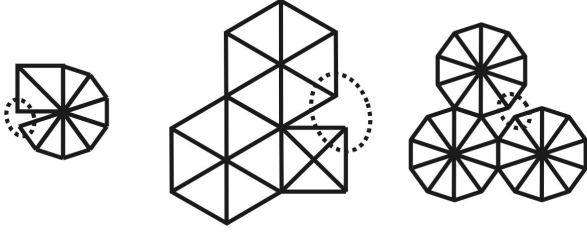
FIGURE 2. Structural frustration in near-zone for the tiling of ET. In the examples shown the tiling produce forbidden *ss* and *bb* pair-distances because they are shorter than the first maximum distances of the corresponding partial PDF.
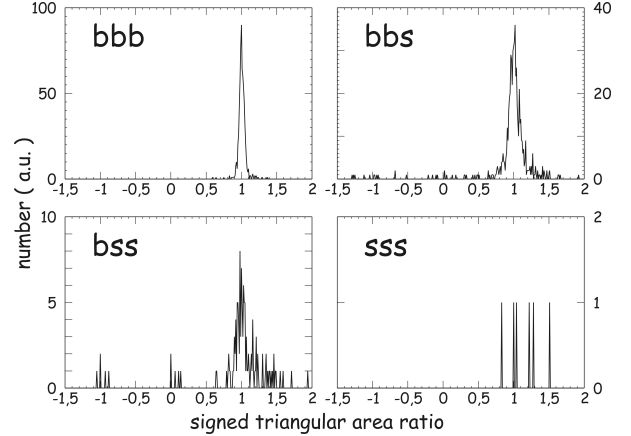

FIGURE 3. Triangle-area ratio for $\Delta t = 3600s$, separated in the different 3-particle combinations. $\Gamma = 142$, $\xi = 0.28$, $\rho = 2.62 \cdot 10^{-3} \mu m^{-2}$, $B_{ext} = 1.9mT$.

The reason for the amorphous structure is that the microscopic particle distribution of the *b* and *s* colloids locally varies in the 2D sample. Thus, the different ET-like TNNP lie side by side in the monolayer and tend to form clusters without structural mismatch. We call such clusters of the same ET 'crystallite clusters' (CC) and of different ET 'multi crystallite cluster' (MCC). However, the mixed tiling of the different ET-like TNNP cannot cover the monolayer without structural frustrations of the local structure (Fig. 2). At that places the repulsive particle interaction bents the shape of the TNNP in the monolayer. Therefore, structural frustrations are responsible for broadened peaks of the short-range order in the partial PDF. Also, the increasing number of possible mixed tilings of ET for increasing interparticle distances lead to the loss of long-range order.

It can be shown [7] that for decreasing system temperature the accumulation points in 3-PCF become less sharp and the TNNP gets more ET-like. This means that the microscopic particle configurations become more ordered as well as more densely packed, which simultaneously corresponds to a slow-down of the particle dynamics displacements and to more pronounced heterogeneous relaxations.

HETEROGENEOUS STRUCTURAL DYNAMICS

In the 2D binary colloidal suspension the TNNP can directly be distinguished in the monolayer by construction rules which are reported in detail in [7], [8]. For the following it is important to note that investigations of the structural dynamics, using the angles, the area or the edges of the TNNP, are independent of the translation or the rotation of the TNNP in the monolayer.

Here, we introduce a new function, called triangular area ratio (TAR), in order to investigate a special structural relaxation process in 2D, the hopping process. We store the particles of each of the N TNNP in the monolayer on the condition that the initial area $F_i(0)$ of each

TNNP with the number i in the first data file ($t = 0s$), which is calculated by vector product between the particle bond vectors, is defined positively. After the time Δt the area $F_i(\Delta t)$ is calculated once again. Dividing the final through the initial area of each TNNP and plotting this ratio $F_i(\Delta t)/F_i(0)$ in a histogram, one obtains the TAR for the four different 3-particle combinations, shown in Fig. 3.

The peaks in Fig. 3 can be interpreted as follows. The peak around 1 represents the TNNP, which have not significantly changed their area during Δt. If the peak around 1 is sharp for a special 3-particle combination, the structure has remained stable. However the peak at -1 for *bbs* and *bss* TNNP represents triangles with the same area, but with opposite direction of the particle arrangement. This peak indicates triangles which we call hopping triangles. There, during the time interval Δt, the hopping particle of such a TNNP has passed through between two neighboring particles, and thus it has changed its neighborhood. Since the final hopping triangle conserves the 3-particle combination, its area as well as its structure are expected to be the same as before. That is why the hopping particle would also give a second peak in the van Hove-function [2], [9] which one uses for the characterization of hopping processes. Because not only the hopping triangle but also the TNNP, which are built up by the hopping particle, typically have a TAR-value unequal to 1 in Δt. We call such TNNP 'hopping connected triangles'. From them there are signals in TAR around zero for aligned particles and somewhere in the positive range for TNNP of the same direction of the particle arrangement. More details can be found in [7] and will be published elsewhere.

Analyzing the TAR of Fig. 3, the following conclusions can be drawn about the structural dynamics of the

different 3-particle combination in Δt. The *bbb* TNNP are the most stable structures. Hopping processes are found for *bbs* and *bss* TNNP. The very low number of *sss* TNNP show no hopping process, but their structure fluctuates strongly. For the sake of completeness it should be remarked that the time period Δt beyond which hopping processes can be observed corresponds to the time range where the cage-effect in the 2D sample starts to crumble [7], [8]. Furthermore, it is also possible to analyze the hopping process directly in the monolayer.

Since hopping processes need less densely packed regions, the reverse statement is allowed that particles which are surrounded by only local density-optimized ET, undergo a 'perfect cage-effect'. Therefore there is, as we say, a 'blocking effect' for microscopic structural dynamics which is why also in fast regions of a monolayer, perfectly captured particles can only follow their neighbors.

CONCLUSIONS

In this paper, the statical structure and the dynamics of the microscopic particle configurations of a binary 2D colloidal suspension are analyzed by means of 3-PCF and of TNNP. Several new conclusions are drawn: First, the amorphous structure of the investigated 2D glass formers can be described by four different idealized ET and structural frustration. Secondly, hopping processes in the 2D sample are responsible for the structural relaxations of the TNNP. The special feature of the TNNP analyses by their areas or their angles is that the translation or rotation of the triangles themselves in the monolayer are ignored. This is why only the microscopic structural relaxations of the triangles are considered.

OUTLOOK

In the free volume theory the idea of 'solid-like' and 'liquid-like' regions and of a percolation, in order to explain the glass transition, has been mentioned more than 40 years ago [10], [11], [12]. Against this background, our new description of the glass transition should shortly be introduced here, which we call concept of local density-optimized crystallite clusters (CLDOCC). Those considerations base on structural and time-dependent analysis of TNNP in the monolayer and allow for the first time to distinguish the dynamics of 2D structures microscopically. Therefore, not single particles but TNNP are in the center of interest.

CLDOCC treats the glass transition as a percolation of the different ET-like TNNP to one big MCC. There, the solidification occurs because different ET-like TNNP sta-bilize each other by the blocking effect of local density-optimized packed particles. In between the connected crystallite clusters less densely packed, spatially separated, and structurally frustrated regions with frozen-in structural relaxations are found. That is why relaxation processes cannot happen in a glassy state any more.

In another paper of this issue [4], where the same 2D binary colloidal suspension is considered, additional aspects of the local and dynamical investigations of the microscopic particle configurations are presented which confirm the idea of CLDOCC. Nevertheless, further analysis is necessary.

In future the predictions of the CLDOCC has to be checked in other experiments. Since the considerations of the microscopic structural dynamics do not involve restriction on the dimension or the mixture of different kinds of particles these ideas can easily be treated also for samples in 3D, of more component systems or with other particle interactions. In 3D, however, the ET have to be transformed into elementary tetrahedrons representing the local density-optimized packing of four particles.

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