Eur. Phys. J. Special Topics **141**, 277–280 (2007)

DOI: 10.1140/epjst/e2007-00053-7

THE EUROPEAN PHYSICAL JOURNAL
SPECIAL TOPICS

Temperature-dependent investigations of locally observed particle configurations in a binary 2D colloidal glass former

H. König[1]

[1] Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany
Institut für Physik, Johannes Gutenberg-Universität, 55099 Mainz, Germany
Present address: System Electric Power Quality GmbH, 63589 Linsengericht, Germany

Abstract. In a binary two-dimensional (2D) colloidal glass former of repulsive interaction, the experimentally observed local particle configurations are studied by the shapes of triangles of nearest neighboring particles (TNNP). Higher order peaks of the partial radial pair distribution functions, which become well-pronounced in strongly supercooled liquids or the glassy state, can be related to local density-optimized particle arrangements of the TNNP. An intriguing interplay is observed between local density-optimized and structurally frustrated regions. It seems that binary 2D glass formers could be excellent model glass formers showing characteristic structural features of normal and supercooled liquids as well as of the glassy state in a simple way.

1 Introduction

For high enough cooling rates nearly all liquids solidify in a glassy state. Thus, a huge number of different glass formers is known consisting of completely different components and bound by almost all possible particle interactions. All of these glass formers are characterized by common static and dynamic features [1,2]. Although or because of the huge variety of different glass formers, no theory or no empirical model could describe the glass transition consistently [3,4].

In supercooled liquids, heterogeneous dynamics strengthen and hopping comes up for decreasing temperature as we know from simulations [5,6] or from microscopically measured relaxation processes in colloidal suspensions [7,8]. Although dynamics dramatically change at the glass transition because the cage effect becomes stable, no abrupt change of local particle configurations happens. But, local relaxation processes are ruled by the amorphous particle configurations since they are responsible for the stability of the cages around each particle.

Before the relation between local particle arrangements and local relaxation dynamics can be studied, we must somehow distinguish between the main characteristic features of local particle configurations in normal as well as in supercooled liquids or in the glassy state. Up to now, such a concept does not exist. One way out could be studying first the local amorphous structure of a very simple model system - in this case of a binary two-dimensional (2D) colloidal glass former. Therein, liquid-like structures of normal up to strongly supercooled liquids can locally be considered depending on the strength of repulsion.

In this paper, the monolayer is subdivided in triangles of nearest neighboring particles (TNNP), which are the smallest local area units. All TNNPs, to which one particle belongs, form its cage. The shapes of the TNNPs were analyzed for the four different 3-particle combinations

of big and small colloids. For each combination, one local density-optimized configuration is found. Less-densely packed TNNP are described as structurally frustrated.

2 Experimental

In a binary suspension of superparamagnetic PMMA (polymethyl methacrylate) spheres, the colloids were confined to 2D due to gravity lying on a completely flat adjusted water-air interface of hanging droplet geometry. The big (b) colloids of diameter $4.7\,\mu$m had a nearly 10 times greater magnetic susceptibility $\chi_\mathrm{b} = 6.2 \cdot 10^{-11}\,\mathrm{Am^2/T}$ than the small (s) ones of diameter $2.8\,\mu$m with $\chi_\mathrm{s} = 6.6 \cdot 10^{-12}\,\mathrm{Am^2/T}$. In the suspension, the thermally fluctuating colloids interact with their induced magnetic moments, tuneable by a homogeneous external magnetic field B applied perpendicular to the water-air interface. Time-dependent particle coordinates were determined by video-microscopy in real time. A more detailed description of the experiment can be looked up in [8,9]. Why the 2D system is a glass formers is explained in [8].

During an experiment the room temperature, T, the number area density, ρ, and the ratio, ξ, of the number $\mathrm{N_s}$ of small particles to the number $(\mathrm{N_b} + \mathrm{N_s})$ of all colloids remain constant. Hence, only B controls the strength of the particle repulsion by the parallelly aligned induced magnetic moments. Other in-plane particle interaction potentials can be neglected. The system is characterized by an interaction parameter, Γ, that is proportional to the magnetic energy $\mathrm{E_m}$ divided by $\mathrm{k_B T}$. Thus, Γ corresponds to an inverse system temperature:

$$\Gamma(B) = \pi^{3/2} \frac{\mathrm{E_m}}{\mathrm{k_B T}} = \frac{\mu_0}{4\pi} \frac{B^2 (\rho\pi)^{3/2}}{\mathrm{k_B T}} \left(\xi \cdot \chi_\mathrm{s} + (1-\xi) \cdot \chi_\mathrm{b}\right)^2 . \tag{2.1}$$

The 2D confined system exhibits several advantages simplifying the observation of particle positions and the analysis of local structures. The restriction to two well-defined types of colloids reduces the number of microscopic particle arrangements. The repulsive potential between induced magnetic moments is known and leads to an energy-landscape with a well for each particle. The highest dividend derives from the access to the time-dependent particle coordinates allowing us to investigate local particle configurations from short-time up to long-time relaxation processes for normal to strongly supercooled liquids [8]. Nevertheless, in this paper, only the amorphous local structure is considered.

3 Results and discussion

Local particle arrangements in glass formers are typically analyzed by partial radial pair-distribution functions $\mathrm{g_{ij}(r)}$. In normal liquids, only a small and broad first maximum is visible for the shortest pair-distances while for higher distances $\mathrm{g_{ij}(r)}$ fluctuates around 1. For increasing temperature T, the first peaks of $\mathrm{g_{ij}(r)}$ become higher and narrower, the first minima decrease and a splitting of the second maxima becomes visible and afterwards more pronounced while no long-range order develops, also for the glassy state. Similar features are found in the $\mathrm{g_{ij}(r)}$ of the binary 2D colloidal glass former [8,9], as shown in Fig. 1.

In this paper, the local particle configurations are characterized not by pairs, but by TNNP [10,11]. These triangles represent the smallest areas, which are defined by the particle positions and cover the monolayer completely.

In the binary 2D mixtures, the amorphous particle configurations are described by idealized local density-optimized triangles, termed as elementary triangles (ET). For a strongly supercooled 2D liquids, their shapes are distinguished by 3-point correlation functions in [11] and by a hard disc approximation in [10]. For each of the four different 3-particle combinations of big and small colloids, one kind of ET is detected. For sss and bbb triangles, the ET are equilateral, bbs ET form right triangles, and bss ET have an angle of 40^o at the big particle.

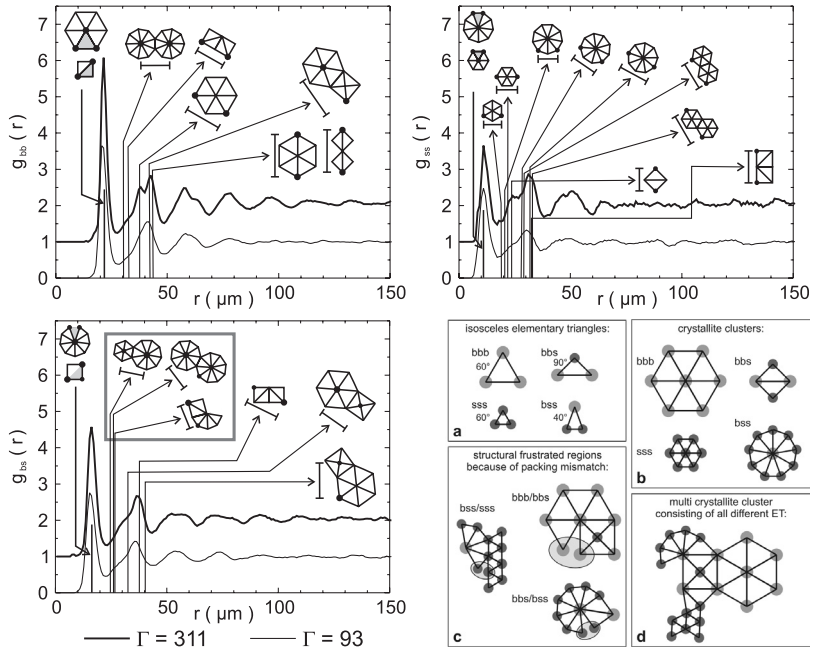

Fig. 1. Partial radial pair-distribution function $g_{xy}(r)$ of the pair combinations bb, bs, and ss as a function of the pair-distance r. A strongly supercooled system ($\Gamma = 311$, $\rho = 0.00300\,\mathrm{m}^{-2}$, $\xi = 0.290$) is compared with a normal liquid ($\Gamma = 93$, $\rho = 0.00335\,\mathrm{m}^{-2}$, $\xi = 0.356$) [8]. Near-zone pair-distances of different CC and MCC up to the split second maximum are sketched by sharp lines. Because of the small ξ-value, sss and bss TNNP are rare, so that the bs pair-distances of the CC and MCC in the grey box give low signals. Such structures are ignored for higher bs pair-distances. In (a) elementary triangles (ET), in (b) crystallite clusters (CC), in (d) multi crystallite clusters (MCC) and in (c) structural frustration are schematically presented. The smallest CC of the 2D glass former consists of one ET-like TNNP and the smallest MCC of two different ET-like TNNPs.

For increasing repulsion the TNNP become more locally density-optimized packed or ET-likely shaped. These TNNP form tiny crystallite nuclei without structural mismatch, termed as crystallite clusters (CC). bbb and sss CCs are hexagonally packed, bbs CCs have a square body-centered lattice, and for bss CCs nine small colloids lie around a big one. CCs of different ET-like TNNP can conglomerate and form multi crystallite clusters (MCC), which are still local density-optimized. Structural frustrated regions occur since the four different ETs cannot cover the monolayer completely because of packing mismatch, as shown in Fig. 1(c). Structural frustrated regions separate neighboring MCCs from each other. The different kinds of ETs and examples of CCs and MCCs are presented in Fig. 1 and Fig. 2.

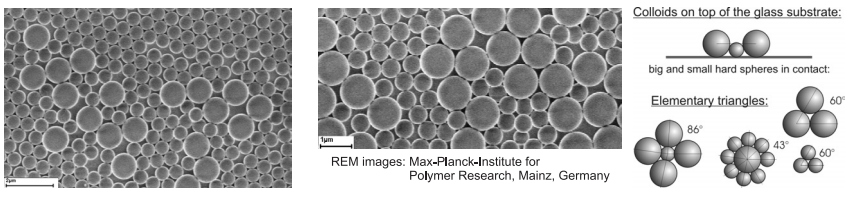

Fig. 2. REM images of air-dried binary colloidal mixtures on top of a glass plate. During the rapid drying process the charged colloids locally form elementary triangles (ET), crystallite clusters (CC), multi crystallite clusters (MCC) as well as regions of local structural frustration. After drying, dynamics are completely frozen and the local particle configurations can be studied.

In Fig. 1, the higher order peak positions are less pronounced for the normal liquid. Since the strength of repulsion is low, thermal fluctuations are able to disturb local order efficiently. Therefore, the shape of the TNNPs are less ET-like. For the strongly supercooled liquid, the peak positions of $g_{ij}(r)$ up to the third peak correspond to bb, bs, and ss pair-distances of the possible CCs and MCCs. The peaks are broadened because of structural frustration and thermal fluctuations. For increasing pair-distance the number of possible combinations of ET-like TNNP increases. Thus, long range order in the strongly supercooled liquid [10] is lost.

4 Concluding remarks

No clear criterion can be defined distinguishing between local density-optimized ET-like TNNP and irregular TNNP of structural frustrated regions. There is a smooth transition. Nevertheless, for decreasing system temperature ET-like TNNP are more pronounced and regions of CC as well as of irregular TNNP can be clearly distinguished [10]. Thus, the glassy solidification is still a dynamic transition. However, global structural relaxations in normal liquids transform to heterogeneous dynamics and finally to local structural relaxations in strongly supercooled liquids or the glassy state. Then, less densely packed regions are caged, surrounded by MCCs of local density-optimized particle configurations. This structurally induced glass transition is called 'concept of local density optimized crystallite clusters'.

The author thanks K. Zahn, G. Maret, J. Horbach, and T. Palberg for discussions and the Deutsche Forschungsgemeinschaft for financial support.

References

1. T.A. Vilgis, in *Disordered Effects on Relaxational Processes*, edited by R. Richert, A. Blumen (Springer-Verlag, Berlin, 1994), p. 153
2. M.D. Ediger, C.A. Angell, S.R. Nagel, J. Chem. Phys. **100**, 13200 (1996)
3. M. Mézard, Physica A **306**, 25 (2002)
4. R. Schilling, in *Collective Dynamics of Nonlinear and Disordered Systems*, edited by G. Radons, W. Just, P. Häussler (Springer-Verlag, Berlin, 2003), p. 153
5. K. Binder, J. Baschnagel, W. Kob, W. Paul, in *Bridging the Time Scales: Molecular Simulations for the Next Decade*, edited by P. Nielaba, M. Mareschal, G. Ciccotti (Springer-Verlag, Berlin, 2002), p. 199
6. D.N. Perera, P. Harrowell, Phys. Rev. E **59**, 5721 (1999)
7. E.W. Weeks, J.C. Crocker, A.C. Levitt, A. Schofield, D.A. Weitz, Science **287**, 627 (2000)
8. H. König, R. Hund, K. Zahn, G. Maret, Eur. Phys. J. E **18**, 287 (2005)
9. H. König, K. Zahn, G. Maret, in *Proceeding of Slow Dynamics in Complex Systems*, edited by M. Tokuyama, I. Oppenheim, AIP **708**, 40 (2004)
10. H. König, Europhys. Lett. **71**, 838 (2005)
11. H. König, in *Proceeding of Slow Dynamics in Complex Systems*, edited by M. Tokuyama, I. Oppenheim, AIP **708**, 76 (2004)