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On the Dynamic Character of "Ordered" Structure in Polymer Latex Suspensions

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Abstract: A detailed microscopic study on polymer latex suspensions has been carried out. Particular emphasis is placed on the dynamic aspects of the ordered structure by using video imagery and an image data analyzer. This technique allows us to treat a large number of particles (usually 200 particles) over a longer time span, which improves considerably the reliability of the data compared to the almost "manual" treatment for a very limited number of particles as in our previous papers. The variation (actually disappearance) of localized ordered structures is demonstrated. The particles in the border regions between the ordered and disordered structures are also shown to be dynamic. The thermal motion of the particles in the ordered regions was found to be substantial at low concentrations. The thermal motion was found to be considerable at 10 and 60 °C but not so pronounced at 30 °C, which can be understood when the temperature dependence of the dielectric constant of water is taken into consideration. The motion of the particles in the coexisting ordered and disordered structures is compared. The results of the dynamical study indicated that a clear distinction must be made between the two coexisting structures, although the ordered structure is far from an ideal lattice.

I. Introduction

The ordering phenomena of ionic species in dilute solutions have recently been investigated intensively.[1] Among them the ordering of polymer latex particles in suspension has been verified directly with the aid of an ultramicroscope. The "crystal" (or ordered region) structure has been established precisely by using the scattering technique[2] and pseudo-[3] and intrinsic[4] Kossel line analysis. In most of the previous work, however, attention was paid to the static aspect of the ordering phenomena. One of the few exceptions is the (phase contrast) microscopic observation by Luck,[5] who described the variation of "crystal" size with time. Some time later, Hachisu et al. reported that the ordered regions coexist with the disordered region and furthermore that at one moment an ordered portion disintegrates into a disordered one and at the next moment an ordered aggregate appears in another place.[6] The coexistence of the ordered and disordered structures was confirmed not to be due to the gravitational sedimentation of (polystyrene-based) latex particles by using mixtures of light and heavy water to adjust the difference in the specific gravities of the particles and the solvent and the existence of non-space-filling, localized ordering (the two-state structure) was noted.[7-10] This confirmed our previous notion that there is a medium-range Coulombic attraction between particles, though similarly charged, in addition to the short-range Coulombic repulsion. In this study, fluctuation of the ordered structure was also noticed, which confirms Hachisu's observation. For example, we observed that some particles in the boundary region between the ordered and disordered structures "evaporated" from the solid-like ordered regions into the gas-like disordered regions, whereas some particles in the disordered regions "condensed" in the ordered regions. This suggests that the ordered structure is not at all static but quite dynamic, at least at relatively low concentrations such as 2%.

As a third example, we show the dynamic aspects of latex particles mentioned in our preliminary paper.[9] In this work, the particles in the ordered regions were found to show substantial thermal motion around their lattice points. However, the analysis mentioned above was done by reproducing the trajectory of the centers of a few particles with the aid of cinematography, virtually "by hand".

In the present paper, we discuss the dynamic aspects of the latex ordering by using modern video imagery and an image data analyzer. This technique, which was partly described in a recent paper,[10] has enabled us to follow a larger number of particles over a longer time span than before, thus improving the reliability of the data obtained considerably.

II. Experimental Section

A. Materials. The latex particles used were commercial products of Dow Chemical Company, Midland, MI (D-series), and Sekisui Chemical Company, Osaka, Japan (N-series), and our own products (SS-43 and SS-45). The SS-series was obtained by copolymerization of styrene and styrenesulfonate with potassium persulfate in methanol–$\mathrm{H_2O}$ as the initiator, with no emulsifier added. The latex suspensions were purified by ultrafiltration with an Amicon Model 202 and Diaflo XM300 with Milli-Q reagent grade water and subsequent deionization by ion-exchange resins.[10] In some runs, a new deionization process was introduced. Previously, deionization was carried out by simply mixing the suspensions and the ion-exchange resins and letting the mixture stand. However, in the present work, the latex container was rotated by placing it between parallel cylinders which rotated in the same direction. This considerably shortened the purification time. This deionization process was finished when the ion-exchange resins started to "float" in the suspensions. This statement requires detailed explanation. The ion-exchange resin particles have a specific gravity of 1.2–1.4 and a diameter of about 0.5 mm. Thus in aqueous suspensions of polystyrene-based latex particles (specific gravity of about 1.05), the resin particles are at the bottom of the suspension container, when the suspension is not purified. However, as the deionization proceeds, in other words, when the three-dimensional lattice-like structures develop, say after 1 week, the resin particles do not sediment down but "float" in the latex suspension when the container is allowed to stand after violent shaking. This phenomenon has already been described.[11] Our interpretation is that the sedimentation of the

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[11] This interpretation seems to be substantiated by our recent dynamic light scattering experiments (ref 13), which showed diffraction peak(s) only when the suspension was purified to such an extent that the floating started to be observed, and diluted for the scattering experiments.

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Table I. Properties of Polymer Latex Used

latex	diameter (μm)	no. of strong acid groups per particle[a]	charge density (μC/cm^2)
Dow samples			
D1A92	0.5	1.3×10^5	2.8
D1B34	0.25	2.2×10^4	1.9
Sekisui samples			
N300	0.3	2.8×10^4	1.3
N400	0.4	2.2×10^5	6.9
our own samples			
SS-43	0.41	3.0×10^5	9.0
SS-45	0.5	6.5×10^5	13.3

[a] Strong acid groups imply sulfonate and sulfate groups.

resin particles is almost completely hindered by the three-dimensional network structure that is formed by latex particles, because the dimension of the resin is larger than the interparticle distance (about 1 μm for particles used in the present paper as will be described below) in the structure. Thus the floating phenomenon of resin particles is a sensitive, though not perfect, indicator of the degree of deionization from latex suspensions. After this stage of purification, the suspensions were introduced into the observation cell as described in the previous paper[10] together with Bio-Rad ion-exchange resin beads [AG501-X8(D)], which had been washed with the freshly obtained Milli-Q water. As before,[9] the Bio-Rad resin was put in a small gauze bag which was held in the suspension. The whole observation cell with the suspension and the ion-exchange resin bag was then shaken by using an Eyela shaker ("Mini" (SS-80), Tokyo Rikakiki Co., Ltd., Tokyo) for 6 h at room temperature. After this process, the cell was kept standing and microscopic observation was started.

As we mentioned previously,[14] the latex particles under consideration are not as stable as thought previously. The sulfate groups from the potassium persulfate initiator were assumed to be oxidized first to OH groups and finally to COOH groups,[15] a transformation that has been reported to be fast.[16] Thus, the titration of the surface charge should be done immediately before or immediately after microscopic observation. The charge density values given in Table I were those obtained in March 1986, when the microscopic investigation in the previous[10] and present papers was in progress. It is thus believed that these values correspond correctly to the true charge states of the latices. If the SO_4H groups of the particles had been oxidized so extensively, the particles would lose most of their charges. It would be then unfeasible to obtain reliable information on the real nature of the interparticle interaction by using such latex systems. (It is to be noted that, when the oxidation is so extensive, the suspensions might become unstable to such an extent that the particles sediment down in acid pH, since the COOH groups do not dissociate. Actually styrene–*acrylate* latex particles studied before[17] precipitated very easily.) The reported hydrolysis rate of SO_4H groups on the latex surface varies from author to author and from latex to latex, as reviewed by Vanderhoff et al.[16] Therefore, it is best to carry out the titration just before or after the microscopic study.

After the micrographs were taken and stored on video tape, the computer work described below was initiated.

B. Microscopic Observation. The microscopes used were a CARL-ZEISS Axiomat IAC, Oberkochen, FRG, and an Olympus microscope Model MG, Tokyo, Japan, as described previously.[10] The observation was made for a horizontal plane or for a vertical plane. The particle distribution in the suspensions was displayed on a TV monitor (SONY PVM-171) with a TV camera (HAMAMATSU C1965.T IKEGAMI CTC-2600). The image treatment was performed with a video tape recorder (SONY VO-5850), a video disk recorder (VICTOR VM-1000M), and an image data analyzer (CARL-ZEISS IBAS). The video image was transformed into a grey image and finally into a binary image by using the image data analyzer, as described previously.[10]

The coordinates of the center of the particle (in the binary image) were stored in the image data analyzer and the interparticle spacing was determined. In order to determine the spacing between particles in the ordered structure, 100 values of the spacing, which was within ±30% of an expected spacing value, were taken and the average value was obtained and denoted as $2D_{exp}$. The standard deviation from this average value was estimated. As mentioned above, 100 spacings, namely 200 particles, were treated. Whether this number is large enough to provide statistically reliable data was unknown. Thus the particle number was increased to 2000 but no significant change was noticed. For example, at 2.0% of D1A92, the $2D_{exp}$ was 1.35 ± 0.10 μm in the 200 particle treatment whereas it was 1.36 ± 0.09 μm in the other. It is thus obvious that the present treatment with 200 particles furnishes statistically significant results as far as the interparticle spacing is concerned. It is furthermore emphasized that the computer-aided present method excludes largely, though not completely, the subjective arbitrariness in judging the distinction between the ordered and disordered regions. This is definitely a substantial improvement over previous treatments in our 1983 and 1985 papers,[7,14] in which the ordered structure was differentiated from the disordered one with the naked-eye. It should be noted that the qualitative aspect of the conclusion drawn is not influenced.

The analysis of the thermal motion of the particles in the ordered regions around the lattice point was carried out as follows: the center of gravity of the particles in one frame was determined and stored and the measurements were extended to consecutive frames taken at an interval of 1/30 s. Then the centers of the particles in a definite time span were regenerated in one new frame. On this frame, the group of particle centers was displayed as one object (see Figure 4), whose area and maximum length (D_{max}) were determined to discuss the thermal motion.

Unless otherwise stated, the microscopic observation was carried out at room temperature.

III. Results and Discussion

A. Micrographs of the Two-State Structure. Figure 1 consists of micrographs showing the coexistence of ordered and disordered structures. These pictures show the organization in a *vertical* plane at various elevations from the bottom of the observation cell. Figure 1a shows the boundary between an ordered and disordered region in a 1% (light water) suspension of a Dow sample (specific gravity of about 1.05) in the vicinity of the bottom of the suspension cell. Obviously an ordered, high-density region is seen to coexist with a less dense disordered region. The direction of the gravitational field is from the bottom to the top of each picture. If the ordering formation is due to a gravitational effect, the ordered structure would be observed in the upper part of the micrograph. This is not the case, however. Again such an observation confirms our previous claim that for (polystyrene-based) particles in light water with a diameter smaller than 5000 Å, the sedimentation effect is not a decisive factor of the ordering, particularly of the localized ordering. Not only the Dow sample but also the Sekisui latex form a localized ordering even at 2%, as is shown in Figure 1c. At a much earlier stage, namely at a short setting time (t), an "island-in-sea" structure was observed (Figure 1d at an elevation (h) of 0.5 cm and (e) at $h = 3.0$ cm). Rather unclear pictures showing the two-state structure are shown in parts f and g of Figure 1, which were taken for the N400 latex sample (latex concentration of 2% and $h = 0.7$ cm) at $t = 3$ and 7 days, respectively. For two-dimensional colloidal suspensions, Clark et al. described the crystal structure separated from the liquid structure by use of cross correlation of the intensity fluctuation.[18] Yoshiyama and Sogami studied the internal structure of latex suspensions by the use of the Lang method originally devised in X-ray topography and took photographs of isolated crystallites.[19] This work is important in that the method provides information on the global situation, which cannot be investigated by the microscopic method. Although the micrographs undoubtedly tell us the true local structures in one place and at a certain time, not all the information derived from them can be generalized. For example, the three-dimensional size and shape of the ordered structure cannot be concluded from the microscopic study, since it allows us to investigate only several layers of (polystyrene-based) latex particles in the aqueous suspensions because of the turbidity of the suspension. Furthermore, the microscopic field of view is limited. Although it is conceivable to repeat the microscopic observation by shifting successively the field of view from one place to another to cover the entire suspension volume, it is impossible

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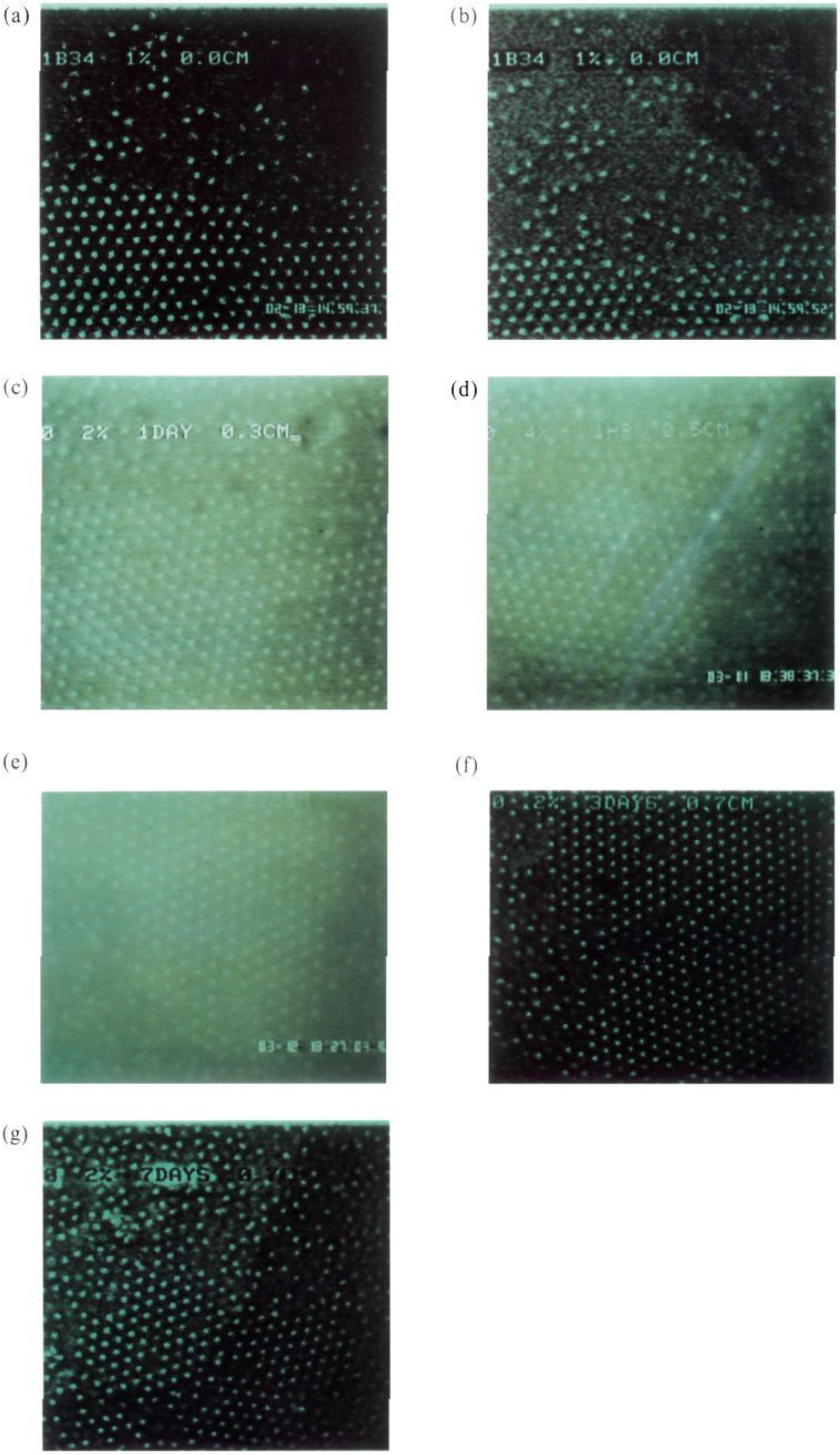


Figure 1. Micrographs showing the coexistence of ordered and disordered structures in latex suspensions (light water) in a vertical plane. Taken from the side of the observation cell by an Olympus microscope at room temperature. For the observation cell see ref 10, Figure 1. The interparticle spacing in the ordered region is of the order of the magnitude of 1 μm for all cases. (a) [D1B34] = 1%, height from the bottom of the observation cell (h) = 0 cm, Setting time of the suspension in the observation cell (t) = 12 h. (b) [D1B34] = 1%, h = 0 cm, t = 12 h. (c) [N400] = 2%, h = 0.3 cm, t = 1 day. (d) [N400] = 4%, h = 0.5 cm, t = 1 h. (e) [N400] = 4%, h = 2.0 cm, t = 1 h. (f) [N400] = 2%, h = 0.7 cm, t = 3 days. (g) [N400] = 2%, h = 0.7 cm, t = 7 days.

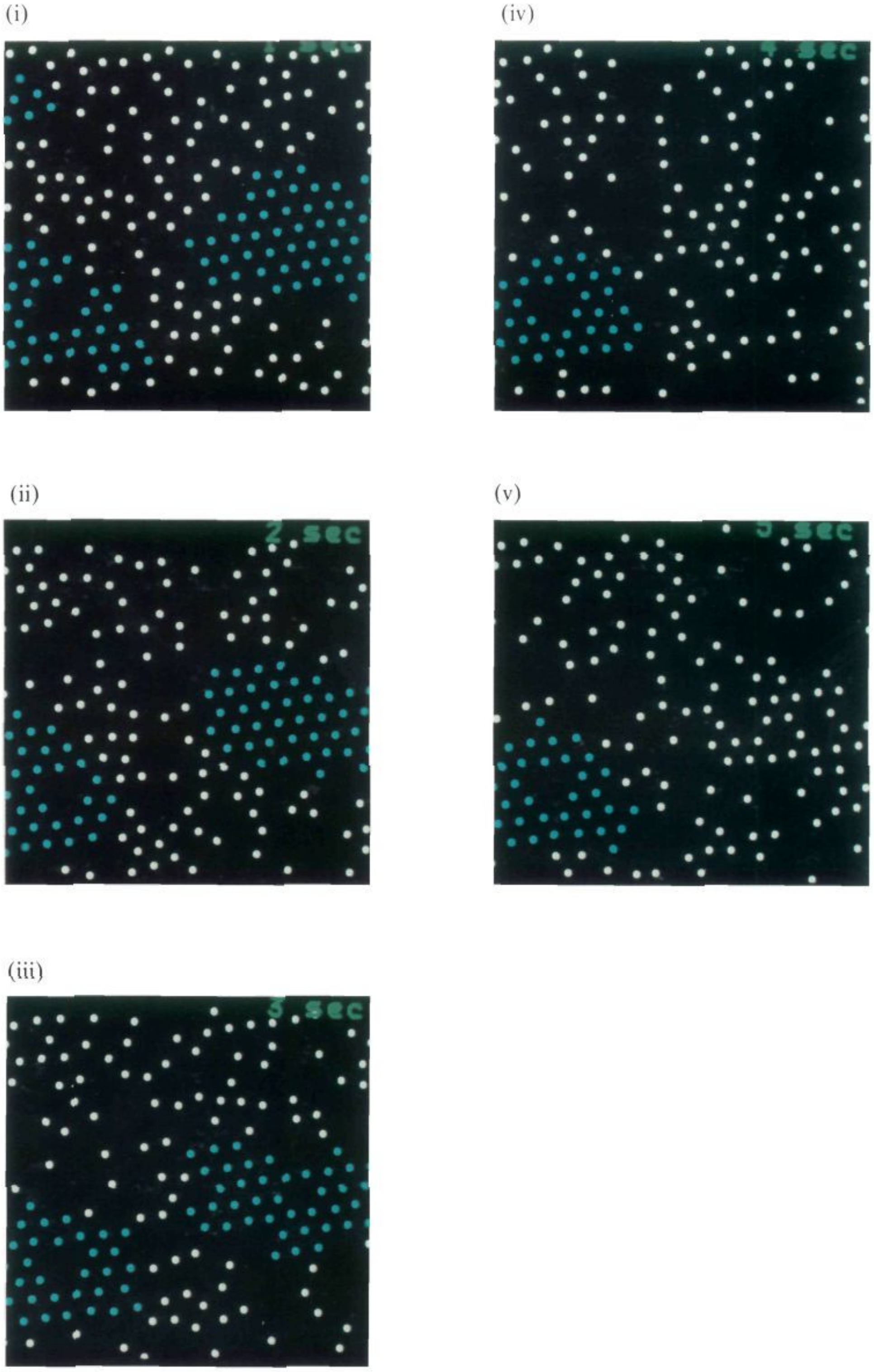
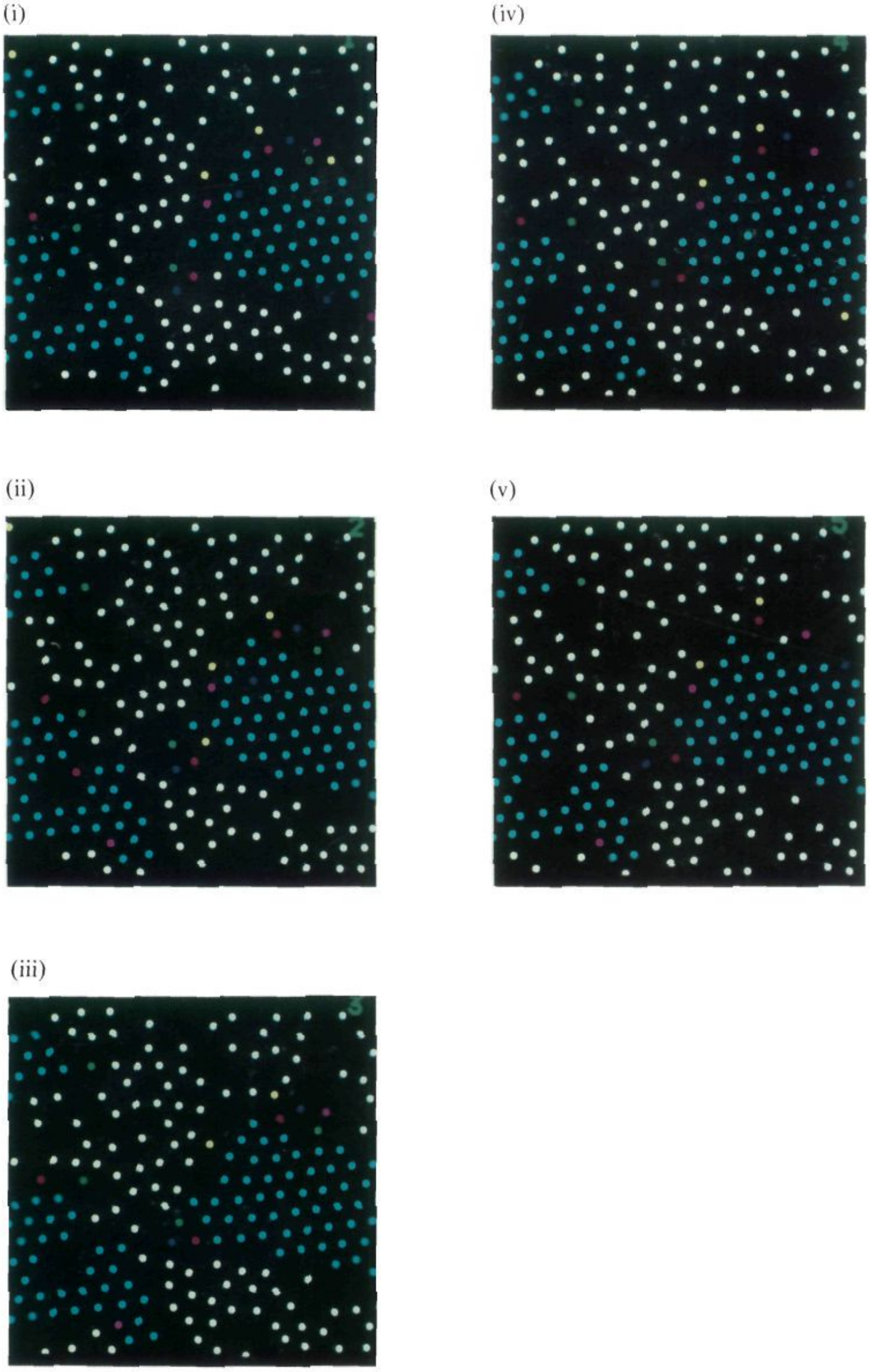

(i) (ii) (iii) (iv) (v)

Figure 2. Variation of the two-state structure with time: latex N300, concentration 2.5%, t = 24 h. The original micrographs were taken by the Carl-Zeiss microscope. The successive five pictures show the particle distribution in a horizontal plane near the bottom of the observation cell at an interval of 1 s.

to do so practically. Under such circumstances, we can claim from Figure 1 with a high certainty that, first, the suspensions are not homogeneous as far as the particle distribution is concerned. Inhomogeneity, in other words, the localized ordering, really exists. It should be noted that this type of ordering is not due to insufficient ripening of the ordered structure: actually the isolated (namely localized) crystallites (about 1mm in diameter) were photographed after several months of ripening by the Lang method, though without coexisting ion-exchange resins and at a higher concentration than those usually used in our micrographic study. However, we have no intention to claim that the ordered structure of the "two-dimensional" size and shape shown in parts d and e of Figure 1 or in Figure 2 of ref 19 can always be found and in all parts of the suspensions under the given experimental conditions. The size and shape of the ordered structure would change with time but it seems most plausible that the inhomogeneity



(i) (iv) (ii) (v) (iii)

Figure 3. The dynamic aspect of the particles near the boundary between the ordered and disordered regions. The original micrographs were taken with an interval of 1/15 s at the same place for the same latex with the same starting time as in Figure 2. The blue circles denote the particles in the ordered structure, the green outgoing ones, the yellow incoming ones, and the red those that have moved in or will move out. This distinction was possible by replaying several times the original video images that had been taken at intervals of 1/30 s.

persists for a prolonged time span. Second, regardless of the size or geometry of the ordered structure, the interparticle spacing in the ordered regions would be physically significant, provided that it is measured for a statistically meaningfully large number of pairs of particles. If the values of the interparticle spacing thus obtained from the micrographs are constant within a certain limit and within the limit of experimental error, the particles under consideration would be distinguished from free particles (in disordered regions). Furthermore, if the interparticle spacing ($2D_{\text{exp}}$) thus determined was smaller from the average interparticle distance ($2D_0$) which can be calculated from the particle concentration and the suspension volume by assuming a uniform dis-

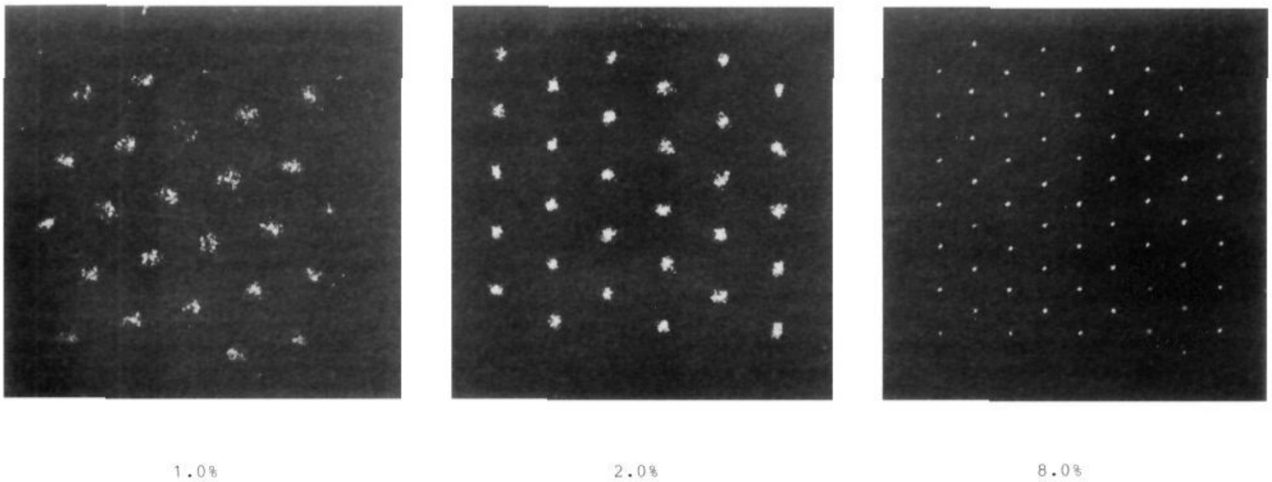


Figure 4. The location of the center of the particles in the *ordered* structure in 8.3 s at room temperature (latex N400). The original picture was taken by a Carl-Zeiss microscope and the video system described in the text at every 1/30 s. After the computer treatment, the particle centers in 8.3 s were reproduced in one new frame and photographed.

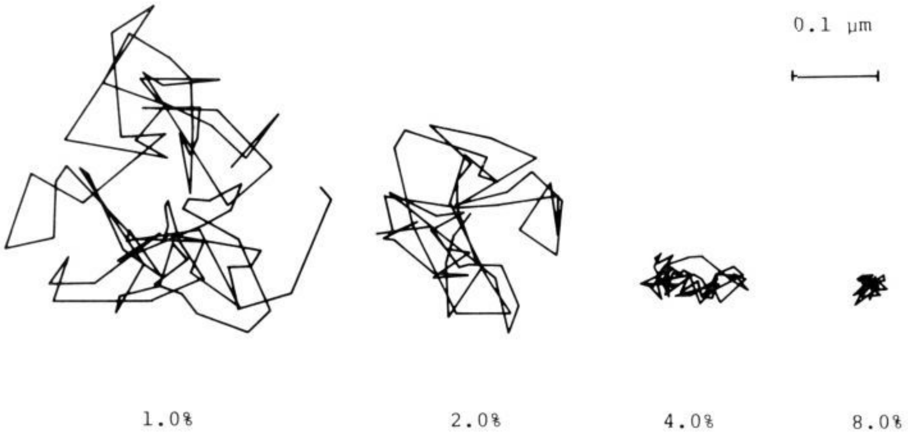


Figure 5. Trajectories of latex particles in the *ordered* structure. For the same sample as in Figure 4, the particle centers were determined by replaying the video tape repeatedly and connecting by straight lines. For 1.0% and 2.0%, 90 centers in 3 s are demonstrated whereas 60 centers in 2 s are shown for higher concentrations.

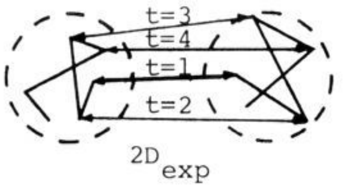


Figure 6. Determination of the spacing between two neighboring particles as a function of time.

tribution, it would imply that there is some kind of attraction between particles.[20] It is reasonable that the difference between the interparticle spacing and the average spacing becomes larger when the inhomogeneity in the suspension becomes more substantial.

B. Instability of the Two-State Structure. Figure 1 clearly shows the two-state structure in the latex suspension but it fails to show the dynamic aspects of the structure. It is fairly difficult to reproduce the dynamic movements in the printed form. In the present work, the video images were transformed finally into binary images and the particles in the ordered structure were colored blue by the image data analyzer while those in the disordered regions were left uncolored. The five pictures in Figure 2 show how the ordered structure changes in one place in a fixed field of view

Table II. Thermal Motion of Latex Particles in the Ordered Structure[a]

concn (vol %)	D_{max} (μm)	G	$2D_{exp}$ (μm)
1.0	0.50 ± 0.08	0.048	1.08 ± 0.08
2.0	0.35 ± 0.07	0.029	1.07 ± 0.07
4.0	0.21 ± 0.07	0.021	0.87 ± 0.07
8.0	0.08 ± 0.01	0.022	0.73 ± 0.03

[a] Latex: N400. The D_{max} and G values at 1.0, 2.0, and 8.0% were estimated for the small number of particles shown in Figure 4.

Table III. Thermal Motion of Latex Particles in the Ordered Structure[a]

temp (°C)	ϵ	D_{max} (μm)	G	$2D_{exp}$ (μm)
10	83.33	0.26 ± 0.06	0.024	0.85 ± 0.08
20	80.20	0.14 ± 0.04	0.023	0.83 ± 0.06
30	76.55	0.11 ± 0.02	0.011	0.75 ± 0.04
50	69.51	0.12 ± 0.03	0.007	0.73 ± 0.04
60	66.81	0.24 ± 0.06	0.048	0.75 ± 0.08

[a] Latex: SS-43, concentration 2.0%. ϵ is the dielectric constant of light water.

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(20) In the microscopic observation of latex suspension, the 111 plane of an fcc or the 110 plane of a bcc structure happened to be parallel to the glass wall of the observation cell, as was mentioned in the previous work (ref 10). Due to the wall effect or otherwise, this situation has enabled us to measure the interparticle spacing in the ordered regions. For disordered regions, the particles move not only in a direction parallel to the glass wall but in all directions. Then the determination of the spacing between the particles in the disordered regions is impossible. If this determination is possible and the measurements were done for a statistically meaningfully large number of pairs of free particles, the spacing thus obtained must be equal to the average interparticle spacing determined from the concentration and the suspension volume by assuming a uniform distribution.

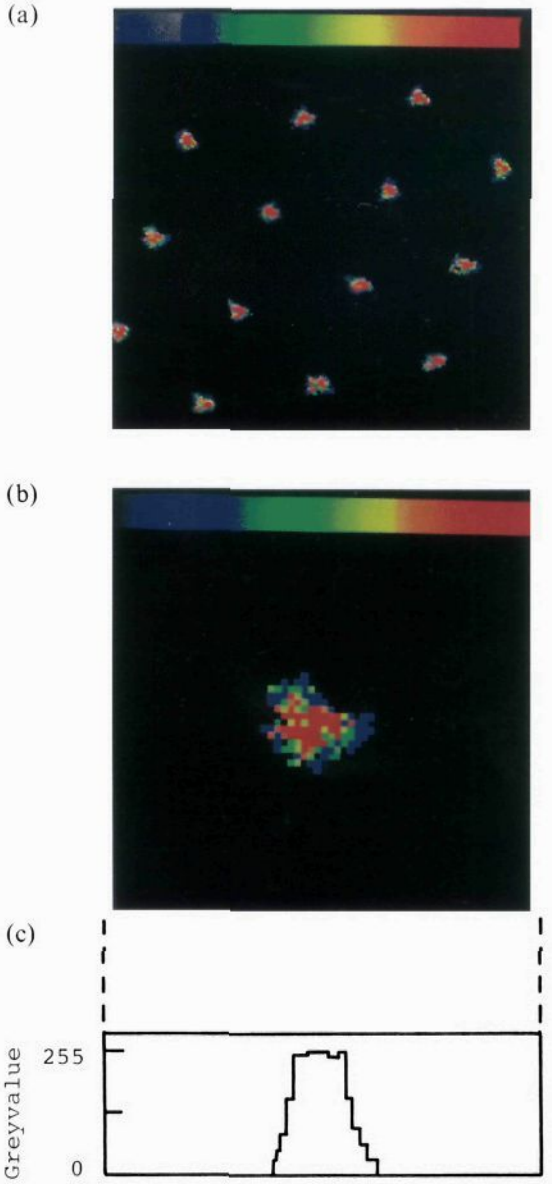


Figure 7. Distribution of the particle center around lattice points: latex D1A92, concentration 1.0%. The original picture was obtained by the Carl-Zeiss microscope. The particle centers in 20 s (600 centers) were regenerated in a new frame and the number of centers at various locations was counted for 20 s. The largest number of centers thus obtained was normalized to the grey value of 255 and the numbers of centers at other locations were expressed in different colors; red corresponds roughly to grey values 255–185, yellow to 180–130, green to 130–75, blue to 73–40, and purple to 37–1. Part b is a magnification of one object in part a, and the histogram in c shows the relative number of centers in a cross section of the object: the abscissa denotes the distance from the origin (the left end of the frame) in pixel.

within 5 s. The structure is not at all stable. For example, the ordered structure seen at 1 s on the right-hand side does not exist after 4 s. Although we do not claim that the ordered structure inside the suspension is always so fragile and dynamic, the present situation shown in Figure 2 reflects at least part of the truth. In such circumstances *it would not be appropriate to assume a stable borderline between the ordered and disordered regions.*

In spite of these changes, it is interesting to note that the interparticle distance inside the ordered regions appears to stay approximately constant. We mentioned the insensitivity of the spacing with respect to time previously;[10] the spacing was found to stay practically constant after letting N400 stand for 11 days at 4.0% and after letting D1B34 stand for 6 months at 2.0% (diameter = 0.25 μm, charge density = 1.9 μC/cm^2) (Tables IV and VI of ref 10). This shows that the interparticle spacing in the ordered regions may be a significant quantity by which the interparticle interaction can be discussed.

Figure 3 again shows the unsteadiness of the borderline. The successive five pictures display the particle distribution in a horizontal plane in an interval of 1/15 s. The particles in the ordered regions are again shown in blue. Incoming particles from the disordered regions are shown in yellow and outgoing ones in green. Red denotes particles that have just come in or will go out in the next moment. It is again evident that there does not exist a clear stable borderline between the ordered and disordered structures.

If we take into consideration both Figures 2 and 3, the localized structure is judged to be time-dependent under the experimental conditions employed. For example, the ordered structure on the right-hand side of Figures 2 and 3 disappeared 4 s later. On the other hand, Yoshiyama and Sogami observed the existence of fairly large, stable crystal grains after letting their systems stand for several months.[19] Probably, the localized structure in our case is in the process of ripening. Nevertheless, such a localized structure is reminiscent of the presence of an attractive interaction between the particles. We shall discuss this point later.

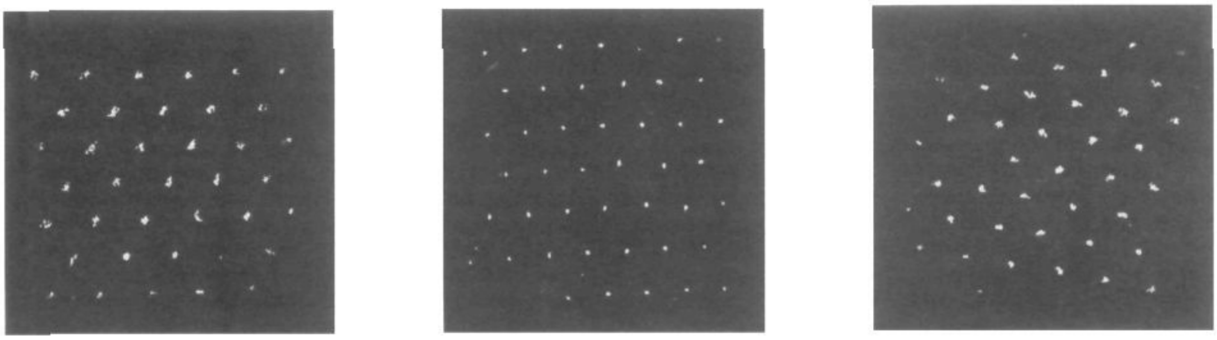
C. Thermal Motion of Particles in the Ordered Structure. By the computer treatment, the position of the center of each particle was determined as a function of time, displayed in one new frame and photographed. Figure 4 is such a picture showing the locations of the particle centers in 8.3 s (about 240 points for each particle) for N400 at three different concentrations. Obviously, the particles show thermal motion around the lattice point and the motion appears to be more violent at lower concentrations, as is expected.

In Figure 5, the centers of one particle (over a time span of 2 to 3 s, depending on latex concentration to avoid too complicated a figure) at every 1/30 s were connected by lines using the image data analyzer to reproduce the particle trajectory for the same sample as in Figure 4 but at four different concentrations. The trajectories are projections of the three-dimensional motion of the particles on a focus plane of the microscope. Figures 4 and 5 indicate that the motion of the particles is restricted to a small area (exactly, space) around the lattice point. Furthermore, the area becomes larger with decreasing concentration, as is easily expected. From Figure 5 it is hard to claim that the particle motion is oscillatory. We have to be careful in judging the mode of the motion from this figure, because the trajectory was constructed by using video images pictured at every 1/30 s; we have no information on the location of the particle centers between two consecutive images.

Taking this fact into consideration, it is relatively safe to analyze the thermal motion in terms of the following two parameters: First, the maximum length of the white area shown in Figure 4 (D_{max}) was evaluated. Second, the spacing ($2D_{exp}$) between two neighboring particles was estimated as a function of time (as shown in Figure 6), its standard deviation ($\Delta 2D_{exp}$) was determined, and the G value, ratio of $\Delta 2D_{exp}$ and $2D_{exp}$, was estimated. From D_{max}, the "amplitude" of the thermal motion would be discussed whereas the relative motion of two neighboring particles would be described by the G value.

In Table II, the values of D_{max} and G are listed for N400 together with the $2D_{exp}$ values. The "amplitude" of the thermal motion is large at lower concentrations and decreases with the concentration, and the G value shows a similar tendency, both of which are easily accepted.

The large D_{max} value at lower concentrations indicates that the $2D_{exp}$ values estimated from micrographs at these concentrations might contain a fairly large error, *unless a statistically meaningfully large number of particle pairs are treated.* In our first publication on latex suspensions,[7] the $2D_{exp}$ value was estimated "as an average of several sets of neighboring spots" in a concentration range between 0.25% and ca. 10%. Quantitatively, the conclusion drawn below 1% in this paper must be viewed with caution in light of the large D_{max} value. Fortunately, however, the qualitative aspect of the previous conclusion ($2D_{exp}$ is smaller than the average spacing $2D_0$ for high charge density particles)



10°C 30°C 60°C

Figure 8. The location of the particle centers in the ordered structure in 8.3 s at 10, 30, and 60 °C: latex SS-43, concentration 2.0%.

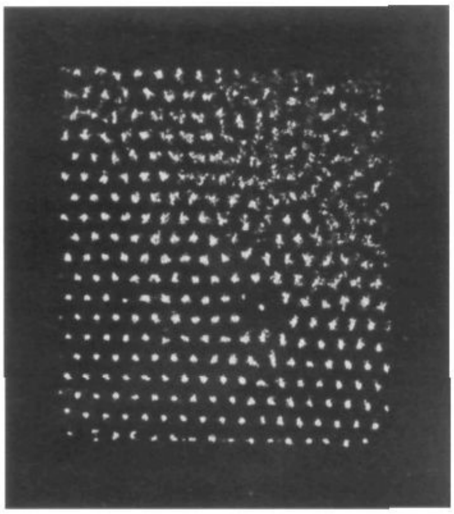


Figure 9. The location of the particle centers in the two-state structure in ca. 3 sec. latex: D1A92, concn.: 1.0%.

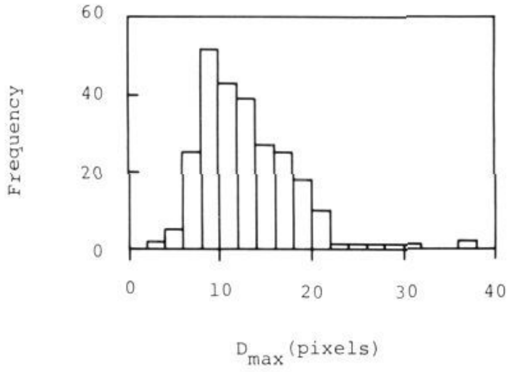


Figure 10. Histogram of the frequency of D_{max}: latex D1A92, concentration 1.0%. D_{max} was determined for the picture shown in Figure 9.

remains unaffected, as was demonstrated recently[10] and by the present work in which at least 100 pairs of particles (not just several sets) were treated.

Another interesting aspect of Table II is that the D_{max} decreased from 0.50 to 0.08 μm (by a factor of 6) when the concentration was increased from 1.0 to 8.0%. In the same concentration range, the G value decreased only by a factor of 2. This difference might be interpreted as indicating that the thermal motion of a particle is dependent on that of its neighbors. This feature seems to be consistent with the nonspherical shapes of the white areas (particularly at 1.0 and 2.0%) shown in Figure 4. The existence of a directional vibration of the lattice planes with low frequency is plausible and we are investigating this possibility.

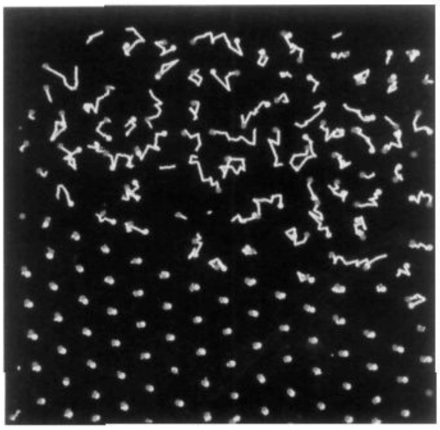


Figure 11. Trajectories of the latex particles in the ordered and coexisting disordered structures: latex N300, concentration 2%, h 3.5 cm. The particle centers in 11/15 s which were photographed by the Olympus microscope from the side of the observation cell and stored in the image data analyzer, were demonstrated in one new frame and connected with lines with the use of the image data analyzer. In order to avoid too complicated a picture, not all of the information obtained in 11/15 s was used. The particle position at a starting time was shown in green and that after 11/15 s in yellow. The white lines without either green or yellow ends or both indicate the three-dimensional movement of the particle.

Figure 4 tells us the area in which the particles are present in a certain time span. The next question is concerned with distribution of the particles inside the area. Figure 7 gives such information, and was obtained by reproducing 600 particle centers (namely, in 20 s) for each particle in a new frame, by counting the number of centers at locations inside the area, and by coloring the relative numbers obtained by normalizing the largest number observed to the grey value of 255. Figure 7b is a magnification of one object in part a and part c is a histogram showing the distribution of the particle center in a cross section of the area. The frequency of the particles is the highest near the lattice point, as would be expected.

The thermal motion of the particles in the ordered structure was studied at three different temperatures. Figure 8 gives the locations of the particle centers (SS-43) in 8.3 s at 10, 30, and 60 °C; these were obtained by the method described for Figure 4. Table III gives the D_{max} and G values for SS-43 at various temperatures. It appears that both these parameters and $2D_{exp}$ decreased with increasing temperature and, after passing a minimum, they increased at temperatures above 50 °C. These trends are understandable, if we accept the fact that the interparticle Coulombic attraction is intensified with temperature, since the dielectric constant of water becomes smaller with increasing temperature. Above 50 °C, the kinetic energy contribution would be so influential that the D_{max} and G values become larger and the ordered structure starts to dilate. The same tendencies were also observed for SS-45, though the experimental data are not shown. The observed temperature dependence of $2D_{exp}$ is consistent with the earlier data reported from this laboratory.[14] It should be noted that the $2D_{exp}$ values increased, or the ordered structure dilated with increasing temperature, when the temperature dependence of the dielectric constant was taken into account. (See Figure 2 of ref 14.)

D. Thermal Motion of Particles in the Ordered and Disordered Structures. Figure 9 shows the locations of the particle centers in a time span of about 3 s (and hence shows 100 locations for each particle) in the ordered structure and in the disordered region, which were observed for a Dow sample. The photograph was taken by the same method as used for Figure 4. The thermal motion of the particles in the disordered regions (right top of Figure 9) is seen to be much more enhanced than that in the ordered regions (left bottom). The motion of the particles near the boundary is intermediate. Figure 10 is a histogram showing the frequency of the D_{max} values determined for about 300 particles in Figure 9. The distribution is far from the normal distribution, because the motion of the ordered particles is much less substantial than that of the free particles.

The trajectories of the free particles in coexistence with the ordered particles are reproduced in Figure 11. The particle centers in consecutive frames were reproduced together in a single new frame and were connected by lines. The particle positions at the starting time are colored green and those after 11/15 s yellow.

It is evident that the motion of the free particles is much more enhanced than that of the particles in the ordered regions to such an extent that the thermal motion of the ordered particles is almost indiscernible in Figure 11, though fairly substantial as shown in Figures 4–8. Once again it should be remembered that Figure 11 reproduces the two-dimensional movements projected on the focus plane of the microscope. Thus, some particles without yellow or green spots or either are seen. This means that these particles have gone away from or have come into the focus plane during the observation period.

As far as Figure 11 is concerned, we may expect at least two diffusion coefficients for particles in the system, which would be detected by an independent measurement such as dynamic light scattering.

IV. General Remarks

In the present paper, we have tried to confirm our previous conclusion (particularly on interparticle distance) and to describe dynamic (time-dependent) aspects of the ordering of latex particles with the aid of an image data analyzer. The interparticle distance observed from the micrographs ($2D_{exp}$) was confirmed to be definitely smaller than the average interparticle distance ($2D_0$) at low concentrations and for highly charged ionic species.[21] This conclusion was drawn by the computer-aided measurements for at least 100 pairs of particles, which were much larger than those in our earlier publication[7] (several particle pairs). Non-space-filling, localized ordered structures of a higher number density were found to coexist with the disordered region of a lower density, and were photographed (Figures 1, 2, 9, and 11). The density difference is consistent with the inequality relation, $2D_{exp} < 2D_0$.

We should like to note that the coexistence of ordered and disordered regions (two-state structure) is observed on a *microscopic* scale: Macroscopically the latex suspension is almost homogeneous, though a concentration gradient develops for large latex particles after the suspension is kept standing for a prolonged period. (See for detail ref 10.) In our experiments, *the suspensions that showed a macroscopic inhomogeniety, such as separation into "precipitated" particles and supernatent solvent, were judged to be "insufficiently purified"*; the purification procedures were reinitiated or the suspensions were abondoned. Our judgment was based on the simple calculations of the sedimentation velocity [u] of a free particle in the gravitational field and the mean displacement of Brownian motion [$(\bar{x}^2)^{1/2}$]. For example, u is found to be only 6.8 nm/s for a particle with a diameter of 0.5 μm and having a density of 1.05. (Polystyrene latex particles are reported to have a density of 1.03–1.05.) The mean displacement for this particle is 1.3 μm. Thus, even when the sedimentation *was* not affected by the Brownian motion, it would take about 7×10^3 days for this particle to sediment down by 4 cm (the height of our suspension cell). Thus the suspension, in which particles were separated from supernatent solvent within a short period (say 7 days), was concluded to be "unstabilized" by impurities or the SO_4H groups were oxidized into COOH groups, as was discussed in the Experimental Section.

The motion of the particles in the ordered structure was demonstrated to be drastically different from that of the free particles. Even though the ordered structure under consideration is far from that of an ideal crystal in various ways, it can be clearly distinguished from free particles. For example, the scattering profiles of latex suspensions display only one or two broad peaks, which have tempted many authors to claim that there is no ordered structure. However, the present study by video imagery indicates that it is necessary to take into account hitherto largely overlooked factors such as thermal motion of the latex particles around the lattice point, the size of the localized ordered structure, its time dependence, and the paracrystalline distortion of the ordered structure. As for the size of the ordered structure and its change with time, it is fair to refer to the earlier work by Luck,[5] who reported that a larger "crystal" continued to grow while smaller ones disappeared quickly. This is the phenomenon called Ostwald ripening,[23] which has been accounted for in terms of surface tension. It must be remembered that the surface tension is a consequence of a net attraction between constituent particles. Thus, Luck's observation is further support for the existence of an interparticle attraction discussed before.[1a,c] A detailed report of this interaction will be made, and the role of the counterions will be clarified.[24]

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Registry No. (Styrene)(styrenesulfonate) (copolymer), 56619-18-2; D1A92, 116076-43-8; D1B34, 116076-44-9; N300, 110391-08-7; N400, 9010-79-1.

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(21) One might argue whether this inequality relation is due to an uncertainty in the latex diameter. The 10% uncertainty would cause a 30% error in the volume fraction of the latex particles, which would lead us to a 10% uncertainty in the interparticle spacing ($2D_0$). When we discuss the relation $2D_{exp} < 2D_0$, we are only concerned with a larger, systematic difference between the two spacings: for example, $2D_{exp}$ for a Dow sample (D1A92, diameter 0.5 μm, charge density 2.8 μC/cm^2) at 1% in a H_2O–D_2O mixture (specific gravity 1.04) was 1.5 μm whereas $2D_0$ was calculated to be 2 μm. Though the inaccuracy due to the polydispersity cannot completely be excluded for polymer latex particles, it should be noted that an even greater difference between $2D_{exp}$ and $2D_0$ (by a factor of about 2) was observed for polystyrenesulfonates of a polydispersity index M_w/M_N of 1.17 (ref 22). Furthermore, similarly large differences in the two spacings were noted even for bovine serum albumin, for which the polydispersity problem is much less plausible than synthetic macroions such as latex or polystyrenesulfonate.

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