Crystal nucleation versus vitrification in charged colloidal suspensions

Abstract We investigated the solidification behaviour of thoroughly deionised aqueous suspensions of polystyrene latex spheres by various optical scattering methods. We found a dramatic increase in the nucleation rate densities with increasing particle number density. Crystalline and nanocrystalline samples showed two relaxation processes on widely separated time scales. For an index-matched suspension of perfluorinated particles an amorphous state was accessible with the glass-typical signature of frozen long-time relaxation. From our results we propose a route into the amorphous state different to that observed in hard-sphere suspensions. It seems that in charged-sphere systems the increased nucleation rate density triggers the appearance of a Bernal-type glass.

Key words Colloids · Charge spheres · Glasses · Light scattering · Shear modulus

Introduction

Amorphous solids are important materials for technical applications and are still a challenge to fundamental research concerning their formation, structure and dynamics [1]. In general, they are obtained by suppressed crystallisation via geometrical mismatch (mixtures, directed interactions), competition to molecular degrees of freedom (polymers) or phase separation (protein solutions). For one-component materials of spherical interaction (e.g. hard spheres, HS) a purely dynamical glass transition (GT) is predicted [2, 3]. However, many real systems (e.g. metals) exhibit fast crystallisation, even when rapid cooling slows the dynamics and shortens the time available for nucleation and growth. This also applies to colloidal suspensions of charged latex particles, a model system with no substantial temperature dependence of its dynamics [4]. How then can an amorphous state be reached, where conventional strategies do not apply? Somewhat counterintuitively, such a state of short-range order, frozen large-scale motion and finite shear modulus may also be obtained via increased nucleation rates.

Owing to their specific time and length-scales and the analytically tractable HS or Yukawa interactions colloidal suspensions have become fascinating and valuable mesoscopic model systems for many condensed matter problems and for vitrification in particular [5]. Many experimental and theoretical studies were performed on both the amorphous state and the GT [2, 5–11]. In colloidal shear melts [12] an increasing packing fraction, Φ, leads to a slowing of large-scale density fluctuations. For HS, this and low crystallisation enthalpies lead to macroscopically long induction times and slow growth. The addition of a second component [13] or polydispersity [7, 14, 15] further supports vitrification. Also in Yukawa systems vitrification was reported for mixtures [16, 17] and polydisperse platelets [18]; there are only a few reports on charged-sphere glasses [19] or their GT [20, 21]. This is conceivable recalling that Yukawa spheres in general reveal considerably larger crystallisation enthalpies [4]. Solids are readily formed at Φ ≈ 10^{-4}, where diffusion is still fast. While a HS-like GT is predicted to occur at about Φ ≈ 0.1–0.2 [8], crystallisation is expected to interfere significantly.
Experimental

We studied two samples [moderately polydisperse polystyrene PS120 and less polydisperse poly(tetrafluoroethylene) PTFE180] with increasing particle number density, \( n \). All the suspensions were prepared from diluted and precleared stock suspensions of approximately 5.15% packing fraction. Thoroughly deionised conditions (residual ion content \( c \leq 5 \times 10^{-7} \) mol l\(^{-1}\)) were achieved either using an advanced conditioning procedure (PS120) [22] or by introducing an ion-exchange resin into the carefully sealed sample cell (PTFE180).

Quasistimultaneous measurements of static and dynamic light scattering and the shear modulus, \( G' \), were performed without the need to transfer the fragile solid to another experiment or sample cell. Details of the novel two-arm light scattering goniometer with counterpropagating illumination and three independent detection schemes are given elsewhere [23, 24].

Results

Our results are shown in Figs. 1, 2, 3 and 4.

Static scattering was recorded immediately after complete solidification as checked via the appearance of a finite shear modulus, \( G' \). Close to the freezing transition both samples form body-centred-cubic (bcc) polycrystalline materials. PS120 shows a transition to face-centred cubic [24] which is absent for PTFE180. Long range order is lost for PTFE180 at \( n = 35 \) \( \mu \)m\(^{-3}\). As the elasticity data (sensitive to the local neighbourhood of a particle [23]) are well described by a single theoretical curve, the observed short-range order remains of bcc structure.

Visual inspection shows a rapid decrease in the crystallite size with increasing \( n \). The average linear dimension, \( L \), of the crystallites (assumed to be cube shaped) was estimated from the full width at half-maximum, \( \Delta q \), using \( L = 2\pi K/\Delta q \), with the Scherrer constant \( K = 1.155 \). For both samples \( L \) decreases with increasing \( n \), with minimum values of a few microns only. Following Aastuen et al. [25] the nucleation rate densities \( J \), were determined using \( J = 1.158 \) \( \sqrt{\rho n}^{4/3} \), where the crystalline number density is \( \rho = 1/L^{3} \) and the growth velocities are \( v \approx 0.1D_{0}/d_{NN} \) (self-diffusion coefficient \( D_{0} \), nearest-neighbour distance \( d_{NN} \)) [4]. The calculated \( J \) values are much larger than for HS and keep increasing.

The PTFE180 intermediate scattering functions [26] show a monoexponential relaxation for the fluid and a short- and long-time decay separated by a plateau for the solids. With increasing \( n \) its height decreases. For both freshly prepared (shaken) and aged amorphous samples the long-time decay is nearly absent. The incomplete short-time relaxation is interpreted conventionally as “rattling in the cage” of nearest neighbours. Possibly, the long-time relaxation is due to grain boundary diffusion [27], ripening processes or crystal stress relaxation. Our observation is consistent with an increase in the ratio of the cluster surface to...