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Recent Study of Counterion-mediated Attraction between Colloidal Particles and between Particles and Interface Studied by the Ultra-small-angle X-ray Scattering

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The application of the 1D- and 2D-ultra-small-angle X-ray scattering (USAXS) methods to the structural study of dilute colloidal silica particle dispersions is reviewed. A single colloidal crystal showed 22 sharp diffraction peaks, which allowed us to uniquely determine the lattice symmetry (body-centered-cubic), lattice constant (around 0.3–0.4 μm) and crystal orientation. In dilute dispersions, the closest interparticle spacing was confirmed to be smaller than the average spacing, pointing to the important role of a counterion-mediated attraction between the particles. The scattering profile had six-fold and four-fold symmetries with $[1\bar{1}1]$ and [001] directions being parallel to the axis of the capillary (dispersion container), respectively. In both cases, the (110) planes, the most densely packed planes of bcc, were in contact with and parallel to the capillary surface, confirming the presence of a possibly counterion-mediated attractive interaction between negatively charged interface and particles. After the capillary was shaken, only the six-fold symmetry was found, which is reasonable in the light of larger contact between the capillary surface and the (110) planes (and hence greater stabilization of the system) than for the four-fold symmetry.

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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INTRODUCTION

Recent experiments on dispersions of well-defined ionic colloidal particles have revealed that an electrostatic attractive interaction exists between similarly charged particles. As reviewed in an article,[1] the essential features of the experimental results are not compatible with the established concept in colloid science, namely the DLVO theory, in which electrostatic repulsive interaction and van der Waals attraction were assumed.[2] One reason for this incompatibility is believed to be that the theory is a mean field theory for two ionic particles immersed in simple electrolyte solutions. In other words, this theory does not satisfy the Gibbs-Duhem (G-D) relationship, which is a thermodynamic requirement for multi-component systems. Therefore it is only at infinite dilution of particles and/or for the infinitely small change of the chemical potential due to the particles that the incompatibility with the G-D relationship and with experiments is permissible. Paradoxical situations were pointed out to arise from ignoring or misusing the G-D relationship.[3]

In the present article, we would like to survey experimental and simulation results testifying further to the presence of the attraction, which were accumulated after the previous review was completed.

STRUCTURAL ANALYSIS OF A SINGLE CRYSTAL OF COLLOIDAL SILICA PARTICLES IN A DILUTE DISPERSION, AS STUDIED BY THE TWO-DIMENSIONAL ULTRA-SMALL-ANGLE X-RAY SCATTERING (USAXS)

We have constructed a 2D-USAXS apparatus using the Bonse-Hart optics,[4,5] which allows us to study X-ray scattering down to 17 seconds of arc and suits the structural study of colloidal crystals. The optical system shown in Figure 1 is composed of two sets of two channel-cut single crystals of Ge to collimate the X-ray beam in both the horizontal and vertical planes. The X-ray (wavelength: 1.54 Å) reflects on the (111) planes of the first and second crystals and the diffracted X-ray reflects on the (111) planes of the third and fourth crystals to reach the proportional counter. The cross section of the beam is about 1×1 mm^2 so that the high collimation as a point focusing geometry is confirmed and the smearing effect is regarded negligible. Extensively purified colloidal silica dispersions were introduced into a quartz capillary, a sample cell for the scattering experiments, in which crystallization proceeded. For further deionization ion-exchange resin particles were confined by a nylon mesh at the top and bottom of the dispersion.

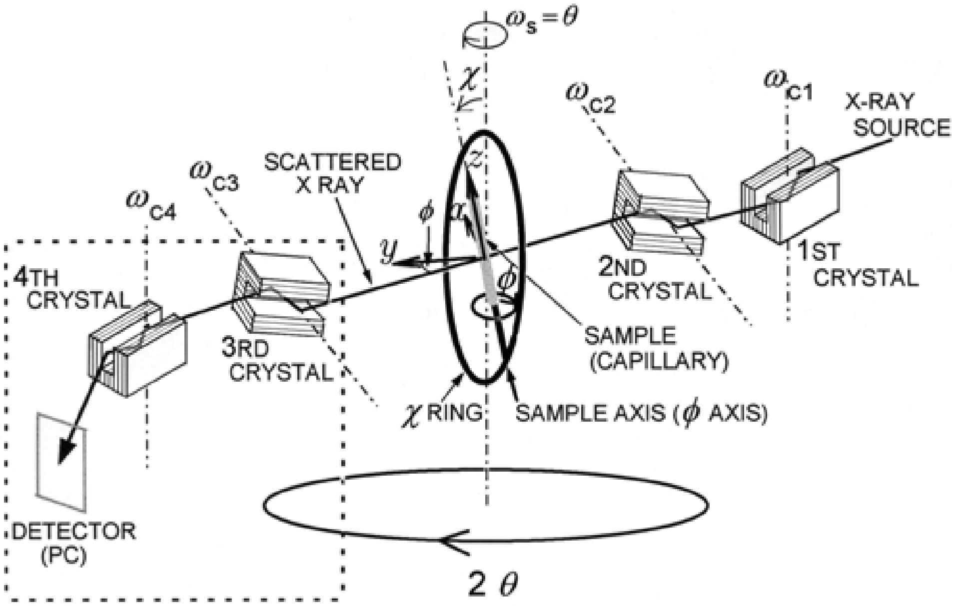

Figure 1. Optical system of the 2D-USAXS apparatus. The mechanism of sample rotation is as follows. The vertical ring (χ ring) can be rotated by ω_s about the vertical axis. $\omega_s = 0$ when the axis of the χ ring is parallel to the X-ray beam. To change the direction of the scattering vector, the sample was rotated by χ in the plane made by the χ ring and by ϕ about the sample axis. $\chi = 0$ when the sample axis is vertical and $\phi = 0$ when the x axis of the coordinate system associated with the samples in the plane of the χ ring. The y axis is normal to the plane of the χ ring when $\phi = 0$ and the z axis constitutes the right-handed rectangular coordinate system with x and y axes. The magnitude of the scattering vector is changed by rotating the third and fourth crystals together with the detector by 2θ about the vertical axis at the sample, while fixing $\omega_{C3} = \omega_{C4} = 0$ and keeping the rotation angle ω_s of the sample equal to θ. Taken from Ref. 5 by permission of the American Physical Society.

The colloidal silica particles had an average radius of 0.056×10^{-6} m, with a standard deviation of 8% (see below). The sample concentration (volume fraction, φ) was about 0.025%. The scattered intensity $I(\boldsymbol{q})$ was measured at scattering vector $\boldsymbol{q}$ and its contour plots are given against χ and ϕ at three scattering angles of 118, 165 and 203 seconds of arc in Figure 2. The components of $\boldsymbol{q}$ are written by $\boldsymbol{q} = (q \cos\chi \cos\phi, q \cos\chi \sin\phi, q \sin\chi)$, where q is the magnitude of the scattering vector, and χ and ϕ are rotation angles of the sample (see the legend to Figure 1). It is clear from twenty-two scattering peaks that an ordered structure is formed in the capillary and is oriented in the light of the ϕ and χ dependence. Using the procedure by

Busing and Levy,[6] the crystal structure was uniquely determined to be bcc with a lattice constant of 0.38×10^{-6} m and with the $[1\bar{1}1]$ direction parallel to the capillary axis.

Conversely, assuming a bcc single crystal with the lattice constant and the direction found above, the peak positions were estimated using the Busing-Levy procedure and indicated by circles in Figure 2. Good agreement between the observed and calculated positions is noteworthy. Thus, it may be claimed that a single crystal of bcc was formed and was the major source of the observed scattering profile.

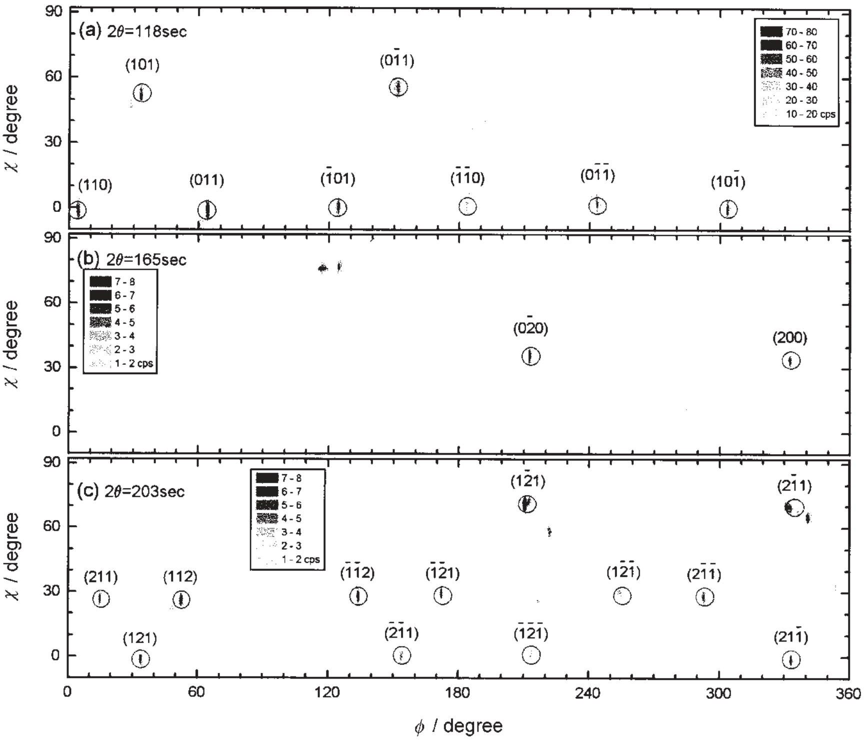

Figure 2. Contour plots of the 2D-USAXS intensities of a colloidal silica dispersion, $\varphi \approx 0.025$, against χ and ϕ. The circles indicate the calculated position of the diffraction peak considering bcc lattice with a lattice constant of 0.38×10^{-6} m and with $[1\bar{1}1]$ parallel to the capillary wall. The diffraction peaks were assigned to the corresponding diffraction planes indicated by Miller indices. There are some extra peaks seen in the figure that do not arise from the proposed structure. They are supposed to be due to separately oriented small crystallites which coexisted in the dispersion. Taken from Ref. 5 by permission of the American Physical Society.

PARTICLE SIZE, ITS STANDARD DEVIATION, AND SYMMETRIES OF CRYSTALS OF COLLOIDAL SILICA PARTICLES IN DILUTE DISPERSIONS AS STUDIED BY THE ONE-DIMENSIONAL ULTRA-SMALL-ANGLE X-RAY SCATTERING

The 1D-USAXS apparatus was also constructed with X-ray of a line focusing geometry (1 mm × 15 mm)[7,8] and used to study the structure of colloidal crystals. (To save space, the optical system of the 1D-USAXS is not shown here. Although the original paper[7] should be referred to for details, the 1D-USAXS optics corresponds to that of the 2D-USAXS without the second and third crystals in Figure 1.) In this case, single crystals of Si or Ge were used for one-dimensional collimation of the X-ray beam. The small-angle resolution was characterized by full width at half maximum of the measured rocking curves of 11.1 and 4.0 seconds of arc for the Ge and Si crystals, respectively.

Characterization of particles was carried out by measuring the intraparticle scattering factor of colloidal silica particles in aqueous 5×10^{-4} M NaCl which had been added to suppress electrostatic interaction between the particles.[9a] The observed scattering intensities in the particle concentration range between 0.00373 and 0.0392 (volume fractions) were extrapolated to zero concentration. When the intensities extrapolated to zero concentration were used, the Guinier plot was linear, which gave a radius value of 0.060×10^{-6} m for a silica sample KE-P10W of Nippon Shokubai Co., Ltd, Osaka. On the other hand, clear deviations from linearity were noticed with unextrapolated intensities. Further, the curve-fitting with a form factor of an isolated sphere gave more precisely the radius to be 0.0560×10^{-6} m and also a standard deviation of the size of 8%.

A salt-free aqueous dispersion of KE-P10W ($\varphi = 0.0376$) gave five peaks at diffraction angles of $(150 \times n)$ seconds of arc with n being an integer, as shown in Figure 3 (curve a). The same profile was also observed at each multiple angle of 60° when the capillary was rotated around its axis (ω), indicating that the crystal is of six-fold symmetry.[9b] Furthermore, the dispersion displayed similarly sharp peaks (curve b) at diffraction angles of $(85 \times n)$ seconds of arc when the capillary was rotated by $(30 + 60 \times m)^{\circ}$, with m being an integer.

It was concluded from all the information that a bcc lattice was maintained in the sample capillary with $[1\bar{1}1]$ direction being parallel to the capillary axis and the profile (a) corresponds to the diffraction from the (110) planes. Further, the first-order peak of the profile (b) was concluded to be the (101) reflection, while the second peak may be the (101) reflection and may be simultaneously the first-order peak of the (020) reflection. The third-order peak is probably due to the (121) reflection. From the peak positions in the profile (a), the interplanar distance d_{110} was determined to be 0.210×10^{-6} m, from which the lattice constant a was 0.300×10^{-6} m and the closest interparticle distance $2D_{\mathrm{exp}}$ was 0.260×10^{-6} m. The average interparticle spacing $2D_0$ for bcc symmetry was 0.290×10^{-6} m. Obviously $2D_{\mathrm{exp}} < 2D_0$, as found out for various cases by us.[10] It is to be emphasized that the inequality relationship is now concluded from several orders of diffraction much less ambiguously than in the previous arguments based on a single peak.

ORIENTATION AND LATTICE STRUCTURE OF MICROCRYSTALS OF COLLOIDAL SILICA PARTICLES, AS STUDIED BY THE USAXS TECHNIQUE: INFLUENCE OF SHAKING

Another interesting finding was that a single crystal of another symmetry could be observed for the same dispersion and at the same concentration but from a different capillary. A bcc lattice of a four-fold symmetry was found with the same lattice constant but the [001] direction was parallel to the capillary axis.[8] It is clear from the crystal geometry that, for these two cases, the (110) planes of the bcc lattice must be parallel to the capillary surface. It should be mentioned that no other orientation could be observed. There remains the question why a large single crystal grew with different symmetries in different capillaries. Our interpretation is as follows: In the initial stage of crystallization, a large number of nascent crystals would be produced in the dispersion as well as near the capillary surface. As a result of the stabilization due to the attraction between charged particles and the glass wall to be mentioned below, their (110) planes are favored to be parallel to the wall. However, at this stage, there is no preference on their orientation, as it has been recently confirmed.[11] All crystals grow according to the Ostwald ripening mechanism and, when they reach the stage at which they are large enough to be affected by a larger glass wall area, a selection process intervenes. Only those crystals survive whose direction is more favored by a larger contact with the glass wall. Thus, we observe a crystal with the $[1\bar{1}1]$ (six-fold symmetry) or [001] direction parallel to the capillary axis, in which three or two of six $\{110\}$ planes are parallel to the wall.

This can be accepted since more of the $\{110\}$ planes can be parallel to the capillary surface in the two orientations than in others. The underlying idea is that the parallelism stabilizes the system. Then, a question arises as to which of the two orientations is more stabilized. A simple consideration of the curved surface of the capillary and crystal geometry reveals that the six-fold symmetry is more favored than the four-fold symmetry (see Figure 3 in Ref. 7 and Figure 3 in Ref. 8).

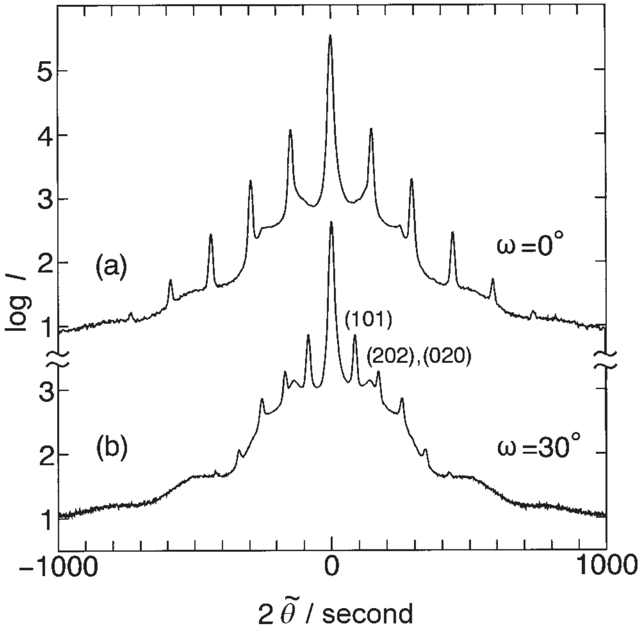

Figure 3. The 1D USAXS intensity $I(2\tilde{\theta})$ in counts per second *versus* the rotation angle $2\tilde{\theta}$ of the crystal on the detector side. Aqueous dispersion of colloidal silica particles (KE-P10W), $\varphi = 0.0376$. Measurements were done 84 days after the dispersion was introduced into the capillary. Temperature: 25 °C. The $2\tilde{\theta}$ is not the true scattering angle 2θ but the angle between a vertical plane including the path of the incident X-ray into the sample and that containing the path of the scattered X-ray. $2\theta = 2\tilde{\theta} / \cos\phi'$, where ϕ' is the angle between the horizontal plane and that defined by the paths of the incident and scattered X-rays. Taken from Ref. 7 by permission of the American Physical Society.

The following experiments[12] seem to provide an answer to the above question. A single crystal was allowed to grow in the capillary at $\varphi = 0.0153$ and then the capillary was violently shaken. The USAXS patterns were measured before and after shaking as functions of the rotation angles around the capillary axis (ω) and that in the plane at right angles to the X-ray beam ($\tilde{\phi}$), where $\omega = 0$ when the scattering was at the maximum and $\tilde{\phi} = 0$ when the capillary was vertical. Before the shaking, four-fold or six-fold symmetry with a lattice constant of 0.440×10^{-6} m was observed. Figure 4 shows the scattering profiles over a period of 1–4 days after the shaking. The profile shown for $\tilde{\phi} = 0$ stayed unchanged between 15 min and 4 days after shaking, indicating that no significant change in the microstructures occurred during this time span. It is remarkable that the same profile was observed for all angles of ω, but it varied with $\tilde{\phi}$. In other words, the new profile is not powder-like, nor due to a single crystal. It was concluded that all the experimental results after the shaking are compatible with a bcc lattice with a lattice constant of 0.430×10^{-6} m and with $[1\bar{1}1]$ being parallel to the capillary axis (six-fold symmetry). Although details should be referred to the original paper,[12] the scattering peaks in Figure 4 could be fitted by a relationship between $2\tilde{\theta}$ and $\tilde{\phi}$ for bcc symmetry.

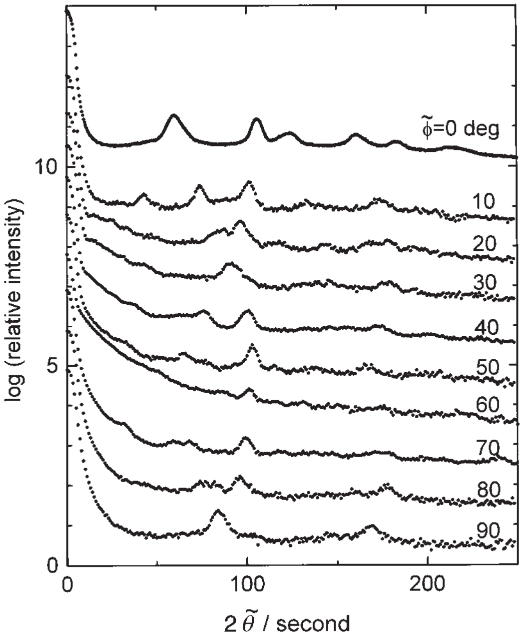

Figure 4. The USAXS intensity $I(2\tilde{\theta})$ in counts per second against the rotation angle $2\tilde{\theta}$ of the Si crystal (detector side) for various $\tilde{\phi}$ of the capillary. The silica concentration (volume fraction) was 0.0153. Taken from Ref. 12 by permission of the American Chemical Society.

Clearly, the large single crystal was broken to produce microcrystals with the same lattice symmetry and the same lattice constant. However, only the six-fold symmetry was observed after shaking, regardless of the symmetry (six- or four-fold) one had before shaking. In the light of the ω independence of the scattering profile, the microcrystals are large in number and their orientation with respect to the capillary axis is the same but the crystals are arranged randomly about the $[1\bar{1}1]$ axis. Figure 5 is a highly schematic view of the orientation of microcrystals in the capillary.

It should be mentioned that, for bcc lattices, the (110) planes are kept parallel to the capillary surface for both six-fold and four-fold symmetries, as shown in Figure 5. This result has been pointed out earlier by several authors. Although they did not mention the reason, the parallelism has much more considerable implications than it may superficially appear, as it will be discussed here. First, let us remind that the (110) planes of bcc lattices are most densely packed. Since the silica particles and glass surface are negatively charged, we questioned why these planes were favored near a similarly charged surface, since a negatively charged surface must repel negatively charged solute entities according to the double layer interaction theory. However, Thomas and Ito independently reported experimental re-

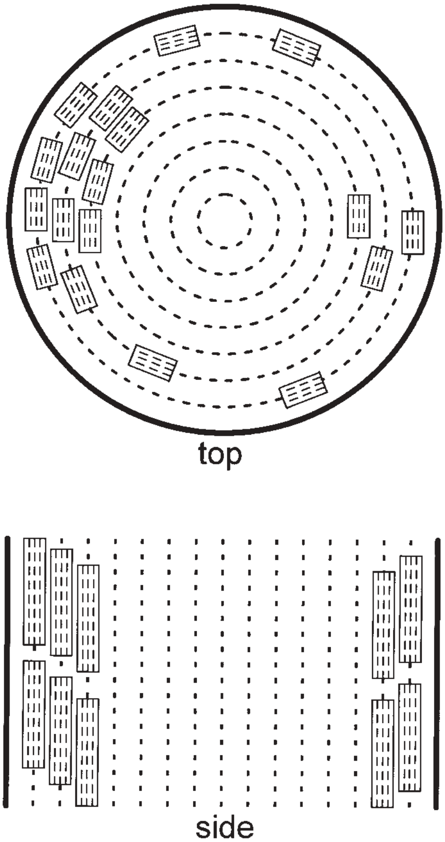

Figure 5. Schematic view of the distribution and orientation of microcrystals shown by rectangles in the capillary (bold lines and curve) after shaking. The (110) planes are denoted by dashed lines. Taken from Ref. 12 by permission of the American Chemical Society.

sults, that question the correctness of the theory. They used the neutron reflection technique for cationic surfactant solutions and the confocal laser scanning microscope for ionic latex particles in dispersion, respectively.[13,14] Their results showed that ionic entities were positively (not negatively) adsorbed near a similarly charged interface. This phenomenon seems to be consistent with the observed orientation. Because of the positive adsorption, the most densely packed planes are favored.

The next question is the origin of positive adsorption. Our tentative interpretation is that the charged entities are attracted by the glass wall through the intermediary of counterions, in other words, counterion-mediated attraction between the charged interface and entities. This is still to be verified experimentally but is consistent with the existing data described by Ito *et al.*

This attraction stabilizes the systems. The more (110) planes are »in contact« with the glass wall, the more strongly the crystals are stabilized. For example, the six-fold symmetry, for which three of six {110} planes are »parallel« to the glass wall, is more stable than the four-fold symmetry with only two of the six being »parallel«. Therefore, after shaking, only the six-fold symmetry, which corresponds to the lowest free energy state, can be observed.

We also studied silica concentrations of $\varphi = 0.0289$ and 0.0380. The same symmetry and orientation were observed for these cases as at $\varphi = 0.0153$. In this concentration range, the closest interparticle spacing $2D_{\mathrm{exp}}$ was smaller than the average spacing from concentration $2D_0$ by 5–9%. This inequality relation has been frequently reported by us for high charge density partcles,[10] indicating the structural inhomogeneity of the dispersion, such as localized ordered structures or voids without particles inside. For example, at $\varphi = 0.0289$, the microcrystals occupy only 74% of the total dispersion volume [= $(2D_{\mathrm{exp}} / 2D_0)^3$ = $(0.280\ \mu\mathrm{m} / 0.310\ \mu\mathrm{m})^3$] while 26% must be occupied by voids and/or free (disordered) particles, according to the mass balance consideration.

GENERAL DISCUSSION

In the above paragraphs, recent USAXS results were reviewed and the importance of the counterion-mediated attraction was emphasized. Although not discussed in the present paper, there are several other advances to be briefly mentioned. The first is the observation of huge and stable voids in macroscopically homogeneous colloidal dispersions.[15] Such a microscopic structural inhomogeneity cannot be explained in terms of the DLVO theory, according to which only repulsive forces exist between two similarly charged particles besides the short-range van der Waals attraction. As a matter of fact, the Monte-Carlo simulation by Tata *et al.*[16] showed that, when the Sogami potential[17] (containing a short-range repulsion and a long-range electrostatic attraction) was used, a homogeneous-to-inhomogeneous transition took place with increasing charge density and ionic strength and voids coexisted with dense ordered and disordered regions. On the other hand, the purely repulsive DLVO potential failed to reproduce the inhomogeneity. Poly(chlorostyrene-styrene sulfonate) particles were synthesized and its dispersions were studied concurrently by the USAXS technique and confocal laser scanning microscope. The glass-like ordering was observed in dilute dispersions, the inequality relationship $2D_{\mathrm{exp}} < 2D_0$ was confirmed, and the void structures were seen. These findings were substantiated by the Monte-Carlo simulation[18] using the Sogami potential.

The second development to be mentioned is the re-entrant phase transition with changing charge density found for silica particle dispersions. By visual observation, supplemented by USAXS measurements, a three-dimensional phase diagram was constructed with salt concentration C_{s}, effective charge density σ_{e}, and particle concentration (volume fraction) φ. The C_{s} values at the boundary between the solid and liquid phases generally first increased with increasing σ_{e} and, passing a maximum around $\sigma_{\mathrm{e}} = 0.4–0.5$ μC/cm^2, decreased between $\varphi = 0.02$ and 0.04.[19] At constant C_{s} and φ, in other words, the liquid-solid-liquid transition takes place with increasing σ_{e}. This trend could not be accounted for in terms of the method of Robins *et al.*[20] using the Yukawa potential, which gave a satisfactory agreement with the observation at very low σ_{e} values. However, it is to be recalled that the re-entrant transition with charge density was reproduced in the homogeneous-to-inhomogeneous transition demonstrated by the Monte-Carlo simulation[16] using the Sogami potential.

A few more words on the simulation. The Monte-Carlo simulation using the Sogami potential was recently extended to cover wider ranges of φ and C_{s}.[21] The computed pair correlation function $g(r)$ showed a fcc crystalline order at high values of φ, which were found to transform to a bcc order upon the lowering of φ. The crystalline order was found to melt into a liquid-like order upon addition of salt. In previous papers, for example in Ref. 20, the Yukawa potential was claimed to be responsible for the formation of bcc and fcc phases and also for the associated order-disorder transition. Now, simulations with the Sogami potential also explain such phenomena equally well.

The simulation in the dilute regime showed vapor-liquid transition upon variation of φ.[21] This transition was noticed experimentally by Tata *et al.*[22] The coexistence of ordered and disordered regions with voids, upon variation of the charge density, was also confirmed by the simulation.

The Yukawa potential or the DLVO potential cannot be claimed to be the only correct one in describing colloidal phenomena because the Sogami potential can afford similarly satisfactory agreement with experiments. The same point was made also for the structure factor, elastic modulus, and thermal expansion of colloidal crystals.[1,3] It should be remembered that the agreement between the Sogami and Yukawa potentials is seemingly true for low charge density particles. When the effective charge density becomes larger, however, the discrepancy between the two potentials becomes outstanding. As mentioned above, void formation and re-entrant transition, which take place at high charge densities, can be accounted for not by the Yukawa potential but by the Sogami potential. Thus, it is clear that the Sogami potential is more realistic than the Yukawa potential.

Finally, it is worth mentioning a recent report by Valachovic[23] who studied solutions of polyamide amine dendrimers. The experimental data obtained for the compact polyelectrolyte system by static and dynamic light scattering techniques were found to be consistent with the two-state structure model. The counterion-mediated attraction causing the structural inhomogeneity thus seems to be quite universal for all ionic species regardless of their geometrical shape and size.

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symmetric, which is due to the smearing effect in the line-focused optical system in the one-dimensional Bonse-Hart camera.

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SAŽETAK

Novija primjena raspršenja X-zraka pod ultramalim kutem na studij privlačenja među česticama i između čestica i površine pod utjecajem protuiona

Norio Ise i Toshiki Konishi

Prikazana je primjena 1D- i 2D-raspršenja X-zraka pod ultramalim kutem (USAXS) na studij strukture razrijeđenih disperzija čestica silike. Koloidni monokristal pokazuje 22 oštra difrakcijska vrha što omogućuje jednoznačno određivanje simetrije rešetke (prostorno centrirana kubična), konstante rešetke (oko 0,3–0,4 μm) kao i kristalnu orijentaciju. Potvrđeno je da je najmanji razmak među česticama u razrijeđenim disperzijama manji od prosječnoga što upućuje na važnu ulogu privlačnih sila utjecanih prisutnošću protuiona. Profil raspršivanja ima šesterostruku i četverostruku simetriju, sa smjerovima $[1\bar{1}1]$ i [001] koji su paralelni s osi kapilare u kojoj se nalazi disperzija. U oba su slučaja najgušće složene plohe (110) bile paralelne s površinom kapilare. Te su plohe bile u kontaktu sa stijenkom što upućuje na privlačnost između negativno nabijene površine i čestica. Nakon potresanja kapilare nađena je samo šesterostruka simetrija, što je razumljivo ako se razmatra znatniji kontakt između (110) plohe i površine kapilare pa je takav sustav stabilniji nego sustav četverostruke simetrije.