Extraordinary Behavior in the Structural Properties of Colloidal Macroions in Deionized Suspension and the Importance of the Debye Screening Length

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Recently, keen attention has been paid to the extraordinary suspension properties of "deionized" colloidal spheres. A suspension of monodisperse colloidal spheres, which is usually milky white in appearance, exhibits beautiful iridescent colors in the deionized state. This iridescence is due to the Bragg reflection of visible light by the "crystal-like" structures. The colloidal crystals behave like the usual solid crystals of identical atoms. However, their physical properties are extraordinary, mainly because they are crystal-like liquids with a fundamental length of about 10^3–10^4 times that of the atomic length scale. Typical examples of the extraordinary properties are (1) existence of a broad peak in the X-ray, neutron, and light scattering curves for the "liquid-like" structures,[1-5] (2) microscopic observation of "crystal-like" structures of colloidal spheres,[6-9] (3) spectroscopic properties of colloidal crystals,[10-15] (4) characteristic dynamic properties of "gas-like", "liquid-like", and "crystal-like" colloidal suspensions,[16-22] and (5) specific viscosity properties.[23-27]

In this Account, the extraordinary properties are explained essentially by the effective hard-sphere model,[6-8] i.e., the electrostatic intermacroion *repulsion* and the elongated Debye screening length (D_l) in the deionized solution. D_l is calculated from eq 1. Here,

$$D_1 = (4\pi B n)^{-1/2} \qquad (1)$$

B is the Bjerrum length, given by $e^2/\epsilon kT$, where e is the electronic charge and ϵ is the dielectric constant of the solvent. The concentration of "free-state" (diffusible) cations and anions in solution is given by $n = n_c + n_s + n_0$, where n_c is the concentration of diffusible counterions, n_s is the concentration of ions from foreign salts, and n_0 is the concentration of hydrogen and hydroxide ions from the dissociation of water. The fraction (β) of the free-state counterions for a flexible macroion depends only on the charge density parameter and remains constant irrespective of the degree of polymerization and the total number of stoichiometric charges (Z).[28-30] For spherical macroions, on the other hand, β changes dramatically, depending on both the size and the charge density of the spheres. In this case the parameter Z is the only factor needed to determine the β value.[31-35]

Recently, mixed beds of cation- and anion-exchange resins, which can eliminate ionic impurities very effectively and *completely* from solutions to levels as low

as 2×10^{-7} M (limited by H^+ and OH^- from water dissociation), have become available commercially. Various distinct extraordinary solution properties are expected to occur for completely deionized solutions, especially for colloidal macroion systems, since the Debye screening length around the macroions is significantly long, to the order of micrometers. Sheaths of double layers are very soft and compressed easily or distorted by an external force. This author believes that the ideas concerning the electrical double layer and the Debye length are much more real than those first proposed in the Debye–Hückel and DLVO (Derjaguin–Landau–Verwey–Overbeek) theories. The following sections discuss in detail how the Debye screening length in the effective hard-sphere model explains very well the extraordinary properties of deionized macroion systems.

(1) de Gennes, P.-G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Paris)* 1976, *37*, 1461.
(2) Schaefer, D. W. *J. Chem. Phys.* 1977, *66*, 3980.
(3) Hansen, J. P.; Haytor, J. B. *Mol. Phys.* 1982, *46*, 651.
(4) Hartl, W.; Versmold, H. *J. Chem. Phys.* 1984, *81*, 2507.
(5) Ottewill, R. H. *Ber. Bunsenges. Phys. Chem.* 1985, *89*, 517.
(6) Kose, A.; Ozaki, M.; Takano, K.; Kobayashi, Y.; Hachisu, S. *J. Colloid Interface Sci.* 1973, *44*, 330.
(7) Crandall, R. S.; Williams, R. *Science (Washington, D.C.)* 1977, *198*, 293.
(8) Pieranski, P. *Contemp. Phys.* 1983, *24*, 25.
(9) Okubo, T. *J. Chem. Phys.* 1987, *86*, 2394.
(10) Luck, W.; Klier, M.; Wesslau, H. *Ber. Bunsenges. Phys. Chem.* 1963, *67*, 75, 84.
(11) Hiltner, P. A.; Krieger, I. M. *J. Phys. Chem.* 1969, *73*, 2386.
(12) Clark, N. A.; Hurd, A. J.; Ackerson, B. J. *Nature (London)* 1979, *281*, 657.
(13) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* 1986, *82*, 3163.
(14) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* 1986, *82*, 3175.
(15) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* 1986, *82*, 3185.
(16) Brown, J. C.; Pusey, P. N.; Goodwin, J. W.; Ottewill, R. H. *J. Phys. A* 1975, *8*, 664.
(17) Mitaku, S.; Otsuki, T.; Okano, K. *Jpn. J. Appl. Phys.* 1978, *17*, 305, 627.
(18) Clark, N. A.; Ackerson, B. J. *Phys. Rev. Lett.* 1980, *44*, 1005.
(19) Lindsay, H. M.; Chaikin, P. M. *J. Chem. Phys.* 1982, *76*, 3774.
(20) Joanicot, H. M.; Jorand, M.; Pieranski, P.; Rothen, F. *J. Phys. (Paris)* 1984, *45*, 1413.
(21) Lindsay, H. M.; Dozier, W. D.; Chaikin, P. M.; Klein, P.; Hess, W. *J. Phys. A* 1986, *19*, 2583.
(22) Okubo, T. *J. Colloid Interface Sci.* 1987, *117*, 165.
(23) Booth, F. *Nature (London)* 1948, *161*, 83.
(24) Mooney, H. *J. Colloid Sci.* 1951, *6*, 162.
(25) Harmsen, G. J.; van Schooten, J.; Overbeek, J. G. Th. *J. Colloid Sci.* 1953, *8*, 72.
(26) Krieger, I. M. *Adv. Colloid Interface Sci.* 1972, *3*, 111.
(27) Okubo, T. *J. Chem. Phys.* 1987, *87*, 6733.
(28) Huizenga, J. R.; Grieger, P. F.; Wall, F. T. *J. Am. Chem. Soc.* 1950, *72*, 2636.
(29) Manning, G. S. *J. Chem. Phys.* 1965, *43*, 4260.
(30) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971.
(31) Vanderhoff, W.; van de Hul, H. J.; Tausk, R. J. M.; Overbeek, J. Th. In *Clean Surfaces: Their Preparation and Characterization for Interfacial Studies*; Goldfinger, G., Ed.; Marcel Dekker: New York, 1970.
(32) Ito, K.; Ise, N.; Okubo, T. *J. Chem. Phys.* 1985, *82*, 5732.
(33) Alexander, S.; Chaikin, P. M.; Grant, P.; Morales, G. J.; Pincus, P.; Hone, D. *J. Chem. Phys.* 1984, *80*, 5776.
(34) Okubo, T. *Ber. Bunsenges. Phys. Chem.* 1987, *91*, 1064.
(35) Okubo, T. *J. Colloid Interface Sci.*, in press.

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Table I
Comparison of $2D_{exptl}$ and D_{eff} in Binary Mixtures of H1001 + D1A92 Spheres ([H1001]$_0$ = 0.212 vol %)[a]

[D1A92]$_0$/(vol %)	$2D_{exptl}/\mu m$			$D_{eff}/\mu m$		
	$2D_{exptl,11}$	$2D_{exptl,12}$	$2D_{exptl,22}$	$D_{eff,1}$	$(D_{eff,1} + D_{eff,2})/2$	$D_{eff,2}$
0	2.25			2.21	1.95	1.69
0.19	2.12	1.80	1.50	2.12	1.86	1.59
0.62	1.95	1.67	1.35	1.96	1.70	1.45
1.87	1.92	1.52	1.22	1.75	1.48	1.22
3.74	1.77	1.39	1.12	1.58	1.32	1.07

[a] Taken from ref 42.

Microscopic Observation of "Crystal-like" Colloids in Sedimentation Equilibrium

Hachisu et al.[6] first developed an ultramicroscopic technique for the direct observation of the ordered structures of latex spheres by using a metallurgical microscope. However, investigating the ordering in dilute concentrations of colloidal particles is often difficult due to sedimentation of the particles. The specific gravity of polystyrene spheres is usually near 1.05, which is larger than that of water. Therefore, when particle size is larger than 200 nm, sedimentation occurs as a result of the Earth's gravitational field. This sedimentation effect was first discussed in detail by Crandall and Williams[7] and later by Furusawa et al.[36]

In sedimentation equilibrium, the distinct sedimentation layers are observed in observation cells in which the ion-exchange resins are hung in small bags. The height of the layers is usually less than 1 mm, and the remaining upper portion is solvent. These equilibrium states are only obtained 5–10 days after the sample suspension has been set into the cell. The microscopic observation is made through a cover glass at the bottom of the cel. Figure 1a shows hexagonal structures of deionized spheres (specific gravity (sg) = 1.50, diameter = 1.02 μm).[9] The center-to-center interparticle distance ($2D_{exptl}$) is 2.5 μm. The spheres move vigorously around the equilibrium points and are distributed regularly along the cover glass, widely separated from each other. Figure 1b shows a picture for bowl-shaped particle (DR728) + sphere (1.02 μm in diameter) mixtures in sedimentation equilibrum.[37] Though the cavities of DR728 are rather large, 5–6 μm in diameter, small spheres fit the cavities. The host and guest molecules do not touch directly, but keep apart from each other.

When microscopic observation was done every day or every other day after the solution was set, surprisingly, $2D_{exptl}$ increased sharply during the first 1–3 days and reached an equilibrium value after 5–7 days.[9,37–43] This fact means that the deionizing process in the observation cell takes longer to be completed than expected. Note here that the Debye length expands more for more dilute suspensions and particles having less charge. The intersphere distance for gold sols, which are very heavy (sg = 19.3) and have a small amount of adsorbed charge on their surfaces, was observed to be surprisingly long, several micrometers.[39] The repulsive forces between highly charged colloids is very strong but only at short range. For slightly charged colloids, on
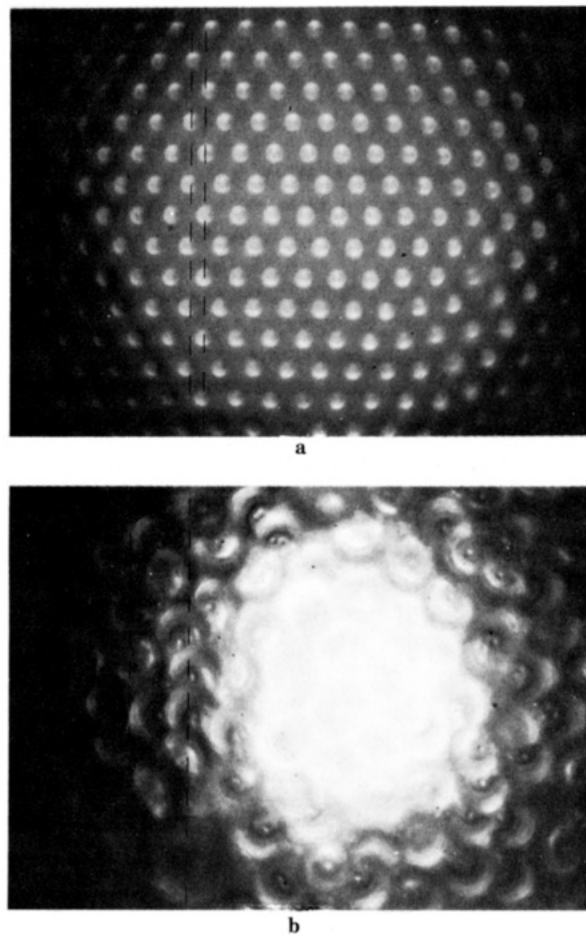
(36) Furusawa, K.; Tomotsu, N. *J. Colloid Interface Sci.* **1983**, *93*, 504.
(37) Okubo, T.; Aotani, S. *Naturwissenschaften* **1988**, *75*, 145.
(38) Okubo, T. *J. Chem. Phys.* **1987**, *86*, 5182.
(39) Okubo, T. *Colloid Polym. Sci.* **1987**, *265*, 522.
(40) Okubo, T. *Colloid Polym. Sci.* **1987**, *265*, 597.
(41) Okubo, T. *Angew. Chem.* **1987**, *99*, 803.
(42) Okubo, T. *J. Chem. Phys.* **1987**, *87*, 5528.
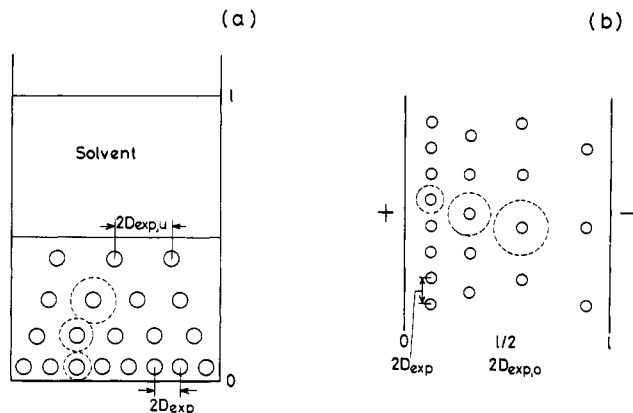(43) Okubo, T. *J. Chem. Phys.* **1988**, *88*, 2083.

a

b

Figure 1. (a) Typical pictures showing the ordered structure of heavy H1001 spheres (code 672) in sedimentation equilibrium. [H1001]$_0$ = 0.212 vol % in a 10 vol % MeOH + H$_2$O mixture. The distance between the dashed parallel lines is 1.0 μm. Reproduced with permission from ref 9. Copyright 1987, American Institute of Physics. (b) A typical picture showing the inclusional association of N1001 spheres in the cavities of bowl-shaped particles (DR728) in sedimentation equilibrium 1 day after the cell was set. [DR728]$_0$ = 0.0199 vol %, [N1000]$_0$ = 0.241 vol %. The distance between the dashed parallel lines is 10 μm.

the other hand, the electrostatic interparticle repulsion is very weak, and the distance between counterions is large, making D_1 large so that the forces prevail to fairly long distances.

Microscopic observation revealed that the particles behave like enlarged particles due to the Debye screening length. The effective sizes (D_{eff}) of the particles, including D_1, decreased as the ionic strength of the solvent increased. Table I shows the comparison of $2D_{exptl}$ and D_{eff} for binary mixtures of spheres, H1001 + D1A92 (sg = 1.05, diameter = 497 nm).[42] Agreement between $2D_{exptl}$ and D_{eff} is excellent. It is clear that the observed value of $2D_{exptl}$ is explained satisfactorily by

Figure 2. Schematic representation of ordered and asymmetric distribution of deionized spheres in a gravitational field (a) and in an electric field (b).

the Debye screening length.

The $2D_{exptl}$ values decreased continuously as ϕ^* (initial concentration) of particles increased. This means that the shells of Debye length around the particle are soft and elastic and can be compressed easily by the weight of other spheres of the upper layers due to the gravitational field (see Figure 2a). In sedimentation equilibrium, Young's modulus (G) is estimated from the slope of the $2D_{exptl}$ vs ϕ^* plots as is given by eq 2.[9]

$$2D_{exptl} = 2D_{exptl,u} - (2\rho_{eff}glD_{exptl,u}\phi^*)/(100G) \quad (2)$$

Here, $2D_{exptl,u}$ is the interparticle distance at the highest suspension layer, ρ_{eff} is the effective density given by the specific gravity of spheres minus that of solvent, g is the gravitational constant, and l is the total height of liquid layer in the cell. Young's modulus was estimated to be in the range 0.11–16 Pa for crystal-like structures of particles with specific gravities between 1.05 and 19.3.[11,43-46] The G values of polystrene spheres determined by Crandall and Williams[7] ranged from 0.1 to 0.3 Pa, depending on the sphere concentrations.

The order of magnitude of G can be estimated by eq 3,[44] where m and U are the density of the spheres and

$$G \simeq mU \quad (3)$$

the energy of electrostatic repulsion between two particles, respectively. If it is assumed that the interparticle distance is $2D_{exptl}$ (μm), the effective charge on a sphere is α, and the dielectric constant of the solvent is ϵ, then G is given roughly by $10^{-5} \alpha^2/\epsilon(2D_{exptl})^4$ (Pa). The observed elasticity of a colloidal crystal is explained reasonably by this rough estimate.

The hexagonal ordering was observed not only in the deionized state but also in the presence of a foreign salt, and $2D_{exptl}$ decreased with increasing salt concentration.[9] Various kinds of "alloy" structure of triangular, square, pentagonal, hexagonal, heptagonal, and octagonal patterns were seen.[42] $2D_{exptl}$ increased by the addition of organic solvents of dielectric constants smaller than that of water, whereas $2D_{exptl}$ decreased in the presence of N-methylformamide or N-methylacetamide, which have a dielectric constant higher than that of water.[42] The influences of organic solvents are ex-
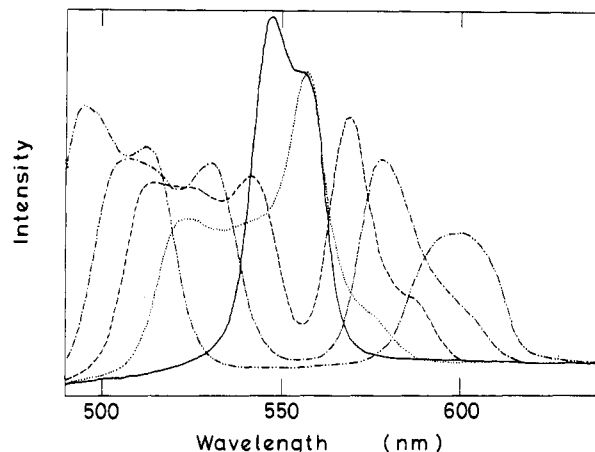

Figure 3. Time-resolved reflection spectra of a D1C27 solution. (2.10 vol %, 0.5-mm cell, applied voltage increased from 0 to 2.6 V, sampling time = 40 ms, interval = 300 ms): (—) 0 s (arbitrary); (···) 0.3 s; (– – –) 2.4 s; (–·–·) 6.9 s; (–··–··) 27.9 s. Reproduced with permission from ref 53. Copyright 1987, Royal Society of Chemistry.

plained reasonably by the changes of β values.

Reflection and Transmitted Light Spectra of "Crystal-like" Structures in Spherical Macroions

Luck et al.,[10,45] Krieger and co-workers,[11,46,47] Fujita and Ametani,[48] Hoffman,[49] and van de Ven and co-workers[50,51] have studied extensively the reflection spectra of polymer colloids, especially at high concentrations (ca. 10–40 vol %). In contrast, this author has discussed the reflection spectra of spheres in solution at relatively low concentrations (0.3–5 vol %).[13] $2D_{exptl}$ was determined from the wavelength at sharp reflection peaks. The face-centered cubic (fcc) distribution was more stable at higher concentrations than the body-centered cubic (bcc) distribution. The bcc structure often appears at a high solution temperature and in the presence of a small amount of foreign salt. The number of crystal layers within a crystallite was estimated to be several hundred and depended on the macroion concentration and solution temperature.[13,52]

Electrically induced changes in the lattice structure have been studied by time-resolved reflection spectrum measurements.[53] A schematic representation of the most plausible manner of ordering in an electric field is given in Figure 2b. $2D_{exptl}$ and $2D_{exptl,0}$ are the interparticle distances at the anode plate and at the mid plane in the electrode cell. The Bragg layers are parallel to the electrode surface, and D_{eff}, which includes the Debye length, is assumed to be close to the interparticle distance. The repulsive force between a pair of spheres for an asymmetric distribution of spheres in an electric field is counterbalanced by the force due to the external electric field.[7,51,53] From the slope of plots of wavelength at the reflection peak against electric field G was determined to be 6.2 Pa for D1C27 spheres (diameter = 91 nm).[53]

(44) Jorand, M.; Koch, A. J.; Rothen, F. *J. Phys. (Paris)* **1986**, *47*, 217.
(45) Luck, W.; Klier, M.; Wesslau, H. *Naturwissenschaften* **1963**, *50*, 485.
(46) Krieger, I. M.; O'Neill, F. M. *J. Am. Chem. Soc.* **1968**, *90*, 12, 3114.

(47) Hiltner, I. M.; Papir, Y. S.; Krieger, I. M. *J. Phys. Chem.* **1971**, *75*, 1881.
(48) Fujita, H.; Ametani, K. *Jpn. J. Appl. Phys.* **1979**, *18*, 753.
(49) Hoffman, R. L. *Trans. Sco. Rheol.* **1972**, *16*, 1, 155.
(50) Tomita, M.; van der Ven, T. G. M. *J. Colloid Interface Sci.* **1984**, *99*, 374.
(51) Tomita, M; van de Ven, T. G. M. *J. Phys. Chem.* **1985**, *89*, 1291.
(52) Okubo, T. *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 516.
(53) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2487.

Time-resolved reflection spectra are shown in Figure 3. The peak at shorter wavelength in the solid curve corresponds to the bcc lattice, and the shoulder at longer wavelength corresponds to the fcc lattice. Faint peaks in the longer wavelength region are attributed to selective Bragg reflection from the lattice layers close to the cathode. The reflection intensity at constant wavelength changed exponentially to reach the equilibrium value. The relaxation time was too short to be determined accurately by the instrument, but was ca. 10 ms.

The ordered fcc structures of polystyrene spheres was analyzed in the presence of water-soluble neutral polymers.[54] $2D_{exptl}$ was found to be in the order poly(ethylene glycol) > poly(vinyl alcohol) > no polymer > poly(vinylpyrrolidone) $\simeq$ (hydroxypropyl)cellulose > poly(acrylamide). Note that this order is very similar to that of the decreasing of the lattice spacing of heavy and monodisperse spheres, observed by microscopy, for the neutral polymers.[40] These effects are explained by intersphere repulsion from the electrical double-layer interaction, which is influenced by the adsorption of the polymer onto the latex surface due to hydrophobic and/or dipole–dipole interactions.

Crystal-like structures were studied at high pressures (1–2000 bar) by using reflection spectrum measurements.[55] Enhancement of bcc lattice formation and/or transformation from fcc to bcc are observed under elevated pressures. The influence of these pressures is explained reasonably by the increase of the effective charge number of the spheres and then the decrease in the Debye screening length as the pressure increases.

This author applied the transmitted light spectrum (TLS) technique for analyzing ordered structures.[14,15] It is surprising that no report has yet been published for a systematic analysis of the TLS of a latex solution. The TLS method provides information about the distance between parallel two-dimensional layers in ordered lattices, and it is especially effective for detecting small changes in lattice structure. Clear peaks showing the selective Bragg diffraction were observed in the transmitted light spectrum. The addition of a small amount of KCl shifted the crystal-like structures from fcc to bcc, and the ordered structure was completely broken down by the addition of KCl above 2×10^{-5} M.[15]

The TLC measurements were used to observe the ordered structure under shear flow using a thin flow cell.[56] The fcc and bcc structures coexisted under flow, although the lattices were deformed and melted at high shear rate. Compression of the Bragg spacing occurred with increasing shear rate at relatively low concentrations. At intermediate concentrations, a sharp increase and/or decrease in the Bragg spacing occurred. At higher concentrations, the spacing simply increased as the shear rate increased. The deformation of the electrical double layer from a spherical shape was deduced under shear flow and was consistent with the sliding-layer model[50] at rather high concentrations.

Time-resolved TLS were obtained during the reappearance of crystal-like structures of deionized spheres after the rapid flow through a thin optical cell was stopped.[57] Fast formation of metastable ordered

Table II
Comparison of Observed D_{tr} ($D_{tr,obsd}$) with Those Calculated ($D_{tr,calcd}$)[a]

[D1C25]/ (vol %)	τ_r/s		$D_{tr,obsd} \times 10^8 (cm^2 s^{-1})$		$D_{tr,calcd} \times 10^8/(cm^2 s^{-1})$
	SPSF	CSF	SPSF	CSF	
0.338	0.05	0.036	0.9	1.2	1.1 (5.8)[b]
0.675	0.02	0.019	1.4	1.5	1.4 (5.8)
1.01	0.025	0.015	0.9	1.4	1.6 (5.8)
1.69	0.0060	0.0091	2.5	1.7	1.9 (5.8)
3.38	0.0047	0.0047	2.0	2.0	2.4 (5.8)

[a] Taken partly from ref 22. [b] $D_{tr,calcd}$ from the crystallographic size of the sphere.

structures finished within 100 ms. Formation of the stable structure was attained after more than 1 s.

Structural Relaxation Times and the Transitional Movement of Spherical Macroions

The structural relaxation time (τ), the time of fluctuation of spheres, is one of the most fundamental dynamic properties. This author observed the τ values of spheres in both crystal-like and liquid-like suspensions by spectrophotometric stopped-flow (SPSF) and conductance stopped-flow (CSF) methods.[22,58] Hitherto, we have studied many chemical and physical reactions intensively using the CSF method.[59-66]

The τ values obtained for the crystal-like structures (D1C25 spheres, diameter = 85 nm) are shown in Table II. In many cases, two kinds of relaxation times, fast (τ_f) and slow (τ_s), were observed. The τ_f values are designated as the real relaxation times for the crystal-like or liquid-like structure formation, and the slower values (τ_s) are for the fluctuation of crystallites and/or their grain boundaries.[18] τ_f is given by eq 4, where $2D_0$

$$\tau_f = (2D_0)^2/6D_{tr} \qquad (4)$$

is the mean intersphere distance and D_{tr} denotes the cooperative translational diffusion constant in strongly interacting colloids. The D_{tr} value of spheres is given by the Einstein–Stokes equation for self-diffusion.

$$D_{tr} = kT/(3\eta\pi D_{eff}) \qquad (5)$$

Here, η is the viscosity of the solvent. The agreement between the observed and calculated values of D_{tr} is excellent when the Debye length is taken into account. These values contrast with the D_{tr} values calculated from the crystallographic size of the sphere (parenthetical values in Table II). Excellent agreement was obtained also for the liquid-like structures.[58] It should be noted that the Debye length does not correspond to the hydrodynamic length quantitatively. A large number of very small counterions move around the colloidal spheres, and this case the counterions are safely as-

(54) Okubo, T. *J. Chem. Soc., Faraday Trans. 1*, 1987, *83*, 2497.
(55) Okubo, T. *J. Chem. Soc., Faraday Trans. 1*, in press.
(56) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* 1988, *84*, 1171.
(57) Okubo, T. *J. Chem. Soc., Faraday Trans. 1* 1988, *84*, 1163.
(58) Okubo, T. *J. Chem. Phys.* 1987, *87*, 3022.
(59) Okubo, T. *J. Am. Chem. Soc.* 1987, *109*, 1913.
(60) Okubo, T.; Kitano, H.; Ishiwatari, T.; Ise, N. *Proc. R. Soc. London, Ser. A* 1979, *366*, 81.
(61) Okubo, T. *Biophys. Chem.* 1980, *11*, 425.
(62) Okubo, T.; Enokida, A. *J. Chem. Soc., Faraday Trans. 1*, 1983, *79*, 1639.
(63) Okubo, T.; Hongyo, K.; Enokida, A. *J. Chem. Soc., Faraday Trans. 1*, 1984, *80*, 2087.
(64) Okubo, T. *Makromol. Chem., Suppl.* 1985, *14*, 161.
(65) Kitano, H.; Hasegawa, J.; Iwai, S.; Okubo, T. *Polym. Bull.* 1986, *16*, 89.
(66) Kitano, H.; Hasegawa, J.; Iwai, S.; Okubo, T. *J. Phys. Chem.* 1986, *90*, 6281.

sumed to have the apparent hydrodynamic volume. The hydrodynamic length will be much shorter than the Debye length because many of the solvent molecules can flow freely through the counterion clouds. A quantitative and theoretical discussion remains to be given.

The τ_f value of a spherical macroion is given by the simple relation[18,21]

$$\tau_f \simeq \rho/G \qquad (6)$$

Here, G denotes the rigidity (local shear elastic modulus) of the latex suspension. G ranged from 0.01 to 1 Pa for spheres smaller than 0.1 μm in diameter, and these values are not far from those of previous reports by the dynamic methods.[17,19,20,67]

Surprisingly, D_{tr} of colloidal spheres in gas-like suspensions increased as NaCl concentration increased; D_{tr} at [NaCl] = 10^{-6} M was one-fourth of that at 10^{-2} M. Furthermore, D_{tr} was rather insensitive to the sphere size.[68] These results are explained beautifully by the Einstein–Stokes equation, if we take account of the Debye length.

Miscellaneous Properties

Quite recently, this author determined the rotational relaxation time and the diffusion constant (D_r) of monodisperse ellipsoidal colloids of tungstic acid in aqueous suspension conveniently and precisely by the SPSF and CSF techniques.[59] The observed D_r values were small than the theoretical values obtained by Perrin's equation, and the deviation increased as the size decreased. This deviation was explained quantitatively by the contribution of the Debye length.

Rheological properties of colloidal spheres have been studied by many researchers.[23–26] However, the theoretical estimation of the electroviscous effect does not always agree with the experimental results, especially for solutions of very low ionic strength.

The reduced viscosities, η_{sp}/c, of deionized colloidal silica were much higher than would have been expected by Einstein's prediction and *decreased* sharply with increasing concentration.[27,69,70] Good straight lines were obtained for plots of η_{sp}/c against c for constant values of n, which appear in eq 1. The linearity was excellent, when we take experimental errors into account. Clearly, the linearity corresponds to the viscosity curves subject to the condition that the concentrations of the diffusible ions are constant, and as a result the effective sizes of the spheres, which include the Debye length, remain constant.[71] This sharp decrease of η_{sp}/c with c is evidence for the important role of the Debye screening length in deionized liquid-like suspensions.

A sharp peak was observed in the reduced viscosity vs concentration curves of deionized colloidal silica and deionized latex spheres.[27,69] The peak shifted to higher concentrations as NaCl was added. The peak corresponds to the transition between liquid-like and crystal-like structures. It is worth noting that this extraordinary transition is very similar to the sharp transition observed for the viscosity of liquid crystals
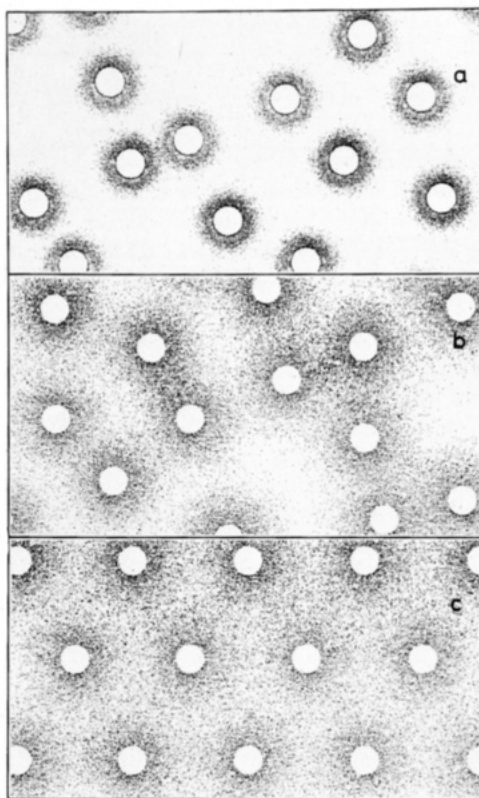

Figure 4. Schematic representation of gas-like (a), liquid-like (b), and crystal-like (c) structures of spherical macroions. Dots show counterions.

of polymers, poly(γ-benzyl glutamate), for example.[72–74]

Concluding Remarks

Distributions of spherical macroions in gas-like, liquid-like, and crystal-like suspensions are shown schematically in Figure 4. The thickness of the electrical double layer expands more for the lower values of n. In the deionized state, the Debye lengths are significantly long, and the electrostatic repulsive forces prevail to a long distance, as long as micrometers, though the forces become *very* weak. Following the effective hard-sphere model, when the D_{eff} of spheres containing D_1 is much shorter than $2D_0$, i.e., $D_{eff} \ll 2D_0$, a gas-like distribution is observed (Figure 4a). When D_{eff} is comparable to or shorter than the $2D_0$ value, the distribution is usually liquid-like (Figure 4b), and spheres move without keeping their positions, though the effective concentration is much higher than the stoichiometric concentration due to the effect of the elongated Debye length. When $D_{eff} \geq 2D_0$, crystal-like ordering occurs (Figure 4c). Thus, the Debye length is the essentially important fact for the characteristic properties, and the inequality between D_{eff} and $2D_0$ is a very useful criterion for distinguishing the three structures from each other. The idea of the relative length scales of the Debye length and interparticle spacing is very similar to the four ionic strength regions proposed by Schmitz et al.[75] several years ago.

The experimental results described above and interpretation by the elongated Debye screening length

(67) Otsuki, T.; Kishimoto, A.; Mitaku, S.; Okano, K. *Jpn. J. Appl. Phys.* **1981**, *20*, 509.
(68) Okubo, T. *J. Phys. Chem.*, submitted.
(69) Okubo, T. *Naturwissenschaften* **1988**, *75*, 91.
(70) Okubo, T. *Ber. Bunsenges. Phys. Chem.*, in press.
(71) Pals, D. T. F.; Hermans, J. J. *J. Polym. Sci.* **1948**, *3*, 897.

(72) Papkov, S. P.; Kulichikhim, V. G.; Kalmykova, V. D.; Malkin, A. Ya. *J. Polym. Sci., Polm. Phys. Ed.* **1981**, *19*, 229.
(73) Kiss, G.; Porter, P. S. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 193.
(74) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 229.
(75) Schmitz, K. S.; Lu, M.; Gauntt, J. *J. Chem. Phys.* **1983**, *78*, 5059.

and the interparticle repulsion are believed to be important in that they bear on the controversial issue of electrostatic intermacroion *attraction* for the deionized systems.[76] As described before,[38] the electrostatic intersphere *attraction* had been proposed to exist from the erroneous assumption of the two-state structure. Furthermore, other evidence for the intersphere attraction was reported to be the rapid *decrease* in single-ion activity of macroions (a_{2p}) as their concentration increases.[76] However, the rapid decrease in a_{2p} does not support the intersphere attraction, because the rapid decrease in a_{2p} is beautifully explained quantitatively by counterion condensation and the Manning theory for gegenion–macroion interactions (not macroion-macroion attraction).[77] The other serious misinterpretation was that a broad single peak, which appeared in small-angle X-ray scattering curves for the salt-free flexible macroions, was believed to be evidence for the existence of a "paracrystal-like" ordering.[76] However, the broad single peak undoubtedly indicates the purely liquid-like nature of the solution, as has been confirmed by the correlation-hole theory.[1,2,5] Overbeek pointed out that Ise–Sogami theory supporting the attraction contained serious errors, and attraction vanished when these errors were corrected.[78]

The extraordinary properties in deionized solution occur more often for the smaller colloids. However, no reliable reports supporting the existence of the crystal-like structures has been published for spherical macroions smaller than ca. 20 nm in diameter. This would be due to the fact that the thermal movement of the very small spheres is very vigorous to a similar extent as that of counterions, and the stable electrical double layers do not form around the macroions.

Although a quantitative discussion still remains to be given, the extraordinary behavior of deionized colloids can be attributed to the important role of the Debye screening length in the hard-sphere model. This idea is consistent with the DLVO theory on colloidal stability.[79]

(76) Ise, N. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 323.
(77) Ise, N.; Okubo, T. *Macromolecules* **1978**, *11*, 439.

(78) Overbeek, T. Th. G. *J. Chem. Phys.* **1987**, *87*, 4406.
(79) Verwey, E. J. W.; Overbeek, J. Th. G. *The Theory of the Stability of Liophobic Colloids*; Elsevier: Amsterdam, 1948.