Review

When does like like like?
Microscopic inhomogeneity in homogeneous ionic systems

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Abstract: Recent experimental results confirm the previous finding that ionic solute species locally form ordered structures in macroscopically homogeneous, dilute solutions. Ionic dendrimers with univalent counterions are found to show a Bragg diffraction peak in the small-angle X-ray profiles, as has been reported for other ionic polymers and colloidal particles. The Bragg spacing is smaller than the average spacing expected from concentration, suggesting the localized ordered arrangements in solutions. The localization testifies to a weak, but undeniable attraction between like-charged dendrimer ions, which is generated through the intermediary of unlikely charged counterions. The *like-like* attraction is shown to disappear for bivalent counterions, however; The diffraction peak is not observed, because the charge number of the dendrimers is lowered more strongly by the bivalent ions than the univalent ones. Neutron scattering profiles for polystyrenesulfonate (PSS) solutions demonstrate diffraction peaks, sustaining the existence of the like-like attraction. The transfer from univalent counterions to bivalent ones increases the Bragg spacing, suggesting weakening of the attraction. Dynamic light scattering indicates the presence of two diffusive (fast and slow) modes for homogeneous PSS solutions, which correspond to the Brownian motion of free macroions and the motion of the localized structures, respectively. With increasing counterion valency, the fast mode becomes smaller while the slow mode is increased. A strong attraction is detected by a direct measurement of the interaction potential using colloidal particles of a high charge density while no attraction but only repulsion is found for low charge particles. This is reasonable in light of the nature of the counterion-mediated attraction. Recent computer simulation works substantiate qualitatively the existence of the like-like attraction. Quantitatively, however, they fail to reproduce the observed fact that the attraction is more intense for univalent counterions than for bivalent ones. The size of the local structure is found to depend on the diameter of filter pores employed in purification process, while the Bragg spacing is not influenced. It is concluded that the structures are ruptured by filtration and thereafter regenerated rather rapidly, suggesting that they are not filtrable aggregates but loose assemblies of macroions containing solvent. The likewise local structure is inferred to exist in simple ionic solution and in "dust" plasma as well, albeit with largely different time and length scales. The structural inhomogeneity (and hence the like-like attraction) thus appears to be one of basic features of dilute ionic systems in general.

Key words: Dendrimers; polystyrenesulfonate; zinc bromide; ordered structure; counterion-mediated attraction; solution structure.

Introduction. Molecules and/or ions had been generally assumed to be more or less uniformly distributed in homogeneous, condensed systems with thermal fluctuation. The concentration of solute species is then defined by its total number divided by the system volume, which is sufficient to describe the physical properties of the system. This rather axiomatic feature was challenged by direct observation on ionic colloidal particles,[1)] which are large enough to be seen by optical microscope. The co-existence of ordered regions having high number density and disordered regions of low

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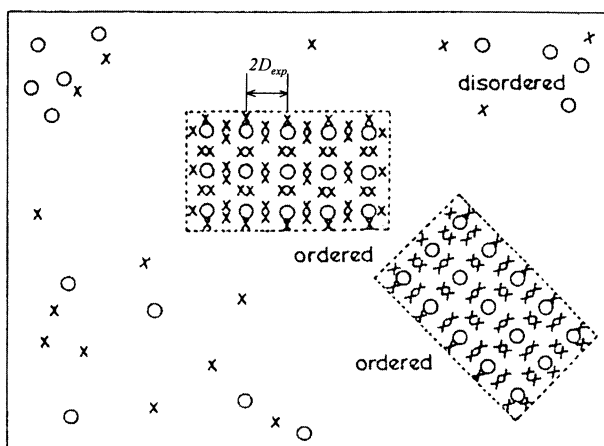**) e-mail: norio@ise.mbox.media.kyoto-u.ac.jp

Fig. 1. Schematic view of the coexistence of ordered regions of high number density of ionic solute species and random regions of low density (the two-state structure). The circle denotes conveniently charged species such as ionic polymers, dendrimers, colloidal particles and so on, while the cross stands for their counterions such as H^+ or Cl^-. Taking advantage of colloidal particles that can be "seen" under microscope, it was verified that the particles in the ordered regions show an oscillatory motion around the lattice points (lattice vibration) and the structure as a whole moves rather slowly, whereas the free particles' motion is approximately described by the Einstein theory of Brownian motion. Thus, at least two (fast and slow) diffusion processes are expected from the homogeneous systems for the free particles and the ordered particles, respectively. Based on this straightforward information, a similar situation is inferred to exist also for other "invisible" solutes such as ionic polymers. The closest distance of approach between the solutes inside the ordered region is $2D_{exp}$, which can be estimated from the Bragg diffraction peak or directly from micrographs for colloidal particles. In view of the difference in the number densities inside and outside the ordered regions, $2D_{exp}$ is smaller than the average spacing between solutes $(2D_0)$ which can be estimated from the overall concentration. It is rather difficult to make a general statement of the size of individual structure, because it depends sensitively on the experimental conditions. However, the total sum of the volume of all structures is $(2D_{exp}/2D_0)^3$ of the whole system volume.

density (the two-state structure, as highly schematically depicted in Fig. 1) was actually video-recorded, when the dispersion was highly purified. Though in an indirect manner, X-ray scattering measurements of ionic polymer solutions including charged proteins[2] substantiated the two-state-structure. Such a microscopic inhomogeneity was accentuated by a subsequent finding of void structure containing only solvent without particles by confocal laser scanning microscope on colloidal dispersions.[3] In short, two concentrations have to be defined in macroscopically homogeneous solutions for complete description of the systems. Since these facts were in direct contradiction to the widely accepted view in condensed matter physics and also to the established theo-

retical framework in colloid science (the so-called Derjaguin-Landau-Verwey-Overbeek (DLVO) theory[4]), they were immediately regarded as experimental artifacts, when made public, so that no ones tried to reproduce them over 14 years until a Chicago group photographed the two-state structure for colloidal dispersions.[5] These findings led us to the conclusion that there must be an electrostatic attraction between like-charged solute species through the intermediary of their counterions, in other words, *like likes like*. Although the attraction is inconsistent with the established views, it is acceptable if one carefully considers the principle discussed by Feynman[6] for ionic systems in a broad sense of words, who claimed that "attraction arises because the repulsion of likes and an attraction of unlikes will tend to bring unlikes closer together and push likes farther apart".

While paradoxes inherent in the established view were clarified by us,[7],[8] it seems that the experimental observation of the attraction is now being accepted,[9] as judged from a large number of publications in the past two years, which deal with direct measurements of the interparticle forces, computer simulation, and theoretical elucidation of the attraction. In the present article, recent experimental results are reviewed. Furthermore, this inhomogeneity is shown not merely to be a characteristic of ionic polymers and colloidal particles but is one of fundamental properties of ionic systems ranging from colloidal particles to simple salt solutions and "dust" plasma, though with different time and length scales: It is important to emphasize that the fact that the inhomogeneity was first observed for polymeric substances is due to the availability of the detection techniques suitable for these systems, not due to their specificity.

Recent study of ordered structure.

(a) *Ionic Dendrimers.* Dendrimers are spherical polymers whose architecture is highly controlled three-dimensionally, as shown in Fig. 2. We carried out small-angle X-ray scattering (SAXS) study of dilute solutions of cationic poly(amido amine) (PAMAM) dendrimers, which is composed of ethylenediamine (or ammonia) as the initiator core and copolymer of ethylenediamine and methyl acrylate as the branch and have primary amine groups at each branch and tertiary amine groups at each branching point, so that they behave as cationic, globular polyelectrolytes in acid solution. The generations 4, 7, and 10 (G4, G7, and G10) have molecular weights of 1.4×10^4, 1.16×10^5, and 9.33×10^5 and 64, 512, and 4096 primary amine groups, respectively. The

Repeating unit:

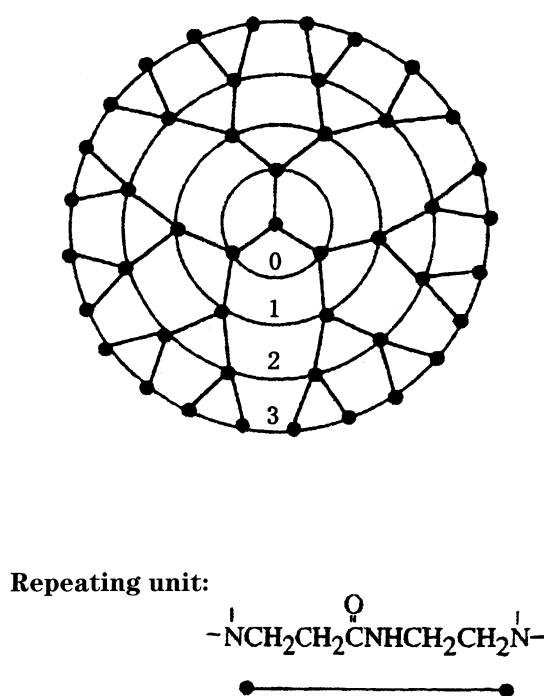$$-\overset{|}{N}CH_2CH_2\overset{O}{\overset{\|}{C}}NHCH_2CH_2\overset{|}{N}-$$

Fig. 2. Molecular structure of an ammonia core PAMAM dendrimer (generation 3). Based on the Ph. D. dissertation of D. E. Valachovic, 1997.

analytical and effective numbers of electric charges of the molecules (Z_a and Z_e) can be experimentally determined. This situation largely reduces ambiguities involved in most of earlier papers in elucidating the electrostatic interaction. Fig. 3 shows SAXS curves for four kinds of acid solutions of G7 dendrimers at a weight fraction w of 0.050 and at a degree of neutralization (α) of unity, where α is the ratio of the equivalent of acid added to the equivalent of the end groups. Clearly a Bragg peak could be observed for the dendrimers with univalent counterions, implying that "ordered" arrangement of the dendrimer ions is formed. The Bragg spacing from the peak position ($2D_{exp}$) was found to be *smaller* than the average spacing estimated from the overall concentration ($2D_0$) by 25 % for G10. This indicates that the distribution of the high-generation dendrimers is not uniform but localized, implying the occurrence of the two-state structure, and hence the attraction. On the other hand, the scattering profile of the bivalent SO_4^{2-} case overlapped with that of the solvent, water, showing the absence of the structure. The observed counterion dependence clearly shows that the attraction between dendrimers is stronger for the univalent counterions than for the bivalent one. The conductivity measurements showed that Z_e of G7 was 44 and 11 for the univalent

counterions and sulfate ions, respectively. This is reasonable since the bivalent ions interact more strongly with the dendrimers than the univalent ions and reduces Z_e, as observed. Thus the absence of the structure with the bivalent counterions is due to weaker interaction (and hence attraction).

(b) *Polystyrensulfonates*. Amis and his associates carried out a systematic study on polystyrenesulfonate (PSS) solutions[11] by neutron scattering (SANS), static light scattering (SLS), and dynamic light scattering (DLS). Fig. 4 shows SANS profiles for PSS with uni- and bi-valent counterions in D_2O. There were observed the so-called "polyelectrolyte" peak (Bragg peak) and the sharp upturn at low scattering vectors q ($= (4\pi/\lambda)\sin(\theta/2)$) with wavelength of the neutron beam λ and scattering angle θ. The latter testifies to the presence of a large scale concentration fluctuation such as the localized ordered structures. The interesting trend is the shift of the peak position (q_m) to lower q with increasing counterion valency, implying that $2D_{exp}$ ($= 2\pi/q_m$) becomes larger (8 nm and 16 nm for the uni- and bi-valent counterions, respectively). Although Z_e was not experimentally determined for PSS, this result is consistent with the finding on dendrimers mentioned above that the multi-valent counterions decrease the macroion charge more strongly than univalent ones to reduce the intermacroion attraction. Furthermore, it can be seen that the $2D_{exp}$ values mentioned above are smaller than $2D_0$ ($= 17$ nm for the experimental condition in Fig. 4) for the univalent cases, substantiating the two-state structure.

The existence of slow and fast diffusive processes in homogeneous ionic polymer solutions was earlier demonstrated by DLS for poly-L-lysine solutions and other ionic polymers, as discussed by Schmitz.[12] Amis *et al.*[11] examined the influence of counterion valency on the diffusive modes. As shown in Fig. 5, when the valency increases, the fast diffusion constant D_f is lowered while the slow diffusion constant D_s increases. D_f is interpreted as a coupled diffusion between the macroions and their counterions while D_s is taken as due to the diffusion of the localized ordered region.[12] Since the diffusion constant of Mg^{2+} (0.706×10^{-5} $cm^2 s^{-1}$) is smaller than that of Na^+ (1.33×10^{-5} $cm^2 s^{-1}$) by a factor of two, the observed reduction of D_f is acceptable. Amis *et al.* ascribed the increase of D_s to decreases in solution viscosity and in the size of the ordered regions by the transfer from univalent to bivalent counterions. The latter factor seems more plausible since the size of regions would be decreased as the charge number of PSS
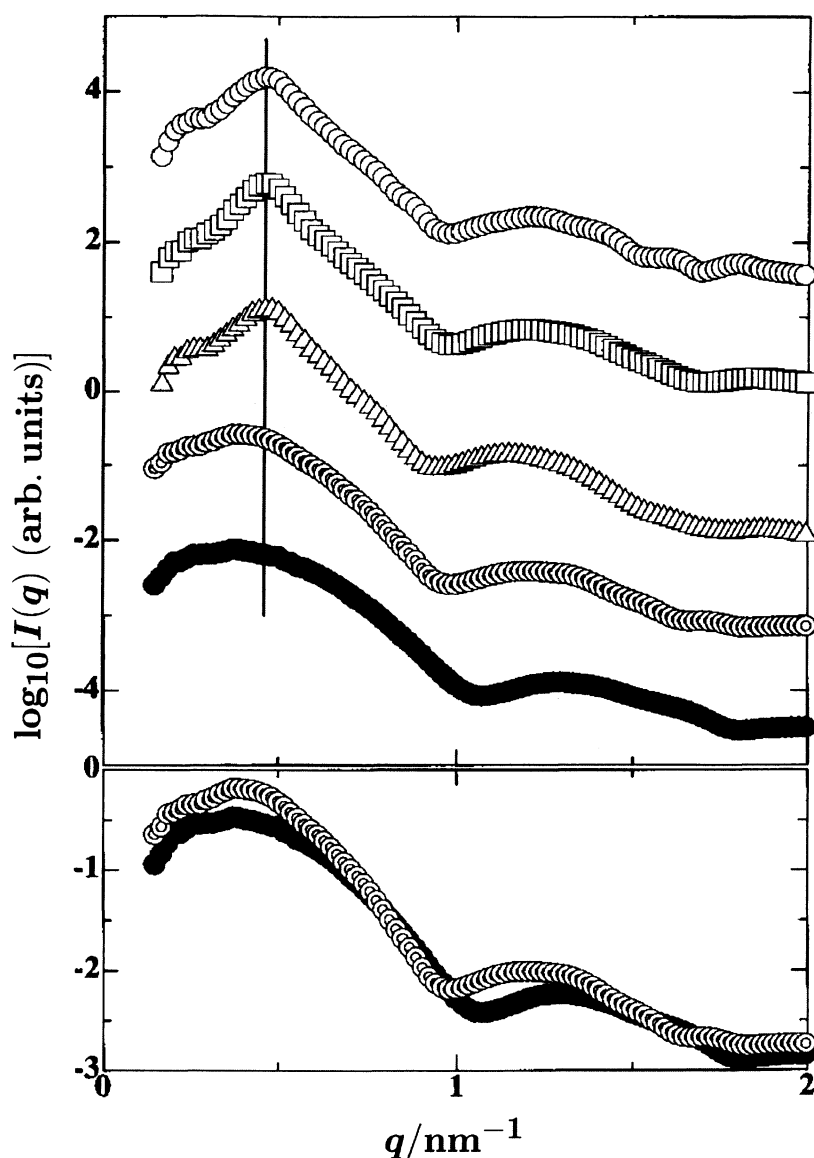
Fig. 3. SAXS curves for G7's with uni- and bi-valent counterions. $\bigcirc$: Cl^-, $\square$: Br^-, $\triangle$: IO_3^-, $\copyright$: SO_4^{2-}, $\bullet$: un-neutralized sample (water). $w \simeq 0.050$, $\alpha \simeq 1.0$ except for water. Each curve was shifted vertically, and the inset reproduces the profiles of the sulfate salt and of the un-neutralized sample on the same scale. Taken from ref. 10) with permission.

ions and hence intermacroion interaction are lowered when monovalent counterions are replaced by those of higher valency.

The size of the ordered region and its stability. It has been well-known that colloidal crystals are so fragile that they are readily broken by shaking or by radiation of strong light. Their elastic modulus is $10^{-2} \sim 10^2$ Pa,[13),14)] depending on concentrations, much lower than that of metals ($\sim 10^{12}$ Pa). By shaking, colloidal crystals are ruptured and microcrystals are soon thereafter

reformed rather quickly while retaining the lattice constant and lattice symmetry, according to the ultra-small-angle X-ray scattering (USAXS) study.[15)] It is plausible that the ordered structure in ionic polymer solutions is likewise fragile. When the solutions are forced to pass through filter pores, the ordered structure would be ruptured and reformed thereafter in a short time. In other words, it is not filtrable aggregates of ionic polymers. As a matter of fact, Matsuoka et al. demonstrated that the SAXS profile of NaPSS solutions stayed
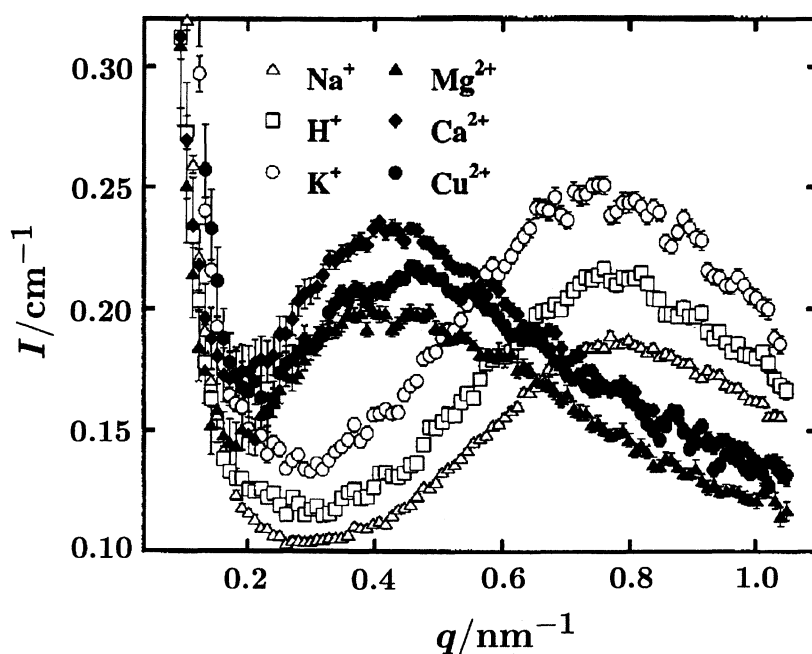
Fig. 4. SANS intensity data for PSS with uni- and bi-valent counterions. PSS concentration: 40 gl^{-1}, molecular weight: 1.24×10^5, degree of sulfonation: 90%. Taken from ref. 11) with permission.

practically the same in three cases of no filtration and filtration through filters with pores of 0.22 and 0.1 µm smaller than the dimension of the local structure (of the order of 0.2 µm for NaPSS), while D_s as determined by DLS depended on pore size.[16] Recently Sedlak systematically investigated the influences of filtration and time on the size of the ordered regions by measuring the scattering amplitude A (relative to a benzene standard), D_s and D_f.[17)-19)] He confirmed for NaPSS solutions that the localized ordered structure (macroion domain according to his terminology) was formed spontaneously by decreasing the salt concentration by dialysis from salt-containing solutions, (in which PSS ions are initially distributed in a homogeneous manner), while such a situation has long been known for colloidal systems. The spontaneous formation of the structure supports that an attraction is in operation between like-charged solute ions. A_f and D_f were practically independent of the pore size (0.1 ~ 0.8 µm), the number of filtration (1~8), and time (after solution preparation up to 10^3 days). On the other hand, A_s decreased and D_s became larger as the pore size decreased and the number of filtration increased. To help understanding, we show here illustrative values for a NaPSS case (mol. weight: 7.1×10^5, salt-free): A_s decreased from 7.49 to 0.34 and D_s increased from 1.63 to 6.70×10^{-9} cm^2 s^{-1} when the pore

size was varied from 0.8 to 0.1 µm, corresponding to the change of hydrodynamic radius of the structure from 0.148 to 0.026 µm according to Sedlak. As the time passed, A_s typically decreased first and then leveled off and D_s showed a tendency to increase. Since the angular dependence of A_s remained the same over the prolonged period, the size of the ordered structure was claimed to stay unchanged. He ascribed the decrease of A_s and increase of D_s to a gradual decrease in scattering contrast inside and outside the structures, and hence in polymer concentration in the structure, which would result in looser structures while keeping the size constant. Strictly speaking, the estimation of the structure dimension from the angular dependence of the intensity is allowed in the absence of the interaction between the structures. In the lack of better treatment, however, Sedlak's argument may be taken as approximately correct, although the anticipated increase in $2D_{exp}$ was not measured. According to Sedlak's statement, the localized structures (domains) can be visualized as soft particles comprised of polyions with a lot of solvent inside (droplets of solutions with higher concentration in a matrix of "regular solution"). This is what we envisioned from SAXS study on ionic polymers and confirmed by microscopic observation for colloidal systems (Fig. 1).
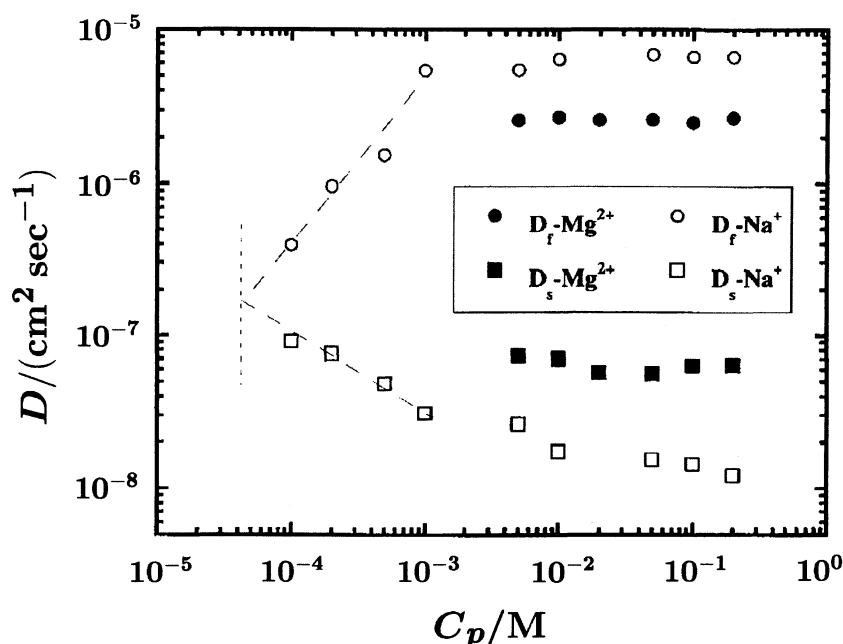
Fig. 5. Polymer concentration dependence of the diffusion constants for NaPSS and MgPSS salt-free solutions. M: monomer molar concentration (1 M for NaPSS corresponds to the mass concentration 200 g l^{-1}). Taken from ref. 11) with permission.

Direct measurements of the interaction potential. The above argument involves intellectual guessing of the interaction potential from various measured properties. This is ubiquitous and unavoidable for real molecular and atomic systems. However, a more direct method is available for colloidal systems. The distribution of the particles in dispersion can be directly determined by microscopy, from which the radial distribution function (RDF) $g(r)$ may be derived and the interaction potential energy $U(r)$ can be calculated according to the basic equation,

$$U(r) = -kT\, ln\, [g(r)] \qquad [1]$$

where kT is the kinetic energy. In this way, for ionic latex particle dispersion in a closed space (near single wall or between two interfaces), Fraden *et al.* observed a long-range attraction, which cannot be described in terms of the DLVO theory.[20] On the other hand, Versmold *et al.* reported that their results are consistent with this theory and contained no indication of the presence of an attraction.[21] By following the relative Brownian motion of a pair of colloidal particles released from the positions where they were fixed by optical tweezers, Grier *et al.* determined the probability density of a particle moving in the potential set up by another particle, from which potential energy was derived, and claimed that the potential was purely repulsive in accordance with the

DLVO theory.[22] Ignoring the basic difficulties inherent in these measurements in the confined geometry (wall effect), we note that the chasm between diametrically opposite results is clear. It should be emphasized that Versmold's and Grier's samples had charge densities of 0.001 and 0.02 μCcm^{-2}, respectively, whereas Fraden's sample was of 2 μCcm^{-2}. Careful examination of previous data shows that attraction could be detected only when particles were highly charged.[8] Though this sounds counterintuitive, higher charge particles naturally repel each other more strongly than lower ones, but the former provide a larger number of counterions in between the particles, which overturn the enhanced repulsion to an overall attraction. This is the Feynman principle mentioned above. It is instructive to realize that a triple ion frequently found in simple ionic solutions has lower potential energy than an ion pair plus a free ion. Therefore, it is not dialectically correct to claim that direct measurements by Grier and Versmold disproved the attraction between like-charge particles.[22] Their measurements have to be extended to higher charge density materials, without the confined geometry if possible, to judiciously conclude the true nature of the intermacroion attraction.

Recent computer simulation. The like-like attraction discussed above has called keen attention of
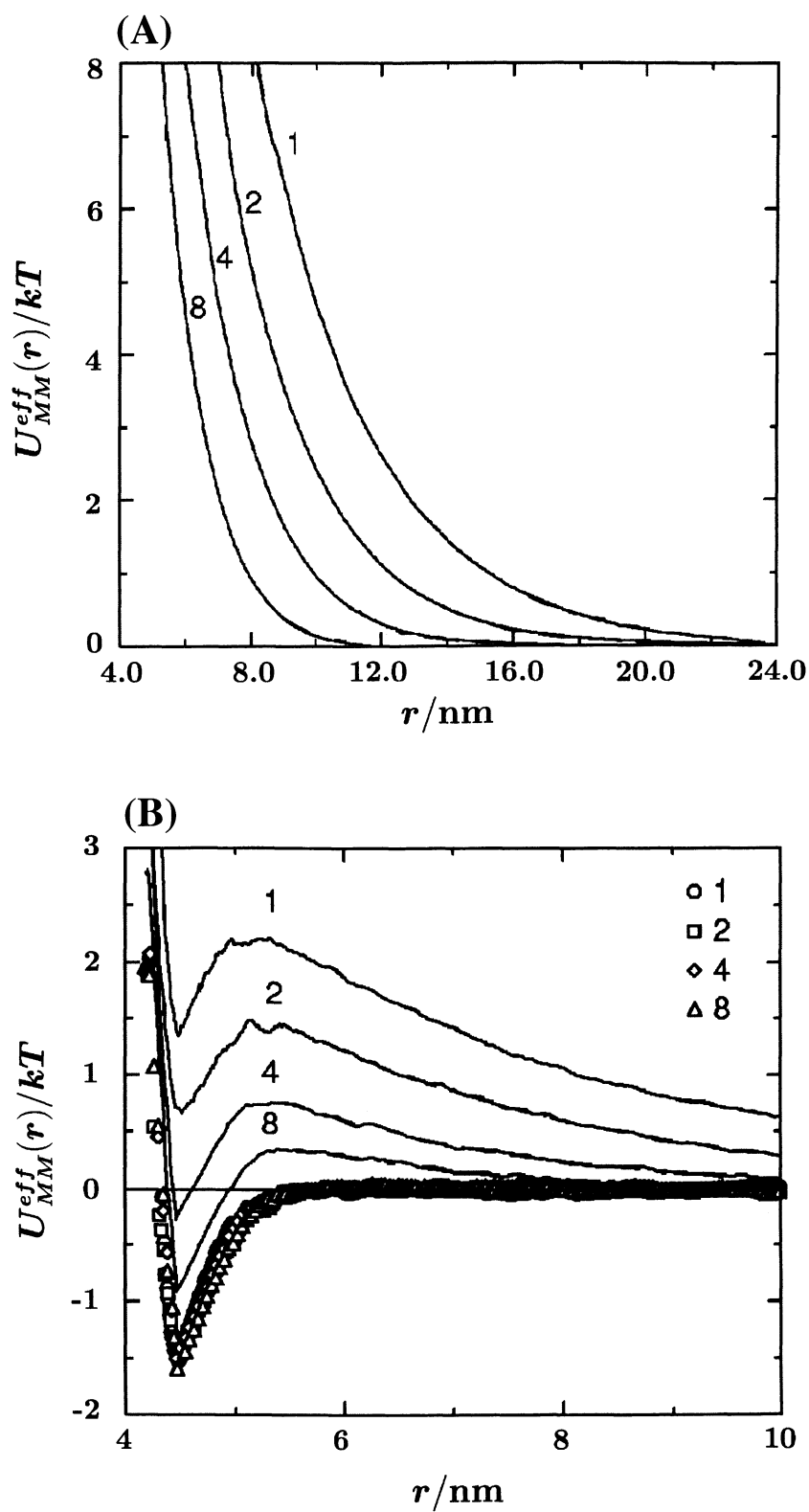
(A)

(B)

Fig. 6. Effective macroion-macroion potentials computed by a Monte-Carlo simulation. Macroion: $Z = 60$, radius $\sigma = 4$ nm, Volume faction, curve 1: 8.4×10^{-3}, 2: $2 \times 8.4 \times 10^{-3}$, 4: $4 \times 8.4 \times 10^{-3}$, 8: $8 \times 8.4 \times 10^{-3}$. Counterion: $\sigma = 0.4$ nm, (A) univalent, (B) bivalent. The symbols in (B) show the residual potentials over the Yukawa-type repulsive potentials.

computer simulation scientists.[23)-25)] In the present section we discuss Monte-Carlo simulations based on the primitive model, in which the solvent is considered as a continuum with a dielectric constant ε. Typical simulations were carried out assuming the pairwise additive potential U_{ij} between ions i and j (macroions or counterions) with valency Z and with radius σ,

$$U_{ij}(r) = Z_i Z_j e^2 / 4\pi\varepsilon r \quad \text{for } r \geq (\sigma_i + \sigma_j)/2 \quad [2]$$

where e is the elementary charge. For systems of 80 macroions having 60 charges with uni- or bi-valent counterions, the macroion-macroion RDF was computed from which the effective macroion-macroion potential energy $U^{eff}_{MM}(r)$ was reconstructed using an inverse Monte-Carlo technique via seven iteration processes. The results (Fig. 6) shows that for univalent counterions $U^{eff}_{MM}(r)$ is purely repulsive, whereas an attraction is found for bivalent cases in superposition with the Yukawa-type repulsive interaction. Though the original authors claimed the success of their simulation, their results are in clear contradiction with the observed fact for ionic dendrimers and polystyrenesulfonates that the attraction is operative even for univalent counterions and becomes weak for the bivalent cases. It is not clear at present whether this failure originates from the inappropriateness of eq. [2], from the very small number of macroions treated, or from some other factors. Anyway, the fact is more complicated than the simulation.

Simple ionic solutions and "dust" plasma. The Extended X-ray Absorption Fine Structure (EXAFS) study of simple ionic systems provided startling information of ionic distributions. According to Sadoc et al.,[26),27)] the interionic distance between Zn^{2+} and Br^- was 0.240 nm in solid crystal of $ZnBr_2$ while that at 0.1 mol l^{-1} in its aqueous solution was 0.237 nm. (Therefore, the spacings between neighboring Zn^{2+} ($2D_{exp}$) are 0.480 nm and 0.474 nm in solid and solution, respectively.) Similarly, the $2D_{exp}$ at 0.05 mol l^{-1} in ethyl acetate ($\varepsilon = 6$) was 0.460 nm. These data indicate that a structure similar to that of solid crystal is maintained in the dilute solutions, albeit in a very short period of time. Interestingly, the average Zn^{2+}-Br^- distance from concentration is roughly of the order of 2 nm at concentrations of 0.1 and 0.05 mol l^{-1}, which leads to the average cation-cation spacings ($2D_0$) by multiplying the factor 2. The ratio $2D_{exp}/2D_0$ is 2 × 0.237/2 × 2 (=1/8.4) at 0.1 mol l^{-1}. This ratio is amazingly small in comparison with those found for ionic polymers (at the smallest, for example, 1/2 for NaPSS[28)] and 1/1.25 for G10 dendrimer), which implies more conspicuous localization of the ordered structure in $ZnBr_2$ solutions than in

polymeric systems. This would be due to extremely high electric field on the surface of simple ions as a result of their *small* size.

Thomas et al. have carried out structural study of colloidal particles in gaseous electrons and ions, namely plasma, which has been regarded as the most disordered state of matter.[29),30)] A set of colloidal particles (for example, melamine formaldehyde sphere of $\sigma = 7$ μm, density = 1.51 g cm^{-3}), which were introduced into the plasma, acquired negative charges and were levitated electrostatically against the gravity in rare gas plasma generated in a radio frequency discharge chamber under reduced pressure. The locations of the particles photographed by CCD camera indicated that the particles formed 3-dimensional crystal structures, hcp, fcc and/or bcc,[29)] with thickness of about 18 layers, at higher gas pressures (at higher plasma concentrations). The crystals were found to melt into disordered states via the "flow and floe" stage, where islands of ordered crystalline structures and free particles coexisted, when the gas pressure was lowered. This is qualitatively what we called the two-state structure (Fig. 1). Most of the phenomena described for dust plasma crystals have been observed for colloidal crystals in solutions by us some years ago.[31)] The existence of localized structure was also claimed under microgravity condition.[32)]

Concluding remarks. First we have to point out that the like-like attraction has been a focus of many theoretical considerations, particularly in the past two years. Because of space limitation, we refrained discussion thereupon in the present paper, in which attention was paid to experimental observations and simulation works. It was demonstrated that solute distribution was microscopically inhomogeneous in macroscopically homogeneous systems for various ionic systems, ranging from polymeric materials to "dust" plasma crystals. Although the length and time scales vary from system to system, a basic feature appears to underlie seemingly different phenomena, which originates from the like-like attraction. To avoid misunderstanding, it is emphasized that, though the opposite has often been claimed, the attraction is not violating the Coulomb law, according to which likes certainly dislike likes and unlikes like unlikes *if* only likes (or unlikes) could exist exclusively. This is physically impossible in reality: there exist likes and unlikes in an equivalent amount to satisfy the electric neutrality. Then, as Feynman described, likes like likes through the intermediary of unlikes. This is the physical basis of the counterion-mediated attraction between like-charged species.

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