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Reviews

On the Distortion of an Ordered Structure of Ionic Particles in Suspension or Solution

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ABSTRACT: Dilute solutions of ionic solutes such as proteins, polynucleotides, micelles, and synthetic macroions show a single broad peak in X-ray and neutron scattering experiments. Suspensions of ionic polymer latex particles, which are confirmed to form regular latticelike structures by naked eye observation, show only two or three scattering peaks. The micrographs of particle distribution in latex suspensions were Fourier transformed to obtain the scattering profile. A single broad peak was obtained from a micrograph showing the coexistence of localized ordered structures with disordered arrangements (free particles). Discrete scattering spots were obtained from highly ordered structures, whereas a completely disordered distribution gave no spots or rings. The lattice factor calculated on the basis of the paracrystal theory was compared with the observed structure factor. Highly distorted latticelike structures were found to exist in the dilute solutions or suspensions.

Introduction

It would not be easy for experts in crystallography to accept the existence of an ordered structure, when they see such a "scattering" pattern as shown in Figure 1. They would claim that liquidlike structure exists in the systems. Definitely we should not think about such an ideal and infinitely large ordered structure as is often described in textbooks. However, according to our interpretation, Figure 1 indicates highly distorted, imperfect, finitely sized, ordered arrangements of solutes in solutions. What we have in mind is shown in Figure 2. This figure is a micrograph taken by an ultramicroscope showing the distribution of monodisperse polymer latex particles (diameter, 0.24 μm) in water (1%). Clearly ordered structures with a hexagonal packing are seen here and there. It is to be noted that the micrographs in Figures 2, 3a, and 4 show two-dimensional organizations. However, the actual ordering is three dimensional, as can be easily confirmed by shifting the focus plane carefully.

According to the principle of the scattering theory, the density function and the amplitude of scattered radiation are interrelated by the Fourier transformation. This is an axion and Figure 1 "was" the scattering profile obtained by a computer using Figure 2 as a density function.[1] The scattering profile (Figure 3b) corresponds to a completely random state (Figure 3a), and Figure 4a is for an almost "completely" ordered arrangement of latex particles. It is clear that discrete scattering spots are obtained for the ordered arrangements whereas no spots or rings are seen for the random situation. When ordered structures coexist with disordered ones (Figure 2), we find a single peak.

For several years, such vague X-ray and neutron scattering patterns (SAXS and SANS) as shown in Figure 1 have been reported for salt-free or low salt solutions of ionic polymers such as proteins, polynucleotides, and synthetic polymers and of ionic micelles.[2-5] Similarly one or two broad peaks were found by other scattering techniques for micelles and polymer latex particles.[6,7] The appearance of the peak(s) has been interpreted in various ways: our interpretation has been that the peak is reminiscent of "ordered" arrangements of these ionic species in solutions. For latices, particularly larger ones, the situation is clearer: the ordering of latices has been confirmed by microscopic methods,[8] as shown in Figures 2 and 4. For latex suspensions, even the Kossel image has been observed;[9,10] Yoshiyama et al. demonstrated intrinsic Kossel images, from which it was rigorously deduced that a face-centered cubic (fcc) structure was stable at higher concentrations whereas a body-centered cubic (bcc) structure was favorable at low concentrations. In the case of simple ions, e.g., solutions of $ZnBr_2$, there is EXAFS evidence showing the presence of local ordering fairly close to that of solid crystals.[11] It should not be forgotton that Bernal and Fankuchen were the first to demonstrate the

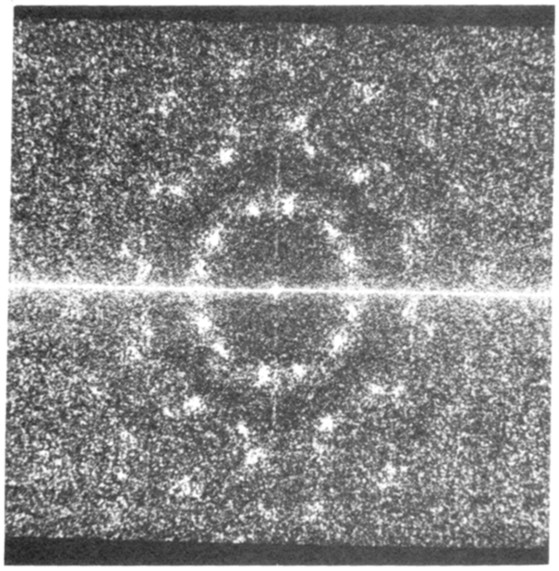

Figure 1. "Scattering" profile from a latex suspension. Latex, D1B34 (a Dow sample): diameter 0.24 μm; charge density, 19 μC/cm^2; concentration, 1%. Reprinted from ref 1 with permission. Copyright 1987 American Institute of Physics.

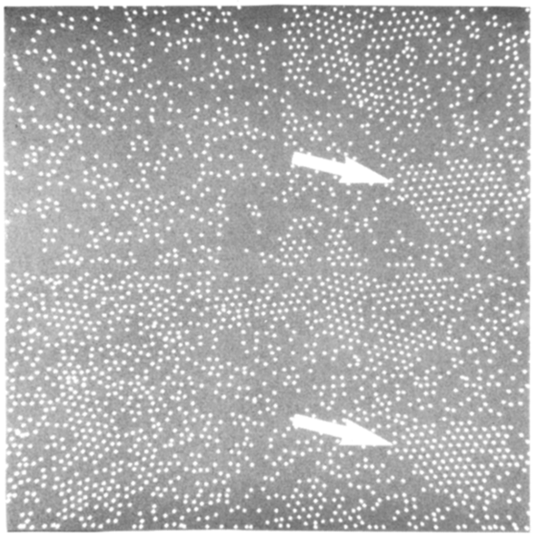

Figure 2. Micrograph showing the coexistence of ordered and disordered regions of latex particles (two-state structure). This is *not* an electromicrograph but a light micrograph of the latex suspension in Figure 1. The micrograph was computer-treated and the latex particles are shown as white circles in the black background (binary image). The binary image was Fourier transformed and shown in Figure 1. Reprinted from ref 1 with the permission. Copyright 1987 American Institute of Physics.

equidistant distribution of tobacco mosaic virus (TMV), although only in dry and wet gels and in a concentrated solution.[12] Thus, it seems that ionic species in general form an "ordered" distribution even in dilute solutions, whatever geometry and mass they may have. Since 1827, however, the thermal motion of solvent molecules has been known to be so influential that it causes the Brownian motion of floating particles. Thus when we talk about the ordered structures in solution, we strongly suspect that the structure is not rigid or perfect to the same extent as expected for a solid crystal: instead of the ideal lattice, we have distorted lattices, namely, paracrystals at the best, as depicted in Figure 5. How strongly distorted is the "ordered" structure in question? This review introduces our recent analysis of this problem. We start with polymer latex particles, which are large enough to be visible, and then we discuss invisible macroions and micelles.

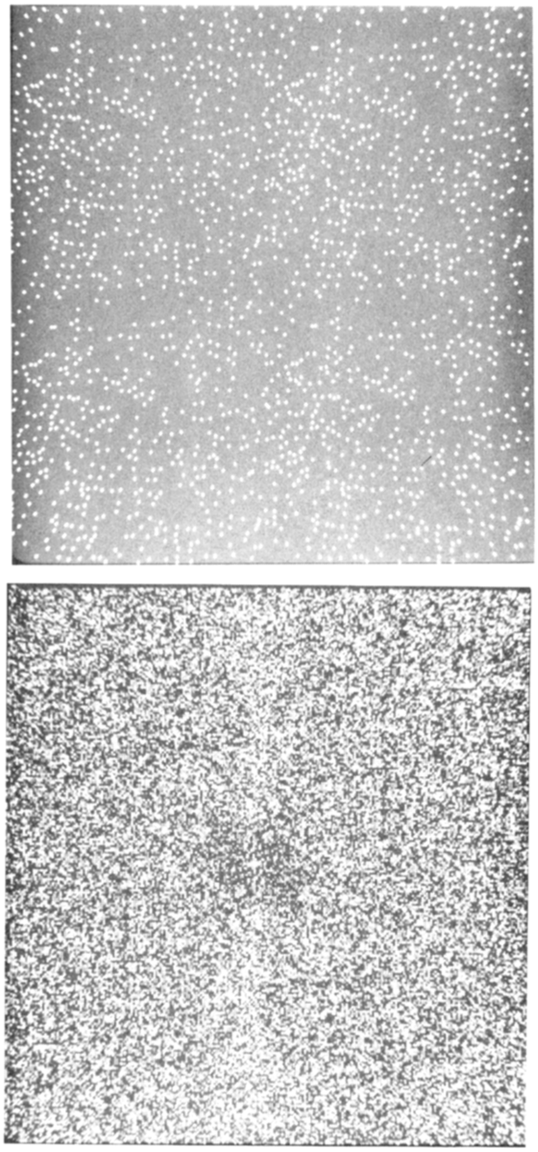

Figure 3. Micrograph showing completely disordered distribution of latex particles (a, top) and the corresponding Fourier pattern (b, bottom). Latex, D1B34 (the same as in Figure 1); latex concentrations, 1%. The random distribution was realized by addition of NaCl at a concentration of 10^{-3} M.

Latex Suspension Studied by the Microscopic Method and Scattering Techniques

The term latex suspension, which originates from the rubber industry, is used here to imply suspensions of spheres of synthetic polymers. The latex particles mostly used in our study were prepared by emulsion copolymerization of styrene and styrenesulfonate. When carefully prepared, the particles are monodisperse. When their diameter is above 0.3 μm, the individual particles can easily be viewed by a microscope (actually used was an ultramicroscope). When ionic impurities are removed from the suspension, the particles show an ordered arrangement. As can be seen from the micrographs (Figures 2 and 4),[13] structures hexagonal in many cases, although not strictly so, are seen. When the latex particles are highly charged, we often see a two-state structure, namely, the coexistence of a localized (non-space-filling) ordered structure and a disordered region as shown in Figure 2. The physical significance of such a situation has already been discussed in detail in the previous reviews,[2] but we must note that hexagonal, distorted packing is seen even in the localized ordered structure.

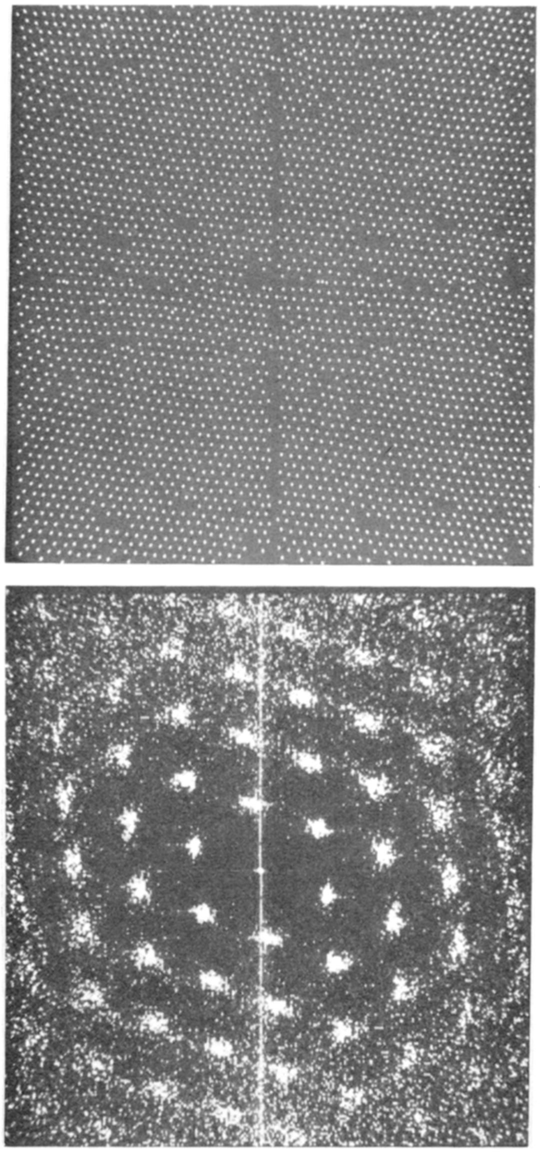

Figure 4. Micrograph of the ordered distribution of latex particles (a, top) and the corresponding Fourier pattern (b, bottom). Latex, D1B34; concentration 0.5%. Because of many lattice imperfections, the Fourier spots are not sharp points.

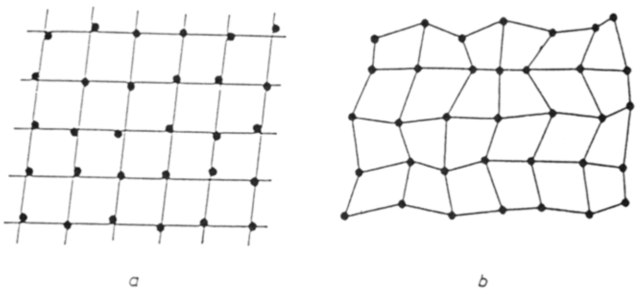

Figure 5. Schematic presentation of the crystal distortion: (a) ideal lattice with thermal vibration; (b) paracrystalline lattice. Reprinted with permission from Vainstein, B. K. *Diffraction of X-rays by Chain Molecules*: Amsterdam, 1966; Figure 65. Copyright 1966 Elsevier.

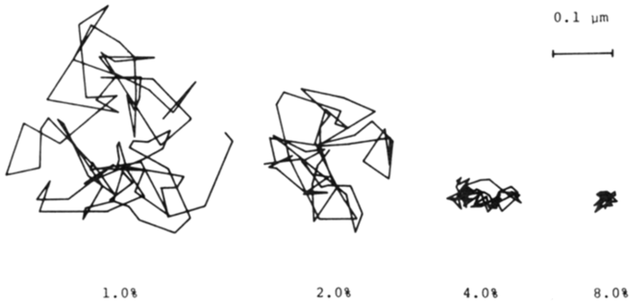

Figure 6. Vibrational motion of latex particles in the ordered structure. Latex, N400; diameter, 0.4 μm; charge density, 6.9 μC/cm^2; latex concentration 1.0%, 2.0%, 4.0%, and 8.0%, as indicated. The particle motion was recorded on a video device and the videoimage was input into an image data analyzer and transformed into 256 grey-level images. After computer treatment, the particles were displayed on a TV monitor as white spots. These spots, which were stored in 8 × 30 monitor fields (8 s), were further transferred on a monitor frame and photographed by a Polaroid camera.

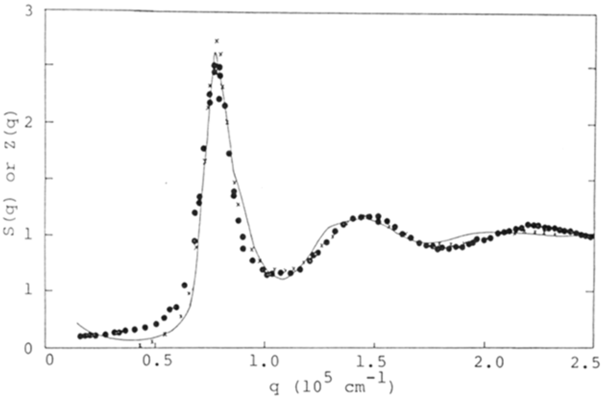

Figure 7. Structure factor $S(q)$ experimentally found and the theoretical lattice factor $Z(q)$ calculated by the paracrystal theory. Filled circles: $S(q)$ for latex (diameter, 0.09 μm) at a concentration of 0.05%. Curve: $Z(q)$ for an fcc structure with the interparticle distance of 0.98 μm and a distortion factor (g) of 0.15. Cross: the $S(q)$ calculated by the rescaled mean spherical approximation method. Experimental data are taken from ref 7 and the figure is reprinted from ref 23 with permission. Copyright 1987 American Physical Society.

These micrographs are quite interesting, but they are misleading in the sense that the actual situation is not so static as imagined from Figures 2 and 4. The particles display a very violent oscillatory motion around the "lattice point".[14] By use of a video device, this motion is recorded and the position of the center of each particle in the ordered region in 8 s is reproduced on one monitor plane (Figure 6).[14] From this figure, the maximum amplitude of the vibrational motion is to be roughly 20, 15, and 7% of the average interparticle spacing (about 1 μm) at concentrations of 1, 2, and 8%, respectively. Although the vibrational motion is so substantial, the particles in the ordered region stay in a rather small space around each lattice point. In other words, *the root-mean-square displacement* is practically zero for the particles in the ordered structure. In contrast, the motion of free particles in the disordered region can be Brownian: their root-mean-square displacements are found to be in agreement with the prediction of the Einstein theory,[15] and even more so when the particle concentrations are low and the concentration of coexisting salt is high.[16]

Such a difference in the particle movements may be hard to imagine from the description given above and from static pictures such as those shown in Figures 2–4, and but it is most easily recognized under the microscope. The situation can be easily understand by comparing the trajectories of the particles,[14] as shown in Figure 3 of ref 2b. Although substantial distortion (as is shown in Figure 4) and vibrational motion are involved in the "ordered" structure, this structure must be distinguished from the disordered regions and accepted as a physical reality.

The scattering curves from such distorted ordered structures must be quite different from what we expect

Table I
Observed Interparticle Spacing ($2D_{exp}$) in H_2O-D_2O Mixtures for Latices with Different Charge Densities[a]

spec. gravity of D_2O-H_2O	$2D_{exp}$, μm	
	D1A92	SS-45
1.00	1.30 ± 0.14	1.06 ± 0.09
1.01	1.25 ± 0.17	1.08 ± 0.09
1.02	1.37 ± 0.15	1.06 ± 0.09
1.03	1.42 ± 0.11	1.09 ± 0.10
1.04	1.37 ± 0.16	

[a] D1A92: diameter, 0.5 μm; analytical charge number (Z), 1.3 × 10^5 per particle. SS-45: diameter, 0.5 μm; Z, 6.5 × 10^5. Latex concentration, 2% ($2D_0$ = 1.65 μm), 20 °C. The specific gravity of the latex is about 1.03. The $2D_{exp}$ was determined by a computer for 100 pairs of particles in the ordered structure.

from ideal solid crystals. In Figure 7 is shown the interparticle structure factor $S(q)$ obtained by light scattering experiments on a suspension of latex particle (diameter, 0.09 μm) at 0.051 vol %, where q is the scattering vector. The $S(q)$ curve has only three broad peaks: higher order peaks are indiscernible. This is mostly due to the distortion of the ordered structure according to our interpretation. This point will be discussed again later.

From the micrographs such as those shown in Figures 2 and 4, we can determine directly the spacing between the particles in the ordered region ($2D_{exp}$). In our recent work,[1,13,14,17] the spacing was determiend by using an image data analyzer for 100–1000 particle pairs. The number of particles is believed to be statistically large enough to warrant the reliability of the results. This comment is important for the following reasons: As we would discuss below, we are interested in the difference between the observed spacing ($2D_{exp}$) and the average interparticle spacing ($2D_0$), which can be calculated from the concentration by assuming a uniform distribution. Depending on the situation in the systems, we have (1) $2D_{exp} = 2D_0$ for a *uniform distribution throughout the system*, (2) $2D_{exp} = 2D_0$ for a *completely random distribution*, provided that the spacing between particles in such a configuration is measurable and a significantly large number of the observed values of spacing are averaged, and (3) $2D_{exp} < 2D_0$ if the *ordered structure of a high number density is localized and coexists with disorered regions of a smaller number density*, as shown in Figure 2. If the relation $2D_{exp} < 2D_0$ is really confirmed, we may conclude that there exists an inhomogeneity in particle distribution in an apparently homogeneous suspension. This is an unexpected situation, which would nonetheless provide most important information in the interparticle interaction. If the population is very low, the interparticle spacing could be smaller than the average distance: Some molecules in the liquid state may come closer to each other than in solid crystals, but if the spacing is averaged over a large population, we end up with an average value. In this respect, what we are trying to do must be correctly understood; we measured the interparticle spacing ($2D_{exp}$) for a *large number of particles in the ordered regions* and compared it with the average value ($2D_0$).

We compiled some recent results in Table I for two kinds of particles having almost the same dimension and different charge densities.[17] First, note that the average interparticle spacing at 2% is estimated to be 1.65 μm. The $2D_{exp}$ values obtained from the two particles are much smaller than $2D_0$. This trend is in accord with our previous finding for highly charged particles[2] and is also consistent with the X-ray data for highly charged macroions[2] to be mentioned below. Furthermore, the $2D_{exp}$ for particles of a higher charge number (SS-45) is *smaller* than that for those of a lower charge (D1A92). This tendency is also consistent with the X-ray data obtained for high-charge-density macroions. The fact that $2D_{exp}$ is smaller than $2D_0$ indicates the coexistence of a localized ordered structure having a high particle density with a less dense disordered structure. This is exactly what was demonstrated in Figure 2.

The next problem is the size of the localized ordering. Luck, who took a phase-contrast picture of polymer latex suspensions, found that the larger ordered structure grew at the expense of smaller ones.[19] This is the well-known Ostwald ripening mechanism.[20] Essentially, the total surface area is forced to decrease so as to minimize the free energy. Our recent microscopic observation shows also that the ordered structure is not stable but quite dynamic in the rather early stage of the crystallization process.[14] However, after being left undisturbed for several months, the solutions produced a stable fairly large "grain" (as large as 1 mm) as photographed by Yoshiyama and Sogami.[21]

Scattering Study of Macroions, Micelles, and Silica Particles. The macroions and micelles have much smaller dimensions than the latex particles. Thus it would be no wonder if the "ordered" structure of the macroions and micelles is distorted in solutions much more than that of the latex particles. It would be possible and necessary to take the single broad peak in SAXS and SANS curves of the macroions and micelles as indicating the existence of more distorted ordered structures. To estimate the magnitude of the distortion, we apply the theory of scattering.

Among various distortions of the crystals, the most important are the distortion of the lattice points (paracrystalline distortion or distortion of the second kind) and the vibrational motion of particles at the lattice points. Furthermore the size of the ordered structure (crystal) affects the scattering curve. As is well-known, the paracrystalline distortion and the crystal size influence the intensity and width of the scattering peak, whereas the thermal motion has an effect mainly on the intensity. First we consider only the paracrystalline distortion to calculate the lattice factor $Z(q)$, for which the paracrystalline theory of Hosemann is applied.[22] In this theory it is assumed that neighboring lattice points are at distance a apart with a Gaussian distribution with a standard deviation of Δa. The parameter of distortion g is defined by $g = \Delta a/a$. Matsuoka et al. extended this theory to three-dimensional lattices such as simple cubic (sc), fcc, and bcc with the assumption that the distortion is isotropic.[23] For fcc symmetry, the theory gives for the lattice factor $Z(q)$

$$Z(q) = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} Z_1(q,\theta,\psi)Z_2(q,\theta,\psi)Z_3(q,\theta,\psi)\sin\theta\, \mathrm{d}\theta\, \mathrm{d}\psi \quad (1)$$

where

$$Z_1(q,\theta,\psi) = [1 - \exp(-q^2\Delta a^2)]/\{1 - 2\exp[-(1/2)q^2\Delta a^2] \times \cos[(1/2)qa(\sin\theta\sin\psi + \cos\theta)] + \exp(-\Delta a^2 q^2)\} \quad (2)$$

$$Z_2(q,\theta,\psi) = [1 - \exp(-q^2\Delta a^2)]/\{1 - 2\exp[-(1/2)q^2\Delta a^2] \times \cos[(1/2)qa(-\sin\theta\cos\psi + \cos\theta)] + \exp(-q^2\Delta a^2)\} \quad (3)$$

$$Z_3(q,\theta,\psi) = [1 - \exp(-q^2\Delta a^2)]/\{1 - 2\exp[-(1/2)q^2\Delta a^2] \times \cos[(1/2)qa(-\sin\theta\cos\psi + \sin\theta\sin\psi)] + \exp(-q^2\Delta a^2)\} \quad (4)$$

with (θ,η,ψ) the Eulerian angles, q the magnitude of the

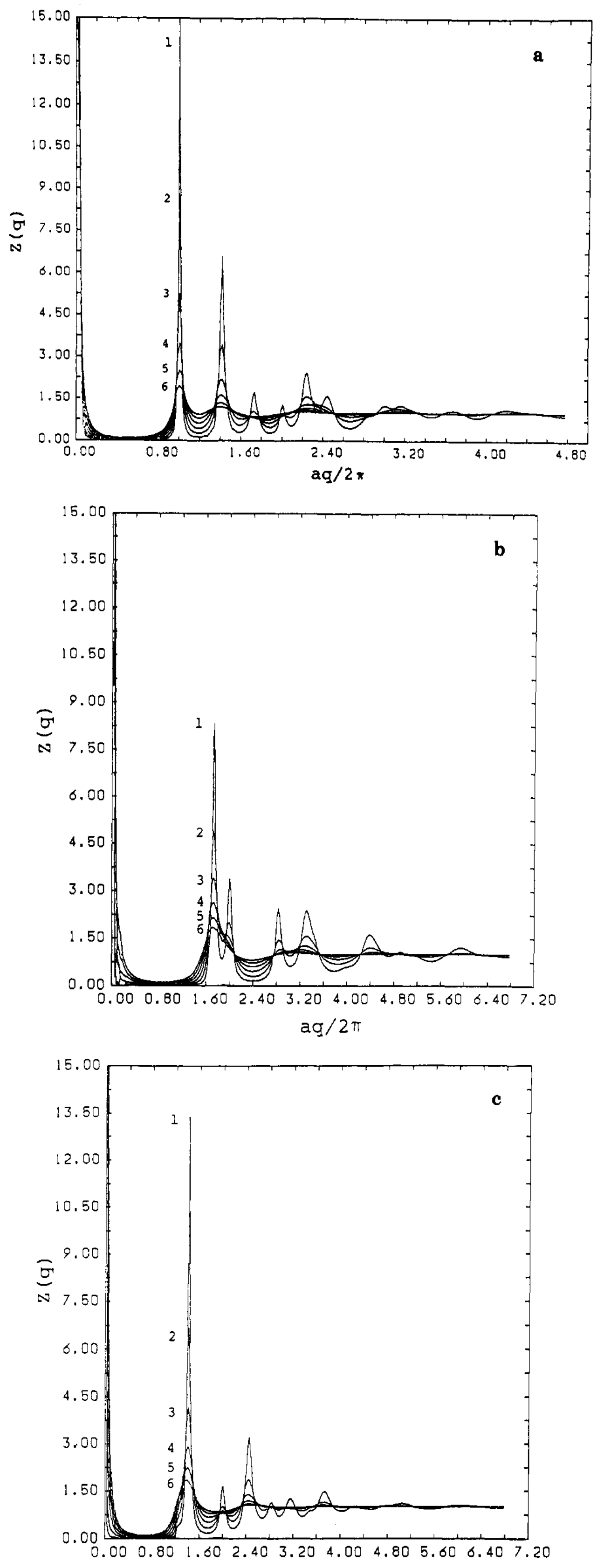

Figure 8. Calculated paracrystalline lattice factors for cubic systems. Reprinted from ref 23 with permission. Copyright 1987 American Physical Society. (a) sc, (b) fcc, and (c) bcc; g (curve no.) = 0.05 (1), 0.07 (2), 0.09 (3), 0.11 (4), 0.13 (5), and 0.15 (6).

scattering vector $\mathbf{q}$, a the magnitude of the unit vector, and Δa the distortion of a real lattice point from an ideal lattice point. The numerical results of the theory are shown in Figure 8 for cubic lattice systems. The $Z(q)$ for an fcc system shows peaks at relative positions of 1, $(4/3)^{1/2}$, $(8/3)^{1/2}$, $(11/3)^{1/2}$, and $4^{1/2}$ for (111), (200), (220), (311), and (222) planes, respectively, when the degree of distortion is very small. However, when the distortion is enhanced, or when the g value becomes large, there remains only the first peak. In the intermediate range, the peak intensity is influenced, but not the peak position. The situation is the same for other lattice systems, for which the peaks appear at different positions characteristic for each system. It seems thus far less legitimate to claim that even when only a single broad peak is observed, the peak is *not* reminiscent of an ordering of solute particles.[24] This statement is furthermore consistent with the results of the Fourier analysis (Figure 1), which gave a single broad halo for a localized ordering (Figure 2).

The theory has been compared with the structure factor $S(q)$ of a latex suspension shown in Figure 7. When an fcc structure with $g = 0.15$ is assumed, the theoretical $Z(q)$ agrees fairly well with the position and width of the first peak of the observed $S(q)$. Although a discrepancy is seen on the height of the second and third peaks, this would probably be because only the distortion of the second kind is taken into account. Similar agreements are obtained for the structure factor of latex suspensions estimated by neutron scattering[6] and by light scattering[25] although their graphical presentation is omitted.

For micellar solutions (dodecyltrimethylammonium chloride), the theoretical $Z(q)$ has been compared with the $S(q)$ derived from the SAXS measurements.[4] In the case of lysozyme, a reasonable fit with the observed intensity of scattered X-ray is obtained for an sc structure with a lattice spacing of 0.006 μm, if the g value is assumed to be 0.38.[26] This value should not be taken seriously, however, because it is so difficult to estimate the $S(q)$ (from the observed intensity) for nonspherical particles, with which the $Z(q)$ should be compared. In the case of linear macroions, even such an approximate analysis would not be feasible, because reliable information on the macroion conformation at the concentrations employed in the scattering experiments is still lacking. Recently a more rigorous discussion was given for silica particles.[27] The particles were found to be nearly spherical by the Guinier plot so that the observed intensity of scattered X-ray $I(q)$ could be separated into the structure factor $S(q)$ and the particle factor $P(q)$ by the following equation[28]

$$I(q) = nP(q)S(q) \tag{5}$$

where n is a constant. The $S(Q)$ thus obtained is demonstrated in Figure 9, together with the $Z(q)$ calculated by the paracrystal theory. $S(q)$ cannot be reproduced by an sc structure but is in agreement with $Z(q)$ for fcc and bcc structures.

Together with the relevant properties of the materials, we compile in Table II the g values obtained from some of the scattering data currently available.

As is clear from Figure 6, the latex particles in the "ordered" struture undergo substantial thermal motion around the lattice point. This motion should not be ignored in any discussion of the ordered structure. Theoretically, we should include the effects of this motion by introducing a Debye–Waller factor, and we know then that the peak height will be lowered and the higher order peaks become indiscernible as the thermal motion becomes more pronounced. Thus, if both the paracrystalline distortion and the thermal motion are considered, better agreement with the experiments might be obtained with g values smaller than those given in Table II.

The crystal size effect is not negligible, either, and is even more of a factor when the two-state structure

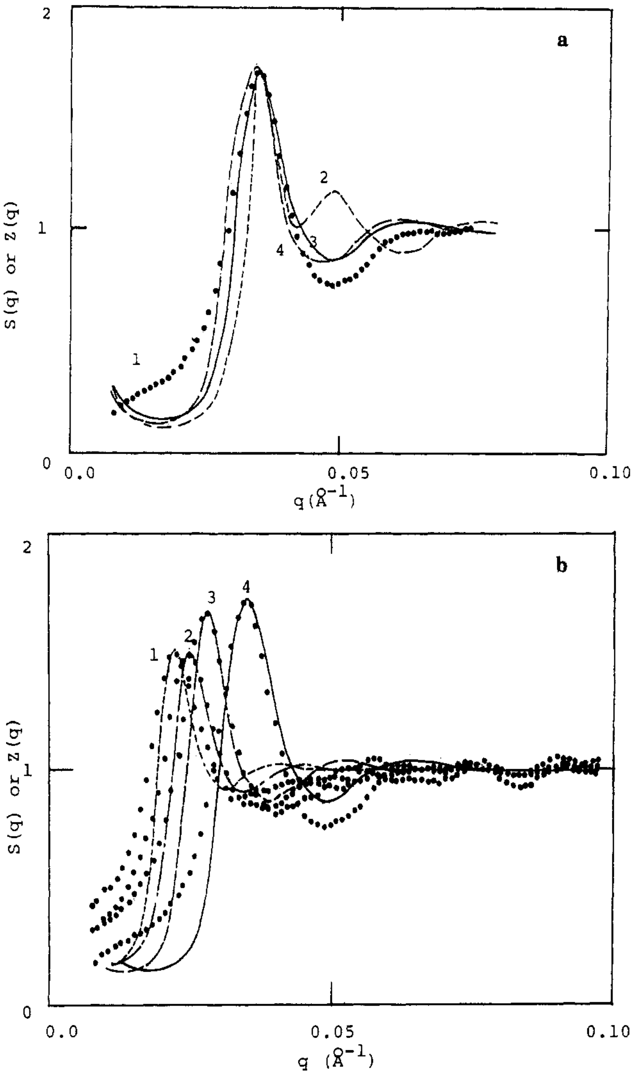

Figure 9. Comparison of the experimental structure factor $S(q)$ (denoted by dots) with theoretical lattice factors $Z(q)$ (given by curves) for aqueous suspensions of silica particles. (a) Silica concentration, 10.98%; curve 1, $S(q)$; curve 2, $Z(q)$ for sc; curve 3, $Z(q)$ for fcc; curve 4, $Z(q)$ for bcc. (b) Concentration dependence of $S(q)$; curve 1, concentration, 2.75%; curve 2, 3.66%; curve 3, 5.49%; curve 4, 10.98%. Taken from ref 27 with permission. Copyright 1988 American Physical Society.

Table II
Distortion Parameter *g* for the Ordered Structure of Various Ionic Species[a]

material	diam, µm	concn, %	lattice spacing, µm	*g*	ref
latex[b] (LS)	0.09	0.05	0.98	0.15	7
latex[b,c] (LS)	0.05	0.1	0.56	0.19	25
latex[b] (SANS)	0.03	4	0.08	0.22	6
		8	680	0.19	
		13	540	0.17	
silica (SAXS)	0.012	2.75	0.0340	0.18	27
		5.49	0.0270	0.17	
		5.49	0.0258	0.19	[NaCl] = 5 × 10^{-3} M
		5.49	0.0251	0.22	[NaCl] = 10^{-2} M
		10.98	0.0219	0.16	

[a] The scattering measurements in Table II were done in the absence of added salt unless otherwise indicated. For all cases fcc strucutres were assumed. [b] These lattices are all polystyrene based. [c] In the presence of 10^{-5} M NaCl.

(coexistence of the ordered and disordered structures as shown in Figures 2) is formed. Recently, the crystal size has been reported to be correlated with the *g* value.[29] This is plausible because crystals cannot grow to larger sizes when their distortion is substantial. From the experimental point of view, however, it is difficult to determine the size of the ordered structure even for the polymer latex systems, because the microscopic vision is limited.

Two-Dimensional Fourier Analysis of a Latex Suspension. A few words are necessary on the Fourier analysis for latex systems. From the halo shown in Figure 1, the interparticle spacing was evaluated to be 0.97 µm. This value is in very good agreement with that (1.06 ± 0.12) µm estimated from the ordered structure of the corresponding micrograph (Figure 2). Similarly, the Fourier pattern (Figure 4b) gave a spacing of 1.21 µm, which agrees well with the value (1.21 ± 0.07) µm from the micrograph (Figure 4a). The agreement is a matter of course and shows the correct execution of our Fourier transformation. Furthermore, the agreement implies that even the single broad peak should prudently be considered.

The interparticle correlation can be destroyed by the addition of a small amount of NaCl to the suspension. Thus, Figure 2b shows almost the complete absence of Fourier rings and spots. This salt concentration dependence is in agreement with the previous microscopic observation[16] and with SANS data reported by Ottewill et al.[6] Although the present Fourier analysis done on the two-dimensional structure and furthermore the thermal motion of the particles is "frozen" in the analysis, it appears to rationalize our previous interpretation of the scattering peak in terms of the intermacroion ordering.

Ordered Liquid or Disordered Crystal?

We have tried to understand the ordered structures of ionic particles in solution as distorted crystals. The opposite viewpoint of course is also possible. One example is the treatment on the basis of a theory of liquids such as the mean spherical approximation (MSA) or the rescaled mean spherical approximation (RMSA).[30,31] It is often claimed that the $S(q)$, or the radial distribution function $q(r)$, experimentally found for micelle or latex solutions can be described satisfactorily by these theoretical considerations. As a matter of fact, the RMSA calculation is in good agreement with the observed $S(q)$ as shown in Figure 7. (Compare the crosses and circles.) It must be pointed out, however, that the agreement with the paracrystal theory is as gratifying as that with RMSA method, a far as the first peak height and width are concerned. If the agreements are real, the ordered structure under consideration would be of an intermediate nature between the structure of a liquid and that of a crystal. Although the problem is to some extent semantic, the "intermediateness" is an interesting problem for future study.

One reservation is made on the approach of the theory of liquids. In this treatment, the effective interparticle interaction is assumed to be purely repulsive. This seems unrealistic to us. As mentioned above, there exist localized, non-space-filling, ordered structures in latex suspensions. In such a case, the interparticle distance ($2D_{\mathrm{exp}}$) measured is smaller than the average spacing ($2D_0$) calculated from the particle concentration. As emphasized already,[2] the intermacroion (Bragg) spacing ($2D_{\mathrm{exp}}$) which can be calculated from the SAXS and SANS curves of macroions is also smaller than the $2D_0$ when they are highly charged. Thus both microscopy and scattering studies reveal $2D_{\mathrm{exp}} < 2D_0$. In this respect, the latex suspensions and the macroion solutions have a common feature, namely, the two-state structure. It should be remembered, as pointed out in the Introduction, that simple ion systems such as $ZnBr_2$ also show localized ordering. Latex suspensions left undisturbed for two to several months show crystal grains of a fairly large size being dispersed in the suspensions.[9,21] For such localized structures to exist in real solutions, we have to admit the existence of an effective attraction between the particles or macroions, although they are similarly charged. Since the addition of simple salts, which shield the electrostatic interaction, prevents the appearance of the structures, this attraction is concluded to be of electrostatic origin.[2] The attraction in question manifests itself in the unusual *decrease* of the activity of macroion or latex species with increasing concentration.[32,33] This is in sharp contrast to the ideal solution for which the activity increases with increasing concentration linearly according to the Raoult law. Such an electrostatic attraction has been noted by Langmuir[34] and Bernal and Fankuchen.[12] Recently Sogami[35] demonstrated theoretically that attraction is possible between similarly charged entities when the role of counterions is duly taken into account. Other recent theories also predict that the electrostatic interaction between colloidal particles can be an attraction,[36,37] and Monte Carlo simulations show that there is a net attractive force between similarly charged surfaces.[38,39] Under these circumstances, we believe it is fair to conclude that the ordered structure in latex suspensions need not always be attributed in terms of the RMSA approach to purely repulsive interactions.

Note Added in Proof. Recently Suzuki[40] extended the ordinary mean-field theory to formulate the super-effective-field theory and pointed out that "effectively attractive interaction" plays an essential role even in the Alder transition, which has been claimed to be explainable in terms of the repulsion-only assumption[41] and the single-occupancy model.[42] Since it seems to us that the single-occupancy model, namely, the confinement of particles in cell compartments, is equivalent to the introduction of an attractive interaction, Suzuki's conclusion is most reasonable.

Concluding Remarks

In the present review, we have tried to emphasize that the ordered structure in latex suspensions can be well described by invoking the concept of paracrystalline distortion. Naturally there remain various questions to be answered in the paracrystal theory. Nonetheless we believe that our conclusion is correct at least to the first approximation. It seems basically wrong to imagine a highly stable, firm, and perfect crystal structure in ionic solutions on the one hand and also to claim an almost complete lack of particle–particle interference on the other. The reality appears to be just in between.

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