RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 1 1 JULY 1991-I

Localized ordered structure in polymer latex suspensions as studied by a confocal laser scanning microscope

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(Received 8 February 1991)

By using a confocal laser scanning microscope and a digital image analyzer, the influence of a glass-suspension interface on colloidal crystals was studied. Particular attention was paid to the interparticle distance ($2D_{expt}$) in the ordered structure and the crystallization process. The $2D_{expt}$ was insensitive to the distance from the interface up to about 40 μm. The crystallization process of the ordered structure was characterized by a strong anisotropy originating at the glass-suspension interface.

Localized ordered structures in polymer latex suspensions have been intensively studied by various methods[1-3] including direct observation by an optical microscope (used as an ultramicroscope).[4-8] A weak long-range electrostatic attraction, in addition to a short-range strong repulsion, between highly charged monodisperse particles plays an important role.[9,10] The direct observation is an excellent technique, providing both real-time and real-space information on the particle distribution in the suspension. However, the observation is limited to the region close to (at most 10 μm, usually 1–2 μm away from) a cover glass (container wall) and we were therefore concerned about whether the ordering phenomena were affected by the glass-suspension interface. Recently, a laser scanning microscope with confocal optics that enables observation of the particles away from the cover glass has been developed.[11] Using the scanning microscope, we studied the colloidal crystals in regions more distant from a cover glass. Particularly, the influence of the glass-suspension interface on the interparticle distance and the crystallization process of the ordered structure have been investigated.

By applying the laser scanning microscope to the direct observation, a high-quality image of the region away from the cover glass can be obtained. This great advantage can be achieved by the following characteristics of the scanning microscope. First, by using optics of a high numerical aperture (NA), only a very narrow part of the object is illuminated by the laser beam ($\sim$0.5 μm in diameter). Obviously, there might be a small obstruction caused by the light scattered from the surrounding background. Second, the light scattered by the object is picked up by a photodetector and the image is composed electronically. This makes it possible to display small differences in contrast on a monitor screen. In the present study, to further improve these advantages, a confocal arrangement of optics was introduced.[11] By using these optics, obstruction to the observation caused by the beam scattered from an object outside the focal volume can be eliminated. The maximum distance which can be reached depends mainly on the concentration of the latex suspension, the size and refractive index of the particle, and the power and wavelength of the laser.

The polystyrene latex used (N300, 0.32-μm diameter, surface charge density of 0.7 μC/cm^2) was a commercial product of Sekisui Chemical Company, Osaka, Japan. The laser scanning microscope (LSM) (Carl-Zeiss, Oberkochen, Germany) was used with an oil immersion objective of 100×, a NA of 1.3, and with a 5-mW Ar laser as a light source. Observed micrographs were analyzed by a digital image processor IBAS (Carl-Zeiss) and further analysis was performed by a workstation Sun 4 (Sun Microsystems Inc., Mountain View, CA). The resolution of the image processor depends on magnification and was 0.1 μm in the present work. The latex sample was carefully purified before use, as described previously.[8] To eliminate the possibility of gravitational sedimentation of the particles, all experiments were carried out in an H_2O-D_2O mixture as the suspension medium. The specific gravity of the suspension medium was checked before and also after the experiment to be 1.05, which was the same as the polystyrene latex particle. A suspension cell of Pyrex glass (22 mm in diameter and 10 mm in height) was used. The top of the cell was made from a cover glass for the microscopic observation. The present microscope is not of a reversed type. The laser beams reach particles from the top of the suspension; thus, the upper part of the suspension could be studied by the present method, while the bottom part could be observed by the Carl-Zeiss Axiomat IAC, which was used in previous experiments.[5-8] For the suspension with a latex concentration of about 1% by volume, the particle distribution up to 40 μm away from the cover glass could be observed.

Previously we found that, at lower concentrations, an inequality $2D_{expt} < 2D_0$ holds, where $2D_{expt}$ is the measured interparticle distance of the ordered structure and $2D_0$ is that calculated from the initial concentration.[9] This inequality was one of our main rationales for accepting a long-range attraction between the particles. However, the influences of the sedimentation of the particles and the glass-suspension interface on $2D_{expt}$ should have been taken into consideration. In the present experiment, the former was eliminated by the density-matching method using an H_2O-D_2O mixture medium.

Table I shows $2D_{expt}$ of the ordered structure at various distances (D_z) from the top of the observation cell. The measurement was carried out as follows: The sample was placed in the cell with analytical grade mixed bed ion-

TABLE I. Interparticle distances of the ordered structure at various distances from the top of the cell. (Latex, N300; concentration, 0.8 vol%; $2D_0$, 1.4 μm.)

D_z (μm)	$2D_{expt}$ (μm)
1	1.3
10	1.3
20	1.3
30	1.3
40	1.3

exchange resin beads [AG501-X8(D), Bio-Rad Laboratories, Richmond, CA] three days before the observation. The observation was performed from the upper part of the cell by the scanning microscope. $2D_{expt}$ was determined by two-dimensional (2D) Fourier analysis of the micrograph showing the particle distribution.[7] Then 2000–3000 particles were treated to obtain each $2D_{expt}$. $2D_{expt}$ (1.3 μm) did not change with D_z and was smaller, though slightly, than $2D_0$ (1.4 μm). The rather small difference between $2D_{expt}$ and $2D_0$ compared with the previous reports might be due to a relatively small surface charge density of the particles used. The effect of the glass-suspension interface on the interparticle distance is not serious.

Crystallization of the ordered structure in the z direction was studied as follows: First, NaCl was added to a purified and ion-exchanged suspension to adjust the salt concentration to $1.0\times10^{-4}M$. The ordered structure which existed in the suspension was destroyed by the added salt. Then, the suspension was introduced into the observation cell with a definite amount (0.3 g/cm^3) of ion-exchange resin beads [AG501-X8(D)]. The added salt was removed from the suspension by the ion-exchange resin beads in about 10 min.[12] The time evolution of the particle distributions at various D_z was observed by the scanning microscope and recorded on a video tape.

As was fully described previously,[12,13] the particles showing Brownian motion at the onset of crystallization began to form 2D hexagonal arrangements in a plane parallel to the cover-glass surface. After the formation of the first layer, the following layers were formed consecutively, layer by layer, from the region close to the cover glass toward the region inside the suspension. In Table II, the number and D_z of the formed layers are listed. The number of the layers increased with time, and after 6 h, more than 22 layers were formed. It is obvious that the formation of the ordered structure is strongly affected by the glass-suspension interface. This may be due to the suppressed kinetic disturbance from the glass-suspension interface in the z direction; inside the suspension, particles are subject to three-dimensional disturbances, whereas those in close proximity to the interface suffer only from disturbance along two horizontal directions.

Figure 1 shows the computer graphs displaying the particle distributions of different layers at a fixed position 6 h after the onset of the deionization. It took about 5 min to complete the observation for 22 layers. The superimposed triangles in Fig. 1 were determined by computer, as described in a previous paper.[13] These triangles were de-

TABLE II. The distance (D_z in μm) of formed layers from the glass-suspension interface after the onset of the deionization. (Latex, N300; concentration, 0.7 vol%; $2D_{expt}$, 1.3 μm; $2D_0$, 1.5 μm.)

Layer	3.0 h	4.0 h	5.0 h	6.0 h	8.5 h	(ΔD_z) [a]
1	1.2	1.2	1.2	1.3	1.2	1.2
2	3.1	3.0	2.7	2.6	2.4	1.1
3	4.2	4.3	4.0	4.3	3.5	1.2
4	5.4	5.5	5.4	5.7	4.7	1.6
5		6.5	6.8	6.8	6.3	1.4
6		8.0	8.3	8.1	7.7	1.3
7		9.6	9.8	9.2	9.0	1.3
8		10.7	10.9	10.3	10.3	1.3
9		12.0	12.3	11.8	11.6	1.3
10		13.4	13.9	13.0	12.9	1.4
11		15.0	· · ·	14.7	14.3	1.6
12			16.4	· · ·	15.9	1.3
13			17.4	17.2	17.2	1.1
14			18.8	18.9	18.3	1.1
15			20.4	20.2	19.4	1.8
16			21.7	21.5	21.2	1.5
17			23.3	22.7	22.7	1.6
18			24.8	24.1	24.3	1.3
19			26.3	25.7	25.6	1.1
20				· · ·	26.7	1.2
21				28.4	27.9	1.1
22				29.8	29.0	

[a]The last column gives the interlayer distance in μm.

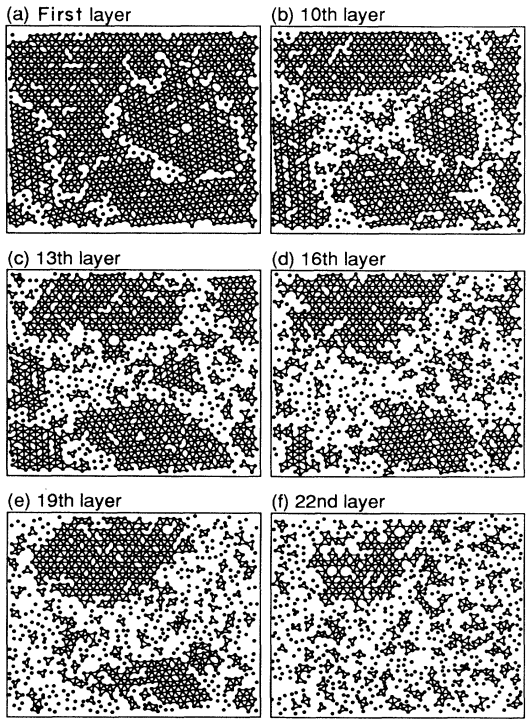

FIG. 1. Computer graphs showing the particle distributions and elementary units in various layers 6 h after the deionization started. Latex, N300; latex concentration, 0.7 vol%; $2D_{expt}$, 1.3 μm; $2D_0$, 1.5 μm.

fined as elementary units of the ordered structure because a regular hexagonal arrangement corresponds to six regular triangles. $2D_{expt}$ was determined for each layer by 2D Fourier analysis. During the growth, $2D_{expt}$ did not change with time or with D_z. The size of the ordered structure in each layer became smaller with increasing D_z. This again shows that crystallization of the ordered structure proceeded, layer by layer, from the region close to the cover glass to the region inside the suspension. The number of particles observed in the field of view increased with decreasing D_z. A similar change was observed in previous work,[12,13] which led to the impression that crystallization was due to gravitational sedimentation of the latex particles. The present observation shows that this impression is not justified; the increase in the number is due to a concentration effect (due to an interparticle attraction) and rearrangement of the particles.[12]

By 8.5 h after the onset of the deionization, the formation of the first 22 layers next to the cover glass was almost complete. Every layer was observed to be covered with a close-packed hexagonal arrangement of the particles just as in the case of Fig. 1(a). When a fcc lattice is formed, the distance between neighboring (111) planes should be $\sqrt{6}/3 \times 2D_{expt}$. However, the interlayer distance (ΔD_z), which is shown in Table II for 8.5 h, was larger, in general, than that predicted from $2D_{expt}$ for the formed layers (1.1 μm). This might be mainly due to the incompleteness of the layer-layer packing. Figure 2 shows the particle distributions of two consecutive layers (6th and 7th layers) at 8.5 h plotted on the same frame. The fcc symmetry is not yet fully developed: The particles in the 7th layer are not always found at the centers of the regular triangles of the 6th-layer particles, as expected for fcc symmetry. Sogami and Yoshiyama have shown by Kossel line analysis that the crystallization process in the polymer latex suspensions can be classified into two stages:[14] layer-structure and cubic-structure stages. The former is characterized by strong anisotropy originating at the glass-suspension interface which initiates the formation of the 2D hexagonal close-packed layers. In this stage, the correlation between the layers is still weak. In the later stage, thermal agitation and interaction among the particles rectify the anisotropy gradually, and complete the ordered structure with the cubic symmetry. In our case, the former stage was almost completed by 8.5 h, at least for the first 22 layers.

In summary, the influence of the glass-suspension interface on the ordering phenomena in polymer latex suspensions has been examined. Confocal laser scanning microscopy turned out to be a powerful method which allowed direct observation of the region inside the suspension. The observed insensitivity of $2D_{expt}$ to D_z confirmed that the inequality $2D_{expt} < 2D_0$ was also valid for the region inside the suspension and was not due to the influence of the glass-suspension interface. Furthermore, the present report using the density-matching method and the laser scanning microscope excluded the possibility that the colloid crystal growth and the inequality relation were due to gravitational sedimentation of the (polystyrene-based) latex particles in aqueous media. These findings, together with other characteristics of the suspensions, such as the coexistence of ordered and disordered regions,[9] indicate the existence of a long-range attraction between the particles.

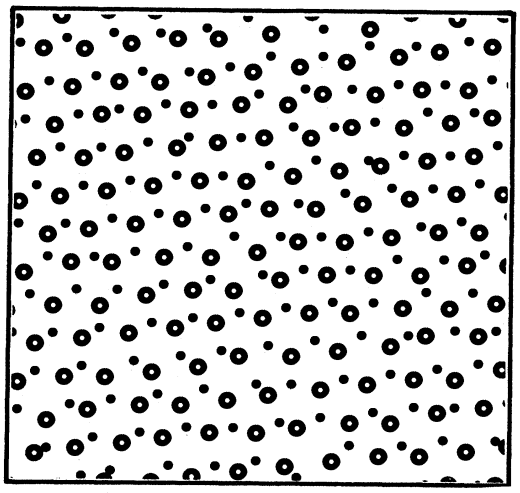

FIG. 2. Computer graphs showing particle distribution 8 h and 30 min after the deionization started. Two consecutive layers are plotted on the same plane. (○) 6th layer; (●) 7th layer. Latex, N300; latex concentration, 0.7 vol%; ΔD_z, 1.3 μm; $2D_{expt}$, 1.3 μm; $2D_0$, 1.5 μm.

The glass-suspension interface played a significant role in the crystallization process of the ordered structure. Consecutive formation of layers consisting of a hexagonal close-packed arrangement of the particles was observed. The ordered structure formed showed 2D symmetry parallel to the cover glass with loose packing between the layers in the z direction. This layer-structure stage should be followed by transitions to form complete cubic symmetry, which will be investigated further.

This work was generously supported by the Ministry of Education, Science and Culture of Japan (Grants-in-Aid for Specially Promoted Research No. 59065004 and No. 63060003). Special thanks are expressed to Carl-Zeiss Co., Ltd. for allowing us to use the laser scanning microscope.

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