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Nucleation and crystal growth in a suspension of charged colloidal silica spheres with bi-modal size distribution studied by time-resolved ultra-small-angle X-ray scattering

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A suspension of charged colloidal silica spheres exhibiting a bi-modal size distribution of particles, thereby mimicking a binary mixture, was studied using time-resolved ultra-small-angle synchrotron X-ray scattering (USAXS). The sample, consisting of particles of diameters $d_A = (104.7 \pm 9.0)$ nm and $d_B = (88.1 \pm 7.8)$ nm ($d_A/d_B \approx 1.2$), and with an estimated composition $A_{0.6(1)}B_{0.4(1)}$, was studied with respect to its phase behaviour in dependence of particle number density and interaction, of which the latter was modulated by varying amounts of added base (NaOH). Moreover, its short-range order in the fluid state and its eventual solidification into a long-range ordered colloidal crystal were observed *in situ*, allowing the measurement of the associated kinetics of nucleation and crystal growth. Key parameters of the nucleation kinetics such as crystallinity, crystallite number density, and nucleation rate density were extracted from the time-resolved scattering curves. By this means an estimate on the interfacial energy for the interface between the icosahedral short-range ordered fluid and a body-centered cubic colloidal crystal was obtained, comparable to previously determined values for single-component colloidal systems. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4902904>]

I. INTRODUCTION

Single-component suspensions of like-charged colloids, almost monodisperse in size and nearly spherical in shape, and binary mixtures thereof, have proven to be suitable model systems for metals and binary alloys.^{1–3} This is due to their ability of spontaneously forming ordered states of condensed matter via their *mutual electrostatic repulsion upon confinement*,⁴ in addition to their spatio-temporal dynamics which favors a comparatively easier mode of experimental observation of their solidification.

Single-component *silica* particles in their suspended state, for instance, show a similar icosahedral short-range order (ico-SRO) as is observed in melts of pure Ni, in particular exhibiting the same dependence of the ico-SRO on undercooling.⁵ However, conceptually, single-component systems mimic the *physics* of metallic elements, e.g., they may show simple phase transitions such as the one from a body-centered cubic (*bcc*) into a face-centered cubic (*fcc*) structure upon a change in density.^{3,6,7}

Bi-disperse systems, on the contrary, mimic the *chemistry* of alloys. Binary mixtures of polystyrene beads exhibit a phase-behaviour well-known from binary metallic alloys, regarding the formation of different types of phase diagrams, such as upper and lower azeotropes or spindle-type ones.^{8–12}

Moreover, a complex fluid structure¹³ up to the onset of compound formation may be observed, ultimately yielding the equivalent for the formation of intermetallic phases. In addition, binary systems may exhibit an enhanced crystallinity.¹⁴ Not least, the additional degrees of freedom, regarding the variation of composition or particle size (charge) ratios, may result in the observation of rather unexpected phenomena: The (chemical and topological) SRO observed in binary metallic melts may differ from that in pure metals and, in particular, need not longer to be icosahedral.¹⁵

In either case the most profound insights are gained by the knowledge of the structure of the colloidal fluid or crystal, with the classical approach using some form of small-angle light scattering experiment. Yet many of the aforementioned features occur only in a suspended state of comparatively high particle number density, naturally resulting in opaque samples. A remedy for this situation is given by changing to an ultra-small-angle X-ray or neutron scattering (USAXS/USANS) setup, the latter allowing, suitable binary samples provided, a scattering contrast variation as a way of obtaining information on *partial* structure factors.

Previous USAXS/USANS experiments on charged colloidal samples focused on single-component systems of polystyrene (PS), poly(methyl methacrylate) (PMMA), or perfluoroalkoxy alkane copolymer (PFA) particles,^{16–18} partially studying the scattering from *oriented* colloidal crystals^{19,20} (mainly using Bonse-Hart type camera setups).

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Binary mixtures of PS/PMMA or PS/PFA were studied by means of a scattering contrast variation using $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures as a medium^{21–24} with binary mixtures of PS/PFA, in particular, via a combined USAXS/USANS experiment.^{25,26}

Comparatively less is known about colloidal silica suspensions,^{20,27,28} despite their advantage of having an enhanced X-ray scattering contrast. Here we report, in continuation of previous own work on a single-component system,⁵ on time-resolved USAXS experiments mapping the phase behaviour and elucidating the nucleation kinetics of charged colloidal silica spheres with a bi-modal size distribution.

II. EXPERIMENTAL METHODS

A. Particle synthesis and characterization

Colloidal silica particles were synthesized using a simplified Stöber process.²⁹ Comparatively high particle volume fractions of $\Phi \approx 10\%$ were reached using a batch process starting from 5 l of starting mixture yielding about 250 ml of stock solution. A solution of tetraorthosilicate (TEOS, Merck) in absolute ethanol ($>99.5\%$, Merck) was combined with a second ethanolic solution of aqueous ammonia of fixed water content (28%–30% NH_3 , Merck) at room temperature. Both solutions were mixed as fast as possible, in order to minimize the timeframe of particle nucleation, and vigorously stirred for approximately 24 h. Thereafter, the mixture was quenched with about the same amount of ultrapure water (GPR Rectapur, Prolabo) and subsequently reduced by boiling away the more volatile components. Finally, the concentrated suspension was filtered using glass-wool and $5.0\ \mu\text{m}$ cellulose nitrate filters (Whatman), de-ionized with mixed bed ion exchanger resin (Amberlite IRN-150, Merck), and stored in a cool, dark place under a protective atmosphere of argon (5.0, Linde). All reagents were taken without further purification from freshly opened vials and no additives were used in order to prevent detrimental side effects with respect to particle interaction.

Following this procedure the average particle diameter is solely determined by the mixing ratio of the two starting solutions. Downscaled test reactions for variable size particle syntheses were monitored by means of electrical conductivity measurements, since the presence of the metastable intermediate silicic acid is expressed by a steep increase of ionic species which subsequently diminishes again slowly due to the formation of the amorphous silicon dioxide nanoparticles. Keeping everything else constant, and as an empirical observation, an expectation value for the average particle diameter can be graphically inferred from the initial slope of the conductivity curve (Fig. 1).

Stock solutions were characterized by means of scanning electron microscopy (SEM), for which a droplet of suspension was allowed to dry on top of a sample holder coated with conducting carbon foil, subsequently sputtered with a thin layer of gold. USAXS samples were studied by transmission electron microscopy (TEM) in order to determine accurate particle diameters (Fig. 4). For this purpose suspensions were diluted to about $n \approx 10\ \mu\text{m}^{-3}$ ($0.1\ \mu\text{mol/l}$) and sampled via a copper grid.

FIG. 1. Conductometric monitoring of the particle synthesis for various mixing ratios of precursor solutions. Mixing occurred at $t = 0$. The initial conductivity for $t < 0$ corresponds to varying ratios of a saturated solution of aqueous ammonia (28%–30%) in ethanol yielding an overall constant volume and was normalized to zero. A steep increase in conductivity is seen upon adding a fixed volume of an ethanolic solution of TEOS. Almost monodisperse silica nanoparticles with sizes between 50 nm (95|1:3|3) and 250 nm (88|8:3|3) were produced. The inset shows a TEM micrograph of a collection of nanoparticles isolated from a typical reaction mixture, emphasizing their spherical shape, comparatively high monodispersity, and amorphous internal structure.

B. Sample preparation

In order to precisely characterize³⁰ and control the interaction between suspended particles a closed-circuit gas-tight sample preparation setup³¹ was used, consisting of (a) a reservoir capable of containing up to 100 ml of silica suspension with a typical circuit pre-filled with about half of this amount; (b) a peristaltic pump (Medorex); (c) a set of three three-way magnetic valves connected such as to allow for a double-bypass to either an ion-exchanger column and/or the flow-through USAXS cell; (d) an ion-exchanger column filled with approximately 5 ml of loosely packed Amberlite IRN-150 mixed bed ion exchanger resin; (e) the flow-through USAXS cell with an optical path length of $\ell = 3\ \text{mm}$, equipped with two exchangeable X-ray transparent Kapton windows of thickness $250\ \mu\text{m}$; (f) a conductometric electrode inside a flow-through cell LR 01 V, D01/T; WTW; (g) a bottle of argon of purity 5.0 and a fixed removal pressure of 500 mbar (Minican, Linde) in order to maintain a protective atmosphere free from airborne carbon dioxide (see Fig. 2). The separate units were connected by means of Tygon ($d_{\text{in/ex}}$: 3.2/6.4 mm; Saint-Gobain) and perfluoroethylenepropylene (FEP) copolymer tubings ($d_{\text{in/ex}}$: 1.58/3.18 mm; Bohlender) and corresponding HPLC-type fittings. Prior to experiments on silica suspensions, ultrapure water was used to check the gas-tightness of a circuit which was ascertained by approaching the ambient-temperature electrical conductivity of pure water of $\chi = 0.055\ \mu\text{S/cm}$ by means of constant cycling. The water was subsequently replaced by an equal amount of maximally concentrated silica suspension. Both water and silica suspension were filtered prior to their use (water: $0.2\ \mu\text{m}$, cellulose acetate; silica: $5.0\ \mu\text{m}$, cellulose nitrate; Whatman).

FIG. 2. Sample preparation setup at BW4 beamline (details given in the text). Note the green iridescence of the strongly crystallizing sample of charged colloidal silica spheres.

C. Static light scattering (SLS) and optical microscopy

In order to determine the particle number density of non-opaque samples, up to $n \approx 60 \mu\text{m}^{-3}$, an in-house goniometer setup for static light scattering was used ($\lambda = 532 \text{ nm}$; $15 < 2\theta/^\circ < 165$; home-built³), as well as a mobile fiber-optic device (AvaSpec, Avantes) for performing reflection spectroscopy ($550 < \lambda/\text{nm} < 1250$; $\sin(\theta/2) = 1$). The particle number density of opaque USAXS samples was determined from the scattering signal according to Equation (6). An inverse light microscope (Leica DMI3000 B) was used in combination with a CCD-camera to study the crystallization behaviour at lower n employing a flat flow-through sample cell made of quartz glass (1 mm wall-to-wall distance). The illumination of the sample was such that only light fulfilling the Bragg-condition contributes to the observed intensity (Fig. 3). This allows for a selective visualization of the colloidal crystals and their relative crystallographic orientation as well as studies of their nucleation behaviour (homogeneous/heterogeneous) and their crystal growth velocity.³²

D. Ultra-small-angle X-ray scattering (USAXS)

In order to investigate opaque suspensions of charged colloidal particles at higher particle number density than possible in light scattering experiments, time-resolved ultra-small-angle X-ray scattering (USAXS) experiments in transmission geometry were performed at the soft condensed matter beamline BW4 located at HASYLAB/DESY, Hamburg, Germany with X-ray synchrotron radiation ($\lambda = 0.138 \text{ nm}$).^{33–36}

FIG. 3. Series of light micrographs obtained by Bragg-microscopy exhibiting the simultaneous nucleation and growth of heterogeneously nucleated wall crystals and homogeneously nucleated ones in the bulk volume (image format $0.4 \times 0.4 \text{ mm}^2$, wall of the flow-through cell at the top). The inset in the first picture illustrates the measurement principle by which light is scattered in the objective only in case of the Bragg-condition for a certain crystal orientation to be fulfilled. As long as free-growth is possible, the wall crystal is characterized by a moving planar front (partly exhibiting a lamellar microstructure of oriented single crystal domains) whereas the growth of the bulk crystals is isotropic (and thus spherical) initially and becomes faceted only latter on by steric exclusion due to neighbouring grains (cf. the spherical cut-offs marked by arrows).

The necessary q -space resolution was obtained by choosing the maximum sample-to-detector distance of $L_{\text{SD}} = 13.800 \text{ m}$. For the necessary t -frame resolution a Pilatus 300K detector (Dectris), consisting of three separated detector modules covering a total of $(487 \times 619) \text{ px}^2$ was used. Here, a single pixel amounts to an area of $(172 \times 172) \mu\text{m}^2$. With a maximum frame-rate of 20 Hz and a minimum readout time of 7 ms the detector allows for measurements of comparatively fast processes, such as the nucleation and growth processes in suspensions of charged colloids. For the calibration of the setup a standard Lupolen sample³⁷ was used.

Data reduction was performed with Fit2D³⁸ (ESRF) and Origin (Microcal). In a first step the two-dimensional diffraction pattern was subjected to an azimuthal integration collecting all intensity values from equivalent scattering angles into a one-dimensional curve of raw data.³⁹ This crucial step includes the assignment of correct q -spacings according to the experimental geometry (sample detector distance, detector metrics) and the optional masking of erroneous (pixel errors) or undesirable intensities (i.e., contributions from heterogeneously nucleated wall crystals). Corrections for the varying incident flux I_0 within the timeframe of all measurements, the background contributed by the sample setup (mainly transmission through water), and intensity losses due to absorption within the colloidal suspension were performed afterwards, namely, when the data were corrected for contributions from the fraction of the sample which remains fluid throughout the crystallization. Yet another major correction is due to the contribution of the scattering regarding the particle form. In order to obtain the spatio-temporal structural information contained within the structure factor $S(q, t)$ the time-independent particle form factor $P(q)$ has to be accounted for. Particle form factors were measured for concentrated suspension in the limit of

screening at exceptionally large salt concentrations induced by the addition of large amounts of NaOH.

III. RESULTS AND DISCUSSION

A. Sample characterization establishing its bi-modal size distribution

The measurement of the time-independent particle form factor $P(q)$ is a crucial prerequisite for the subsequent extraction of the time-dependent structure factor $S(q, t)$. In addition, knowledge of $P(q)$ allows for an accurate determination of the particle properties, namely, their shape, average diameter and size distribution. TEM experiments on as-prepared samples proved the amorphous nature and uniform density of the particles (cf. the inset shown in Fig. 1). In particular, an overwhelming number of particles observed in the transmission electron micrograph exhibit a circular projection according to their expected spherical shape, which allows for the modeling of the particle form factor in an analytical ansatz.

A closed form analytical expression for $P(q)$ of comparative simplicity, yet considering both the average particle size and its size distribution is offered by the *Schulz distribution function*^{40,41} (SDF):

$$S(R) = \left(\frac{z+1}{\langle R \rangle} \right)^{z+1} \frac{R^z}{\Gamma(z+1)} \exp \left(-\frac{z+1}{\langle R \rangle} R \right), \quad (1)$$

Here, $\langle R \rangle$ denotes the average particle radius defining the barycenter of the distribution function, while $z+1 = \langle R \rangle^2 / \sigma^2$ is a parameter related to the width of the distribution and $\Gamma(\cdot)$ denotes the gamma function, i.e., a generalized factorial function. For vanishing polydispersity the SDF defines a Dirac delta distribution centred at $\langle R \rangle$, whereas for low polydispersity it resembles a Gaussian distribution. However, for larger polydispersity the SDF accounts for an asymmetry in the size distribution, which may be described by a comparatively steep increase for smaller particle diameters and a comparatively gradual decrease for larger ones (compare Fig. 4).

The SDF is determined, except for an overall particle number density dependent scaling factor S by only two free parameters, namely the average radius $\langle R \rangle$ (diameter) of the particles and their size distribution given by a polydispersity index $\text{pdi} = \sigma / \langle R \rangle$, where σ is the standard deviation of the distribution. Thus, the SDF gives a simple model of a real colloidal dispersion and has the further advantage that an analytic solution

$$P(q) = \frac{S}{q^6} - \frac{\cos[(z+1)B]}{A^{\frac{(z+1)}{2}}} + (z+2)(z+1) \left\{ \frac{1}{\alpha^{(z+3)}} + \frac{\cos[(z+3)B]}{A^{\frac{(z+3)}{2}}} \right\} - 2(z+1) \frac{\sin[(z+2)B]}{A^{\frac{(z+2)}{2}}},$$

where

$$A = 4 + \alpha^2, \quad B = \tan^{-1} \frac{\alpha}{2}, \quad \text{and } \alpha = \frac{z+1}{q \langle R \rangle}, \quad (2)$$

can be derived for $P(q)$ as it is the case for monodisperse spheres.⁴¹

FIG. 4. (Top) Particle form factor $P(q)$ of silica particles as measured by USAXS in the limit of excessive screening of particle interaction, for which $S(q) \rightarrow 1$ (solid line) and calculated assuming a Schulz distribution function of particle radii (dashed line) yielding an ensemble average of $\langle R_{AB} \rangle = 98.3/2$ nm with a polydispersity of $\text{pdi}_{AB} = 0.121$. The inset shows a TEM micrograph of the corresponding sample. (Bottom) Histogram of the particle size distribution as determined from the diameters d of a total of 454 single particles visualized by means of TEM (bin width $b = 5$ nm). The frequency of occurrence $H(d)$ accounts for the absolute number of particles within each bin. Shown are also a summarized fit curve (magenta) matching a suitably smoothed histogram and its underlying distribution functions for a bi-disperse model consisting of small (blue) and large (red) particles.

This is of some importance in our case, since the size distribution as determined from 454 single particle diameters observed via TEM (Fig. 4) is very broad and, at a first glance, appears as belonging to a single-component sample of low monodispersity ($\langle R \rangle = 98.3$ nm, $\text{pdi} = 0.121$).

Indeed, a $P(q)$ calculated on the basis of this SDF approximates the measured $P(q)$ quite well. However, no single

SDF is able to reproduce the experimentally determined size distribution of the particles, since either the height or width of the size distribution may be described properly but never both simultaneously. Furthermore, a pronounced drop of the frequency of occurrence at intermediate particle sizes favors an interpretation as a *bidisperse* sample. In order to establish and substantiate this view, two independent procedures were followed, namely (i) a fit of $P(q)$ and (ii) a suitably smoothed $H(d)$ taking into account a total of five free parameters: an (arbitrary) overall scaling factor s , two average particle radii $\langle R_A \rangle$, $\langle R_B \rangle$ for each component, a single pdi_{AB} for both components, and a mixing ratio w according to an ansatz,

$$s\{w\mathcal{S}(\langle R_A \rangle, \text{pdi}_{AB}) + (1-w)\mathcal{S}(\langle R_B \rangle, \text{pdi}_{AB})\}. \quad (3)$$

Note that the shapes of SDFs for two species with different average radius and common overall scaling factor and pdi_{AB} differ significantly, which may result in counter-intuitive relative heights of the SDFs (Fig. 4). In combination, however, both the observed $P(q)$ and $H(d)$ are well reproduced with a bi-disperse sample characterized by the following parameters: $\langle R_A \rangle = 104.7/2$ nm, $\langle R_B \rangle = 88.1/2$ nm, $\text{pdi}_{AB} = 0.086$, $w = 0.6$.

B. Mapping of the phase behaviour

Prior to the study of nucleation and growth the phase behaviour of the silica suspension was explored by varying the particle number density n and the sodium hydroxide concentration c_{NaOH} as control parameters. The latter in particular and the state of the suspension in general were monitored by in-line conductometry.^{30,42–44} The conversion between the measured electrical conductivities at a given particle number density and the sodium hydroxide concentration was probed by a conductometric titration.⁴⁵

The measurements started with a maximally concentrated ($n = 201 \mu\text{m}^{-3}$), fully de-ionized stock solution which was subsequently step-wise diluted with filtered, ultrapure water. For each dilution step the *fully de-ionized reference state* was reached by thoroughly cycling the suspension through the mixed bed ion-exchanger column.

Charging of the particle's surface was achieved by adding a specified amount of sodium hydroxide solution (NaOH, $c = 1$ mol/l). During the addition of base the suspension was thoroughly stirred in order to ensure a homogeneous distribution and simultaneously prevent salt-induced coagulation. NaOH has two effects upon the silica suspension: First, the hydroxide anions effectively de-protonate the free R-SiOH silanol groups far beyond their autoprotolysis reaction thereby increasing the negative surface charge of the particles, whereas second, the sodium cations contribute to a screening of this charge thus influencing the particle's interaction. Since the number of free silanol groups on the surface of the particle and therefore their net charge is limited, according to their size, the continuing addition of base leads to an ever-increased screening such that the particles in the limit, although charged, behave like hard spheres. In this case their interaction is sufficiently diminished such that $S(q) = 1$ and one is able to measure the pure particle form factor $P(q)$ even for these highly concentrated samples (compare Fig. 4). For

our specific sample this state was reached beyond an electrical conductivity around $200 < \chi/\mu\text{S cm}^{-1} < 400$ corresponding to a NaOH concentration in the millimolar range.

After obtaining a measurement of the screened state for a given particle number density the suspension was step-wise de-ionized again taking a time-series $I(q, t)$ for each intermediate point between the screened and the fully de-ionized state thereby establishing the phase diagram of the suspension with respect to n and c_{NaOH} . Here, the state of the suspension and the residual amount of sodium hydroxide was monitored by conductometry with the measured electrical conductivity values subsequently converted into calculated sodium hydroxide concentrations based on an independent conductometric titration of the stock solution complementing the determination of the phase behaviour.

The results obtained by USAXS on optically dense samples (Fig. 5) were complemented by SLS measurements on diluted samples (Fig. 6).

The n - c_{NaOH} phase diagram of a silica suspension of given size is characterized by the presence of an inclined wedge outlining the crystalline regime and flanked by two fluid regions.⁴⁶ At low particle number densities the crystalline region is delimited by a minimal value denoting the freezing density n_F below which the charge-induced crystallization upon confinement will not occur any more. Within the crystalline region exists a line representing the interaction between fully de-protonated, i.e., maximally charged silica particles at which, in general, the mutual repulsion is strongest, the growth velocity of 110-oriented wall crystals is fastest³² and the shear modulus of the colloidal crystal passes through its maximum³ (inclined dashed line in Fig. 6). In our case, the line of maximum interaction was inferred from the growth velocity of 110-oriented wall crystals, as observed by optical microscopy.

It should be noted that the nucleation and crystal growth of like-charged silica particles is solely due to their electrostatic repulsion upon confinement, whereas attractive van der Waals interactions set in only at much shorter particle distances than those occurring in our experiment.⁴⁷

FIG. 5. Phase diagram of bi-disperse silica particles obtained by USAXS. Note the good agreement of the data with the phase boundaries extrapolated from SLS data (Fig. 6) for $n < 100 \mu\text{m}^{-3}$ and the strong deviations for $n > 100 \mu\text{m}^{-3}$.

FIG. 6. Phase diagram of bi-disperse silica particles obtained by SLS. Highlighted are the crystal-melt phase boundaries (solid lines) and the line of maximum interaction (dashed line) corresponding to fully charged, not-yet screened particles as determined by optical microscopy. In addition, the regions of predominant homogeneous and heterogeneous nucleation and growth are emphasized (dashed line and micrographs).

For the bi-disperse sample used in this study the SLS data shows the expected phase behaviour, indeed matching the case of a single-component system. At higher particle number densities, above $n \approx 100 \mu\text{m}^{-3}$, a shift of the phase boundaries to higher NaOH concentrations occurs. At the same time a “bifurcation” of the crystallization was observed as illustrated in Fig. 7.

However, it has to be admitted, that the data obtained so far, due to their scarcity, unfortunately are not sufficient to establish an anomalous crystallization behaviour. On one side, a maximum crystallization was observed by means of USAXS for *two* distinct instances in two separate dilution series of constant particle number density $n = 134 \mu\text{m}^{-3}$ and $n = 149 \mu\text{m}^{-3}$, respectively (denoted optimum crystalliza-

FIG. 7. Scattering curves $S(q)$ for $n = 149 \mu\text{m}^{-3}$ and varying sodium hydroxide concentrations showing fluid and crystalline structure factors. For ease of comparison all curves are subject to the same offset in the y- and x-direction.

tion in Fig. 5; “optimum” in terms of the overall quality of the diffraction pattern, i.e., number of visible peaks and their relative intensity above the background). Measurements in-between both crystallization maxima furthermore indicated a continuous de-ionization between these sampling points. On the other side, a general shift in the measured conductivity values cannot be ruled out completely. This may be traced back to sample inhomogeneities due to the high particle number densities and the resulting strong interaction of the particles. Although care was taken to maintain homogeneous samples, primarily by means of vigorously stirring the suspension inside the reservoir maintaining an otherwise constant flow through the sample preparation circuit, this may be not successful inside the flow-through conductivity cell, where crystallized regions could have been prevented from shear-melting due to turbulent flow or other means of flow-excluded volume. The overall crystallization behaviour in terms of the specific diffraction patterns obtained for the *bcc*-type colloidal crystal remained similar however (Fig. 8).

Upon establishing the phase behaviour and as a consequence of time-resolved measurements one is able to study simultaneously the nucleation and growth of colloidal crystals including their long-range ordered structure as well as the development of short-range order (SRO) in the fluid state.

C. Measurement of nucleation kinetics

Time-resolved ultra-small-angle X-ray scattering experiments were performed on an aqueous colloidal suspension of charged amorphous silica spheres with an ensemble radius of $\langle R_{AB} \rangle = 98.3/2 \text{ nm}$ ($\text{pdi}_{AB} = 0.121$; $P(q)$ -Fit) which may be attributed to an actual bi-disperse suspension consisting of particles with $d_A = (104.7 \pm 9.0) \text{ nm}$ and $d_B = (88.1 \pm 7.8) \text{ nm}$ in diameter (TEM; composition ratio $A : B = 0.6 : 0.4$) and reasonably low polydispersity of $\text{pdi}_A = \text{pdi}_B$

FIG. 8. Scattering curves $S(q)$ for optimum crystallization observed at varying particle number densities. Scattering intensities were normalized to $|S(q)_{110}| = 1$. For ease of comparison all curves are subject to the same offset in the y-direction. Note that the apparent offset of the diffraction patterns in the x-direction reflects the change in the particle number density!

$= 0.086$ in order to facilitate spontaneous crystallization upon confinement. A systematic scan of the phase behaviour in a wide range of the control parameters, particle number density n and sodium hydroxide concentration c_{NaOH} , was undertaken, in order to study the nucleation and growth of the resulting colloidal crystals. Although the method in principle allows for a separate treatment of homogeneous and heterogeneous nucleation, by means of selectively masking corresponding scattering contributions from the data prior to azimuthal integration,⁴⁸ we focus on the *homogeneous* case.

After obtaining the time series of structure factor curves $S(q, t)$ each dataset for a given pair of control parameters (n , c_{NaOH}) was subjected to another intensity-correction regarding the contribution of scattering from the fluid background of the colloidal suspension following the approach of Harland and van Megen.⁴⁹ For this purpose the first shot within each time series, recorded at $t_1 = 250$ ms after interrupting of the suspension's flow, which marks t_0 , was taken as a reference for the fluid state of the sample lacking any signs of crystallization. In order to subtract the fluid's contribution and due to the effect of peak sharpening upon crystallization, which diminishes intensity at both flanks of each peak, a peak scaling is performed according to the following formula:

$$S_{\text{crystal}}(q, t) = S(q, t) - \beta(t) \cdot S_{\text{fluid}}(q), \quad (4)$$

where $\beta(t)$ is a time-dependent scaling factor to be determined by a least-squares alignment of each $S(q, t_{>1})$ curve to the one of the fluid $S_{\text{fluid}}(q, t_1)$.

In order to determine key parameters of nucleation and growth of the single-component silica suspension we focused on the detailed analysis of the time-evolution of the strongest reflection, 110, which corresponds to the largest interplanar spacing of the *bcc* lattice. In the crystal structure the (110) plane is the most densely occupied one and the [110] direction perpendicular to it is the dominant growth direction of the colloidal crystal. Thus, the time-evolution of the scattered intensity from the 110 reflection maps the growth of the colloidal crystal (and, eventually, relates to the growth velocity, although more direct methods other than USAXS exist for its determination, e.g., optical Bragg-microscopy of oriented wall crystals, cf. Fig. 3).

Crystallization commonly sets in after a few seconds and is finished after some minutes, thus the timeframe of the measurement was chosen to be 60 s with intermediate steps every 0.25 s yielding a total of 240 frames for a single time-series. A tiny offset in time due to the finite detector read-out time (in the order of milliseconds) was neglected. Figure 9 shows a time evolution from an icosahedral short-range ordered fluid to a body centered cubic colloidal crystal.

The icosahedral SRO was inferred upon comparing the fluid structure factor curve with previous USAXS experiments on colloidal silica suspensions and corresponding simulations of the structure factor assuming distinct models for the SRO for which the icosahedral (dodecahedral) one exhibits the best agreement with the measurements.⁵

The *bcc*-type LRO was assigned on the basis of the observed interplanar spacings d_{hkl} and with respect to the reflection conditions of a *bcc*-type lattice by using the Scatter

FIG. 9. (Top) Time-evolution of the structure factor $S(q)$ —of a silica suspension at intermediate particle number density $n = 83 \mu\text{m}^{-3}$ and close to maximum interaction—from a fluid state with icosahedral SRO into a crystalline state with *bcc*-type structure. (Bottom) Initial and final structure factor $S(q)$ for the same time-series. Up to 10 reflections of a *bcc* crystal can be indexed. Note the shoulder in the second oscillation of the fluid structure factor which indicates the presence of icosahedral SRO.

software.⁵⁰ The crystalline structure factor is shown with its proper indexation. A possible transition into an *fcc*-type structure at high particle number densities and salinities was not observed for the particles under consideration.

D. Evaluation of key parameters of nucleation

Reviews on the crystallization kinetics of charged colloids, mostly referring to monodisperse systems other than silica, have been given by one of the authors.^{51,52} The crystallization kinetics of polydisperse colloidal *hard spheres* were reported by van Meegen *et al.*^{53,54} Here, we restrict ourselves to mention the details of the data evaluation applied within the present study, focused on bi-disperse charged silica spheres. Since the colloidal crystals formed are that of a substitutional alloy, with no observable superstructure formation present, the evaluation scheme used for single-component systems applies.

The 110 region of the structure factor curves of a time-series $S(q, t)$ were multiply fitted by a non-linear least squares routine with a Lorentzian line profile,

$$S(q, t) = \frac{2 A_{110}(t)}{\pi} \cdot \frac{\Delta q_{110}(t)}{4(q - q_{110}(t))^2 + \Delta q_{110}(t)^2} \quad (5)$$

and manually estimated starting values for the peak position q_{110} , width Δq_{110} , and area A_{110} . From the fitted profile one obtains derived quantities in two steps. First, one calculates: (i) the particle number density

$$n(bcc) = \frac{2}{g^3} = 2 \left(\frac{2\pi \sqrt{h^2 + k^2 + l^2}}{|q_{110}|} \right)^{-3} \quad (6)$$

from the peak position (via the lattice parameter g), (ii) the average crystallite size

$$\langle L(t) \rangle = \frac{2\pi K}{\Delta q_{110}} \quad (7)$$

from the peak width (with $K \approx 1$ the Scherrer constant), and (iii) the crystallinity

$$X(t) = c \cdot \underbrace{\int S_c(q, t) dq}_{A_{110}} \quad (8)$$

from the normalized ($A(t_{\text{final}}) = 1$) peak area. Second, one derives: (iv) the crystallite number density

$$n_x(t) = \frac{X(t)}{\langle L(t)^3 \rangle} = \frac{X(t)}{\alpha \langle L(t) \rangle^3} \quad (9)$$

from the crystallinity and the average crystallite size (with $\alpha = 1.25$), (v) the nucleation rate density

$$J(t) = \frac{1}{1 - X(t)} \cdot \frac{d}{dt} n_x(t) \quad (10)$$

from the crystallinity and the crystallite number density, and finally (vi) the solid-liquid interfacial energy γ from the nucleation rate densities,

$$\ln J_{\text{max}} = \ln J_0 - \frac{16\pi \gamma^3}{3 k_B T} \cdot \frac{1}{(n \Delta \mu)^2}. \quad (11)$$

These formulas were previously derived within the conceptual framework of classical nucleation theory (CNT) and proven to yield a basic but essentially correct approach for a quantitative treatment of nucleation phenomena of charged colloids.⁵⁵

Figure 10 depicts a time evolution for the aforementioned nucleation and growth parameters. Note the typical steep in-

FIG. 10. Overview of the nucleation kinetics of bi-disperse colloidal silica. Shown are the time evolution of the crystallinity $X(t)$, the crystallite size $\langle L(t) \rangle$, the volume fraction Φ , the crystallite number density $n_x(t)$, and the nucleation rate density $J(t)$ for the sample shown in Fig. 9.

crease of the crystallinity $X(t)$ after a short induction period and its following saturation after cessation of crystal growth. The average crystallite size $\langle L(t) \rangle$ is in the range of a few micrometer and rises slowly with time. The crystallite number density $n_x(t)$ rises accordingly. The nucleation rate density $J(t)$ traverses an intermediate maximum (due to a decrease in the free volume remaining available for crystal growth) which can be used to yield an estimate of the interfacial energy between the fluid and the *bcc* colloidal crystal.

Within the formalism of CNT the solid-liquid interfacial energy γ determines the surface contribution to the total free energy, i.e.,

$$\Delta G(r) = 4\pi r^2 \gamma + (4/3)\pi r^3 n \Delta \mu \quad (12)$$

whereas the undercooling $\Delta \mu$ acts in a similar way for the volume term.

In our case, the undercooling is obtained from a Wilson-Frenkel-type plot (not shown; compare Fig. 5 in Ref. 3) of the growth velocity

$$v_{110} = v_{\infty} \left\{ 1 - \exp \left(- \frac{\Delta \mu}{k_B T} \right) \right\} \quad (13)$$

of 110-oriented *bcc* wall crystals at maximum interaction,⁵⁶ as determined by Bragg-microscopy (Fig. 3), versus the particle number density, which determines the undercooling via

$$\Delta \mu = B k_B T \frac{(n - n_F)}{n_F}. \quad (14)$$

Here, the limit velocity v_{∞} , the particle number density of freezing n_F , and a parameter B , determining the asymptotic behaviour (v_{∞} , n_F) and curvature (B) of the growth velocity curve, are treated as fit parameters. For the sample under investigation the following values were determined: v_{∞}

FIG. 11. Arrhenius-type plot of the estimated nucleation rate densities $J_{\max}$ at maximum interaction versus $1/(n \Delta\mu)^2$.

$= 10.1(9) \mu\text{m/s}$, $n_F = 11.1(5) \mu\text{m}^{-3}$, and $B = 5.67 \pm 2.66$ in units of $k_B T$. The crossover n_C between predominant heterogeneous ($n < n_C$) and homogeneous ($n > n_C$) nucleation and growth was observed about $n_C \approx 23 \mu\text{m}^{-3}$.

From the total number of measurements the interfacial energy γ between the body centered cubic colloidal crystal and the fluid can be inferred, in particular from a plot of $\ln(J_{\max})$ versus $(n \Delta\mu)^{-2}$ (Fig. 11). The data points correspond to values determined close to maximum interaction of the particles at ten distinct particle number densities.

Although CNT predicts a linear decreasing slope, strong deviations are observed, suggesting a concentration dependence of the interfacial free energy of the nuclei. This may be emphasized by a point-by-point determination of γ employing the local slope at each point and plotting the result versus the particle number density n (Figure 12).

The interfacial free energy increases almost linearly from about $0.4 \mu\text{J/m}^2$ to about $4.0 \mu\text{J/m}^2$. While the absolute val-

FIG. 12. Plot of the absolute interfacial energy in dependence of the particle number density n exhibiting a linear trend with the solid-liquid interfacial energy being of the order of $\mu\text{J/m}^2$.

FIG. 13. Turnbull-type plot of $\gamma n^{-2/3}$ versus $\Delta\mu$.

ues are about one magnitude larger than for a comparable monodisperse silica system, consisting of particles of 77 nm in diameter (Si77), the linear trend is comparable. However, aside from the influence of polydispersity, the observed larger interfacial energy matches the diminished crystallization tendency of the bi-disperse sample for comparable undercoolings.

In the case of colloids both the particle number density and the undercooling are related to the interfacial free energy

$$\gamma = C_T \cdot \Delta\mu \cdot n^{2/3}, \quad (15)$$

via the dimensionless Turnbull coefficient C_T . Equation (15) thus offers a way of evaluating this dimensionless interfacial free energy for colloidal systems, since C_T simply represents the linear slope in a plot of $\gamma n^{-2/3}$ versus $\Delta\mu$ (Fig. 13).

The Turnbull coefficient relating the *bcc* substitutional polycrystal of this study, formed from charged colloidal particles exhibiting a bi-modal size distribution, and its melt is determined to be $C_T = 0.267(7)$. This corresponds well with reported values from either simulations or experiments comparing *bcc*- and *fcc*-type colloidal crystals: while one determines

$$C_{T,\text{sim.}} \approx 0.29(\text{bcc}) \quad \text{and} \quad 0.55(\text{fcc}) \quad (16)$$

from simulations, the corresponding experimental values are

$$C_{T,\text{exp.}} \approx 0.31(\text{bcc}) \quad \text{and} \quad 0.43(\text{fcc}). \quad (17)$$

Here, the approximate experimental value for *bcc* crystals represents a recently determined average from six distinct, mostly single-component colloidal systems,⁵⁷ employing polystyrene-poly-n-butylacrylamide ($2 \times$), polystyrene ($2 \times$ single-component, $1 \times$ binary mixture), and silica ($1 \times$, $C_{T,\text{exp.}}(\text{Si77}) = 0.241$) particles, respectively. In fact, depending on the mode of evaluation, averaged Turnbull coefficients of either $C_{T,\text{exp.}} = 0.31(3)$ or $0.25(2)$ result, the latter one taking into account low-uncertainty data derived from growth measurements (a comprehensive compilation of Turnbull coefficients, with a particular emphasis putting on their comparison with the ones determined for pure metals, is given in Ref. 3).

IV. CONCLUSION

The phase behaviour of a bi-disperse sample consisting of charged colloidal silica spheres with diameters $d_A = (104.7 \pm 9.0)$ nm, $d_B = (88.1 \pm 7.8)$ nm, and composition $A_{0.6(1)}B_{0.4(1)}$ as well as the time-resolved homogeneous nucleation and growth of colloidal polycrystals from their icosahedral SRO melt into substitutional *bcc*-type crystal structures was studied by means of SLS (in combination with optical microscopy) and, in particular, USAXS. At particle number densities below $n \approx 100 \mu\text{m}^{-3}$ a similar phase behaviour was observed as would be expected for a monodisperse, single-component sample. However, at particle number densities above $n \approx 100 \mu\text{m}^{-3}$ and below the maximum achieved $n = 201 \mu\text{m}^{-3}$ a change in the phase behaviour was observed, resulting in—yet unexplained—(i) shifts of the phase boundaries to higher sodium hydroxide concentrations and (ii) a bifurcation in the qualitative crystallization behaviour, with respect to the specific emergence of the obtained *bcc*-type crystal structure. Quantitatively, an attempt was made to obtain key parameters of nucleation from the USAXS data, yielding an estimate on the (particle number density dependent) solid-liquid interfacial free energy in the order of $\mu\text{J}/\text{m}^2$ and a Turnbull coefficient of $C_T = 0.267(7)$.

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