

Non-Affine Structural Evolution of Soft Colloidal Crystalline Latex Films under Stretching as Observed via Synchrotron X-ray Scattering

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A polymer dispersion consisting of soft latex spheres with a diameter of 135 nm was used to produce a crystalline film with face-centered cubic (fcc) packing of the spheres. Different from conventional small-molecule and hard-sphere colloidal crystals, the crystalline latex film in the present case is soft (i.e., easily deformable). The structural evolution of this soft colloidal latex film under stretching was investigated by in-situ synchrotron ultra-small-angle X-ray scattering. The film exhibits polycrystalline scattering behavior corresponding to fcc structure. Stretching results not only in a large deformation of the crystallographic structure but also in considerable nonaffine deformation at high draw ratios. The unexpected nonaffine deformation was attributed to slippage between rows of particles and crystalline grain boundaries. The crystalline structure remains intact even at high deformation, suggesting that directional anisotropic colloidal crystallites can be easily produced.

Colloidal crystals have gained much attention not only because of their relevance to many fundamental physical studies on crystallization and jamming^{1–5} but also because of their potential use in photonic applications. Although there are many ways to produce colloidal crystals, the most straightforward one is simply carefully drying a latex dispersion. Latexes are aqueous dispersions of surface-charged polymeric particles of colloidal size and are widely used in the paint industry.⁶ The polymeric particles are periodically arranged at higher concentrations because of the electrostatic interactions between the particles; this phenomenon has been known for a long time.⁶ The periodicity is retained even after completely drying the system.^{4,5} The densely packed colloidal particles normally deform into polyhedra upon drying because of the low glass-transition temperature of the polymer and capillary forces.^{7–9} Finally, the polymeric chains interdiffuse between adjacent particles, forming a mechanically stable film.^{10–12} However, because the latex film also contains

nonpolymeric material such as salt and surfactants, which to a large extent are located in the interstices between the closely packed particles, the internal structure of the latex film can be easily investigated by scattering techniques. For example, it is found, that the crystalline order is of the face-centered cubic (fcc) type and that the initial packing structure is still detectable after prolonged annealing above the glass transition.^{4,5} Latex films thus provide excellent examples of crystalline systems where the building blocks (“the atoms”) of the crystallites are soft particles. To our knowledge, most of the studies in the field were focused on structure development during film formation.⁶ Relatively little attention was paid to the microstructural evolution of the dried film upon deformation, but compare refs 13 and 14.

In this letter we report on the deformational behavior of a soft colloidal crystalline structure of a latex film during stretching by means of in-situ synchrotron ultra-small-angle X-ray scattering (USAXS). USAXS measurements indicate that the crystalline fcc structure is preserved after film formation despite the low glass-transition temperature of the latex particles. This soft colloidal crystalline latex film exhibits high deformability (draw ratio larger than 3). Different from conventional crystalline materials, the crystalline lattice deforms largely although it follows

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(1) Trappe, V.; Prasad, V.; Cipelletti, L.; Segre, P. N.; Weitz, D. A. *Nature* **2001**, *411*, 772.

(2) Gasser, U.; Weeks, E. R.; Schofield, A.; Weitz, D. A. *Science* **2001**, *292*, 258.

(3) Pusey, P. N.; van Megen, W.; Bartlett, P.; Ackerson, B. J.; Rarity, J. G.; Underwood, S. M. *Phys. Rev. Lett.* **1989**, *63*, 2753.

(4) Rieger, J.; Haedicke, E.; Ley, G.; Lindner, P. *Phys. Rev. Lett.* **1992**, *68*, 2782.

(5) Rieger, J.; Dippel, O.; Haedicke, E.; Ley, G.; Lindner, P. In *Colloidal Polymer Particles*; Buscall, R., Goodwin, J. W., Eds.; Academic Press: London, 1994; p 29.

(6) Winnik, M. A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 192.

(7) Visschers, M.; Laven, J.; German, A. L. *Prog. Org. Coat.* **1997**, *30*, 39.

(8) Routh, A. F.; Russel, W. B. *Ind. Eng. Chem. Res.* **2001**, *40*, 4302.

(9) Routh, A. F.; Russel, W. B. *Langmuir* **1999**, *15*, 7762.

(10) Eu, M. D.; Ullman, R. *Small-Angle Neutron Scattering Studies of Polymer Interdiffusion during Latex Film Formation*; American Chemical Society: Washington, DC, 1996.

(11) Joanicot, M.; Wong, K.; Cabane, B. *Macromolecules* **1996**, *29*, 4976.

(12) Oh, J. K.; Tomba, P.; Ye, X. D.; Eley, R.; Rademacher, J.; Farwaha, R.; Winnik, M. A. *Macromolecules* **2003**, *36*, 5804.

(13) Rharbi, Y.; Boue, F.; Joanicot, M.; Cabane, B. *Macromolecules* **1996**, *29*, 4346.

(14) Oberdisse, J. *Macromolecules* **2002**, *35*, 9441.

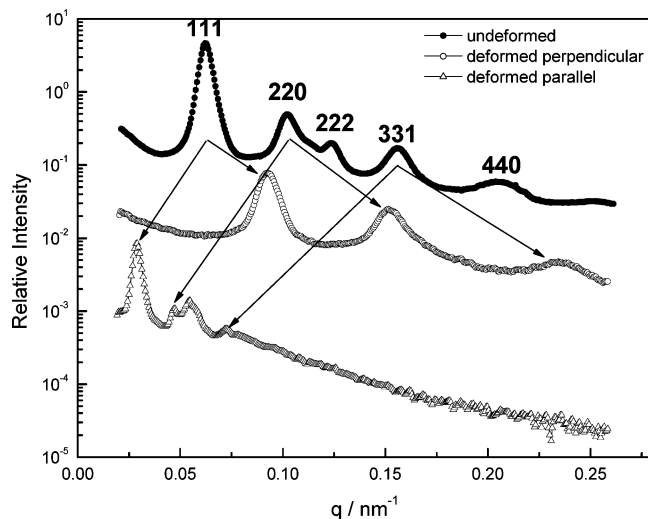


Figure 1. Integrated 1D ultra-small-angle X-ray scattering intensity distribution of the undeformed latex film (●) and the film after a deformation of $\lambda_{m,v} = 3$ in directions perpendicular (○) and parallel (△) to the stretching. The Miller indices of a fcc crystalline structure are indicated. Arrows indicate the shifts of the (111), (220), and (331) peak positions after deformation.

a nonaffine deformation with respect to the macroscopic draw ratio. This observation can be explained only by assuming that a slippage mechanism along the rows of particles or the grain boundaries of the colloidal crystallites inside the latex film is active during deformation.

Experimental Section

An aqueous neutral (pH 6–7.5) latex dispersion consisting of styrene/butadiene (55/45 w/w) copolymer particles was used in this study. The latex was prepared through a seeded semibatch emulsion polymerization process by continuously feeding monomers and initiator. Sodium lauryl sulfate was used as the emulsifier. The solid content was 50%. The glass-transition temperature of the copolymer is 5 °C. The diameter of the latex particles is 135 nm as determined by laser light scattering. The latex films were obtained by evaporating the water from the latex dispersion at room temperature for 4 weeks, yielding a transparent film of about 1.5 mm thickness. Online tensile synchrotron USAXS measurements were carried out at BW4, HASYLAB at DESY, Hamburg, Germany. The X-ray wavelength was $\lambda = 1.3808$ Å. The sample-to-detector distance was $L_{SD} = 12\,533$ mm. The effective scattering vector q ($q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle) at this distance ranges from 0.025 to 0.25 nm^{-1} . Tensile specimens of 10 mm width were cut from the latex film and mounted onto a tensile tester at the beamline.

Crystalline Structure

It has long been established that latex films possess internal ordered structure despite their optically transparent appearance. The crystalline structure in the current system was elucidated by the USAXS pattern of the undeformed latex film exhibiting Debye–Scherrer rings of a polycrystalline material. Figure 1 presents the 1D (azimuthally averaged) USAXS intensity distribution of the latex film where five X-ray diffraction peaks are clearly identifiable. The position of the X-ray diffraction peaks clearly indicates an fcc structure of the colloidal domains. The Miller indices of the corresponding peaks were also included in the plot. Some of the fcc peaks are absent because of the interplay between the form factor of a single latex particle and the structure factor of the fcc lattice.^{4,5} The latex film is polycrystalline as evidenced by the 2D USAXS patterns shown in Figure 2. USAXS patterns in Figure 2 exhibit typical powder diffraction features of the Debye–Scherrer ring type. No

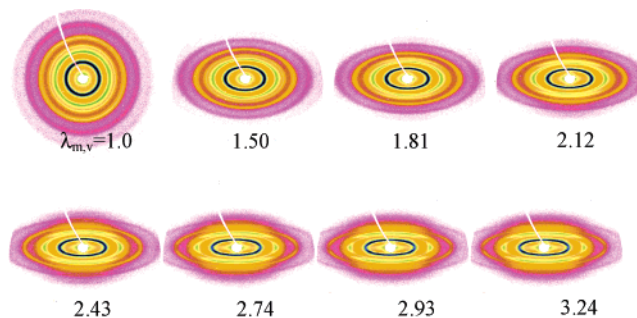


Figure 2. Selected USAXS patterns taken during stretching of the latex film indicating the structural evolution of the colloidal crystallites under extension. The macroscopic elongation ratio ($\lambda_{m,v}$) is indicated on each pattern. (The tensile direction is vertical.)

preferential orientation of the crystallographic planes is observed. It must be mentioned that from the diffraction data one obtains a center-to-center distance of 124 nm between two adjacent particles in the film. This distance is smaller than the diameter of the original particles in the dispersion because of the polyhedral shape of the particles after film formation.

Tensile Deformation

Unlike conventional crystals made from molecules or hard-sphere colloidal crystals, the building block of the crystalline latex film under study is soft. It is thus interesting to investigate how the crystalline structure changes under external stress. It is well known that the pure crystallographic deformation ratio of conventional crystals and hard-sphere colloidal crystals is quite limited (i.e., not over a few percent).¹⁵ The macroscopic deformation in those systems is normally accomplished by the development of dislocations and slippage of crystalline grain boundaries.^{15–17} In the current sample, the deformation of the building block of the colloidal crystallites—the soft colloidal particle—is much more easily accomplished than in other crystalline systems. To identify the deformation mechanism in soft colloidal crystals, it is therefore necessary to compare the crystallographic deformation ratio, as indicated by the positions of the Bragg peaks, and the macroscopic one. Figure 2 presents selected USAXS patterns of the stretched latex film taken at different macroscopic draw ratios ($\lambda_{m,v} = l/l_0$ where l_0 is the length of the latex film before stretching and l is the length of the latex film after deformation). The film was stretched up to 324%, showing excellent deformability. The Debye–Scherrer rings deform into ellipsoids during stretching, indicating that the crystal structure deformed. It must be emphasized that the scattering patterns at larger draw ratios do not show additional scattering intensity close to the beam stop, suggesting that no cavitation occurred during the process, at least not on the length scales accessible with the present setup (i.e., up to 500 nm). To quantify this crystallographic deformation, the draw ($\lambda_{c,v}$) and compression ($1/\lambda_{c,h}^2$) ratios of the crystalline lattices along and perpendicular to the stretching direction were calculated by integrating the scattering intensity within a thin rectangular box along the respective directions, yielding 1D scattering intensity distributions as a function of the scattering vector. The scattering peak positions were used to derive the corresponding crystallographic distances of the (111), (220), and (331) planes along and perpendicular to the stretching direction. As was shown in Figure 1, these three diffraction peaks can be easily followed

(15) Nadai, A. *Theory of Flow and Fracture of Solids*, 2nd ed.; McGraw-Hill: New York, 1950.

(16) Men, Y.; Strobl, G. *Macromolecules* **2003**, *36*, 1889.

(17) Men, Y. F.; Rieger, J.; Strobl, G. *Phys. Rev. Lett.* **2003**, *91*, 095502.

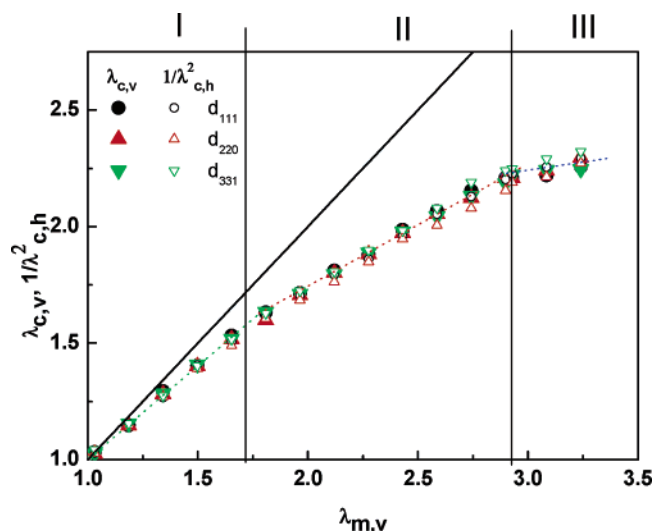


Figure 3. Crystallographic draw and compression ratios of the colloidal crystallites along ($\lambda_{c,v}$) and perpendicular ($1/\lambda_{c,h}^2$) to the stretching direction as a function of the macroscopic draw ratio ($\lambda_{m,v}$). The respective values are calculated from the shifts in the positions of the Bragg peaks. The solid line indicates the case of affine deformation. The three regions I, II, and III can be separated according to the increasing nonaffine deformation behavior of the soft colloidal crystal.

after large deformation both along and perpendicular to the stretching direction. The results are shown in Figure 3. One observes that the draw and compression ratios of different crystalline lattices follow the same trend, indicating that the volume of the crystallites in the system was conserved upon deformation. But more interestingly, the deformation ratio of the colloidal crystallites does not follow affine behavior with respect to the macroscopic draw ratio. The deformation behavior can be divided in three different regions. (1) At small draw ratios ($\lambda_{m,v} < 1.7$), most of the macroscopic deformation was accomplished by the deformation of the crystalline cells. (2) At intermediate draw ratios ($1.7 < \lambda_{m,v} < 3$), the fraction of nonaffine deformation progressively increases. (3) Finally, at large draw ratios ($\lambda_m > 3$), further deformation was mainly accomplished by the nonaffine deformation mode. The nonaffine deformation mode can be mediated either by the development of screw dislocations along specific crystallographic directions or the slippage of the grain boundaries of the crystallites. The appearance of screw dislocations is considered not to be favored in the present case because the interdiffusion of the polymeric chains between adjacent particles creates effective mechanical linkages among the crystalline lattices which in turn prevent the relative movement of single particles in the crystallites. Thus, it is proposed that the nonaffine deformation proceeds via slippage of rows of adjacent particles. We present in Figure 4 a schematic representation of the deformation mechanism of the latex film while being stretched. The drawing in the upper part of Figure 4 gives the structure of the undeformed latex film. The middle drawing presents the structure of the system at small deformation where the coupling between the crystallites is strong enough to ensure that the deformation of the crystalline lattice proceeds affinely. However, when the draw ratio is further increased, the system reacts in such a way that rows of particles pass each other, a phenomenon that is well known from fibers.^{18–20} The coupling mediated by interdiffused polymer chains, between adjacent rows, is not strong

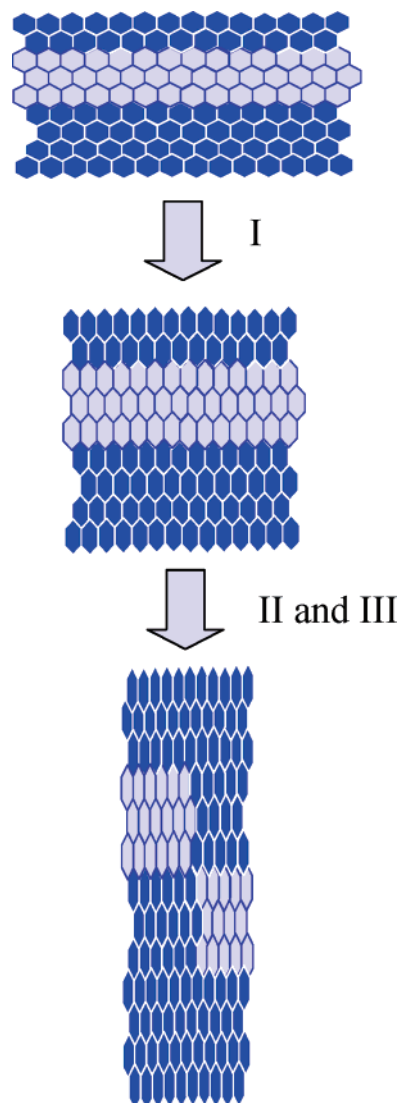


Figure 4. Schematic representation of the structural evolution of the crystalline latex film. Top, the undeformed state; middle, at small to moderate deformation; bottom, at large deformation where a group of particles slipped out of its original position. The marked particles are of a different shade for better visualization of the phenomenon.

enough to prevent slippage, but capillary forces prevent the formation of voids. It can clearly be excluded that such slippage boundaries run through the whole system; this would lead to macroscopic failure. Again referring to the deformation of fibers,¹⁸ it is assumed that slippage occurs locally, comprising a limited number of particles.

In summary, in this letter the evolution of the colloidal crystalline structure in a soft latex film upon stretching was investigated by means of synchrotron USAXS. In the polycrystalline fcc films, the deformation of the crystalline lattices was nonaffine with respect to the macroscopic draw ratio despite the softness of the crystalline lattice building blocks. This nonaffine behavior was attributed to the activation of the slips along crystal planes or grain boundaries. It was shown that the crystalline structure of the soft latex film is retained even at high deformation ratios. This study suggests an easy way to produce colloidal crystals with different optical properties in the respective

(18) Peterlin, A. *Colloid Polym. Sci.* **1975**, 253, 809.

(19) Men, Y. F.; Rieger, J.; Lindner, P.; Endeler, H. F.; Lilge, D.; Kristen, M. O.; Mihan, S.; Jiang, S. C. *J. Phys. Chem. B* **2005**, 109, 16650.

(20) Rieger, J. In *Neutrons, X-rays, and Light Scattering Methods Applied to Soft Condensed Matter*; Lindner, P., Zemb, Th., Eds.; North-Holland: Amsterdam, 2002; p 481.

directions by simply mechanically stretching an isotropic colloidal crystalline material.

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