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IIIII The Kikuchi-Kossel Experiment - Colloidal Crystals under Microgravity IIIII
(Review)

Long-range Attraction between Like-charged Colloids: Simulations and Microgravity Experiments

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Abstract

Deionized dilute charged colloidal systems exhibit gas-liquid and gas-solid coexistence and re-entrant transitions depending on suspensions parameters such as volume fraction, charge density and ionic strength. These observations constitute evidence for the existence of long-range attraction between like-charged colloids. Monte Carlo (MC) simulations using Sogami-Ise pair-potential, which has a long-range attractive term, could explain the above mentioned experimental observations. MC simulations, which correspond to zero gravity conditions, revealed coexistence of liquid-like droplet with rare phase (gas-like) and voids coexisting with dense (solid-like) phase clusters. These predictions will be verified by the project of microgravity experiments in space and the outcome is expected to provide evidence for the existence of long-range attraction between like charged colloids.

Keyword(s): Charged Colloids, Long-range attraction, Simulations, Light Scattering, Confocal microscopy, Microgravity experiments.

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1. Introduction

Among the various soft matter systems, charge-stabilized colloidal suspensions (e.g., micron or submicron sized polystyrene latex and silica particles dispersed in water) have gained recognition as tremendously useful model condensed matter systems because of their structural ordering and rich phase behaviour [1), 2)]. Ensembles of uniformly sized charged colloidal particles undergo phase transitions from gas to liquid, fluid to solid, and from crystal to glass[1,2)]. Such structural orderings and phase transitions are amongst the phenomena that colloidal systems have in common with atomic systems. Hence, these systems are of considerable interest to study fundamental questions, which are also relevant for atomic systems. Understanding of this simple model system is, however, far from complete with respect to the effective inter-particle interaction, $U(r)$ between the charged colloids arising due to the basic electrostatic interactions among the constituents. The phenomena such as aggregation, fluid-crystal and body centered cubic (*bcc*) to face centered cubic (*fcc*) phase transitions, observed in bulk charged colloidal dispersions[1,2)] have been understood using Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1), 2)]. In this theory, a pair of spherical like-charged colloidal particles immersed in an electrolyte solution repels each other at large inter-particle distances, r, due to screened Coulomb repulsion; they can experience strong attraction (van der Waals attraction) at very short surface-to-surface distances (~1 nm) in the presence of high salt concentration. Nevertheless it failed to explain several new and important observations [2–8)]. The most striking of these observations include equilibrium phase separation (gas-liquid) between colloidal fluids of widely different densities [3), 4)], re-entrant order-disorder transition [5)] and stable voids coexisting with dense ordered or disordered regions (gas-solid coexistence) [2), 5–8)]. None of these should be possible in a system with purely repulsive interactions, and hence their occurrence suggests existence of long-range attraction between like-charged colloids.

The above mentioned equilibrium phase behaviour is strongly influenced by gravity as the colloidal particles are large in size (particle diame*ter* $d \sim 100$ to 1000 nm) and the buoyant weight of the colloidal particle ($F_b = \pi d^3 \Delta\rho g/6$, where $\Delta\rho = |\rho_p - \rho_s|$ is the density mismatch between the particle and the solvent and g is the acceleration due to gravity) is not negligible. Two quantities that characterizes the influence of gravity are gravitational length l_g and Pècklet number P_e, which are defined[9)] as follows,

$$l_g = k_B T / F_b = 6k_B T / \pi d^3 \Delta\rho g \quad (1)$$

$$P_e = \tau_B / \tau_s = d/2l_g = \pi d^4 \Delta\rho g / 12 k_B T \quad (2)$$

In Eq. (2), τ_B and τ_s represent the time scales for Brownian diffusion and sedimentation respectively. The gravitational length characterizes the height at which gravity plays important role in the equilibrium phase behaviour. Further one cannot

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Table 1 Gravitational length, l_g and Péclet number, P_e for two sizes (d= 100, 1000 nm) of different colloidal particles suspended in aqueous medium at 25°C.

Particle	d (nm)	$\Delta\rho$ (g/cm^3)	l_g (μm)	P_e
Polystyrene	100	0.05	16040	0.31×10^{-5}
Polystyrene	1000	0.05	16.04	0.031
Silica	100	1.65	487	1.03×10^{-4}
Silica	1000	1.65	0.487	1.03
Titania(Rutile)	100	3.23	249	2.08×10^{-4}
Titania(Rutile)	1000	3.23	0.249	2.08

neglect the effect of gravity on suspension behaviour for Pècklet number $P_e > 1$. **Table 1** summarizes the values for l_g and P_e for two different size particles of polystyrene, silica and titania dispersed in water. It is clear from **Table 1** that gravitational effects cannot be neglected in suspensions of large size particles of small l_g or large size particles of large $\Delta\rho$. Gravitational length and Pècklet number are single particle properties and interactions responsible for the structural ordering in suspensions modify the effects of gravity. Because of this fact, phase separation (gas-liquid or gas-solid) phenomena reported in charged colloids are also influenced by gravity.

In order to understand the above mentioned phase separation and ordering phenomena in charged colloids, Tata *et. al* have performed Monte Carlo (MC) simulations [4), 10–12)] using Sogami-Ise (SI) pair-potential [7), 13)], which has a long-range attractive term in addition to the usual screened Coulomb repulsive term. These simulations have showed homogeneous fluid-solid transition in dilute charged colloids of low charge density and at low ionic strength[11)]. A liquid-like ordered homogeneous suspension with low salt concentration, C_s was found to freeze into a homogeneous crystalline solid with *bcc* structure at low volume fraction, ϕ and *fcc* structure at relatively high volume fraction[12)]. Earlier to the report of these simulations, it was widely believed that repulsive screened Coulomb pair-potential given by DLVO theory is responsible for the crystalline order observed in charged colloids. Further, MC simulations with SI pair-potential also provided good qualitative understanding for the experimental observations of gas-liquid [3), 4)] and re-entrant gas-liquid transition [4)], voids coexisting with ordered/disordered regions [6–8)], gas-solid transition [2), 7)] and re-entrant liquid to crystal transition [2), 5)] reported in dilute deionized charged colloids. Further, the recent observation of stable bound pairs [14)] in highly charged colloids under very dilute conditions constitute direct evidence for the existence of long-range attractive term in the effective pair-potential between like charged colloids. MC simulations correspond to the zero gravity conditions whereas most of the experimental phenomena mentioned above are not free from gravitational effects. Here we review the above mentioned experimental and simulation results and then go on to discuss MC simulation results that can be verified by microgravity experiments in space.

2. Monte Carlo simulations

Sogami and Ise [8), 13)] have proposed an effective pair-potential $U_s(r)$ which has an attractive term in addition to the usual screened Coulomb repulsive term given by Eq. (3) and is shown in **Fig. 1** for different suspension parameters.

$$U_s(r) = A\frac{e^{-\kappa r}}{r} - Be^{-\kappa r} \tag{3}$$

with

$$A = \left[2\frac{Z_e\sinh(\kappa d/2)}{\varepsilon\kappa d}\right]^2\left(1+(\kappa a)\coth(\kappa a)\right) \quad \text{and}$$

$$B = \left[2\frac{Z_e\sinh(\kappa d/2)}{\varepsilon\kappa d}\right]^2\frac{\kappa}{2}$$

where Z_e - the effective charge on the particle and is related to the surface charge density by $\sigma = Z_e/\pi d^2$, ε is the dielectric constant of the solvent, n_p is the particle concentration, T is the temperature, k_B the Boltzmann constant and κ is the inverse Debye screening length given by $\kappa^2 = 4\pi e^2\left(n_pZ + C_s\right)/\varepsilon k_BT$. Notice that the potential minimum R_m and its depth U_m vary with suspension parameters. When the average interparticle separation l (defined as $l = P(1/n_p)^{1/3}$ where P = 1.091 for *bcc* co-ordination and 1.127 for *fcc* coordination) is greater than R_m (**Fig. 1** black curve) the particles experience repulsive potential and remain homogeneous and the structural ordering is liquid-like or solid-like depends on the strength of interaction $U_s(l)/k_BT$. In the case of $R_m < l$ the particles experience long-range attraction and suspensions are expected to exhibit phase separation either in the

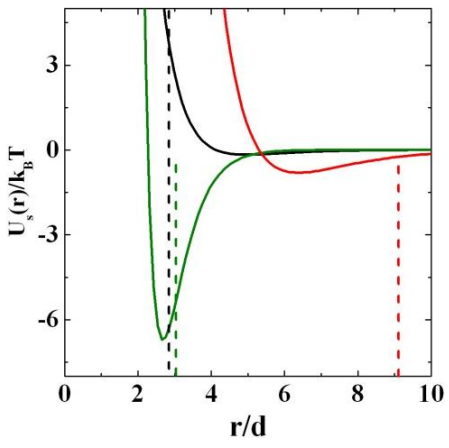

Fig. 1 Sogami-Ise pair-potential $U_s(r)$ vs r for different suspension parameters with d=110 nm. Black curve: ϕ = 0.03, σ =0.085 μC/cm^2, C_s= 0.5 μM; Red curve: ϕ = 0.0009, σ = 0.21 μC/cm^2, C_s= 4 μM and Green curve: ϕ = 0.024, σ =0.45 μC/cm^2, C_s= 1.5 μM. Dotted lines represent respective values of the average interparticle separation l.

form of gas-liquid (*i.e.* for small well depths, $U_s(l)/k_BT < 1$, blue curve) and/or gas-solid transition (for large well depths $U_s(l)/k_BT >1$, red curve). Thus SI potential provided a simple explanation to the experimental observations mentioned above.

Though SI theory [8), 13)] qualitatively predicts most of the experimental observations, there exists criticism and counter-criticism in the literature [2), 13)]. This necessitates more experiments on large size charged colloids with monovalent counterions. Since large size colloids suffer from gravitational sedimentation, experiments in microgravity environment are expected to provide valuable information about colloidal interactions.

3. Experimental and MC Simulation results

3.1 Gas-liquid and Re-entrant phase transitions

Tata *et. al* have reported occurrence of gas-liquid transition [3), 4)] in aqueous dilute suspensions of charged polystyrene particles. Homogenous weakly interacting (gas-like) suspensions are found to undergo gas-liquid condensation upon lowering the salt by exhibiting phase separation in the form of a dense phase and a rare phase as shown in **Fig. 2(A)**. The structure factor $S(q)$ (where q is the scattering wave vector) measured using static light scattering (SLS) in the dense phase showed liquid-like order and that in the rare phase showed gas-like (**Fig. 2 (B)**) disorder. Above a critical concentration suspensions that are homogeneous and weakly interacting at high salt concentrations exhibit gas-liquid condensation for the intermediate salt concentrations and reenter into a homogeneous state having a liquid-like order at low salt concentration [4)].

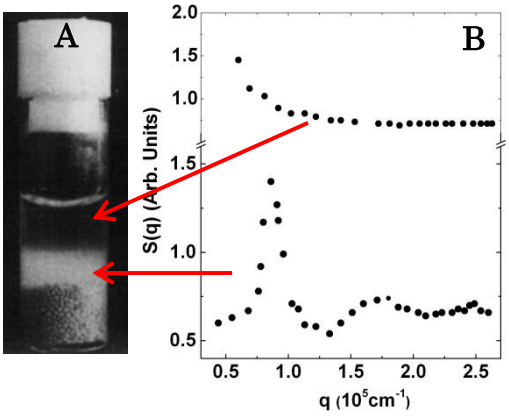

Fig. 2 Gas-liquid coexistence in deionized dilute aqueous suspension of polystyrene particle with d =110 nm and ϕ =0.001. (A) Photograph of the sample cell showing a macroscopic phase separation in the form of dense phase at the bottom coexisting with a rare phase at the top. (B) $S(q)$ vs. q measured in the rare phase (top curve) shows gas-like disorder and that measured in the dense phase (bottom curve) shows liquid-like order. Mixed-bed ion exchange resin used for deionisation can also be seen at the bottom of the cell. Pictures A and B are adopted from Ref. 3 with the permission of the American Physical Society.

MC simulations by Tata *et. al* using SI potential have shown occurrence of gas-liquid and re-entrant phase transitions as a function of salt concentration [4)]. **Figure 3** shows a homogenous gas-like disordered suspension exhibiting gas-liquid coexistence upon lowering the salt concentration. Single peak in the pair-correlation function, $g(r)$ with homogeneous distribution of particles in the MC cell (top panel **Fig. 3(A)**) characterize the structural ordering in the suspension at high salt concentration to be gas-like. Upon lowering the salt concentration suspension showed gas-liquid coexistence (bottom panel **Fig. 3(A)**) in the form of a big droplet in the back ground of single particles and a few small particle clusters. The $g(r)$ showed short-range (liquid-like order) among the particles within the droplet. Upon further reduction of salt, MC simulations showed re-entrant behaviour by exhibiting liquid-like order through the suspension [4)].

Gas-liquid coexistence observed by Tata *et. al* was in the form of macroscopic phase separation (*i.e.* dense phase at the bottom of the sample cell separated by rare phase, **Fig. 2(A)**). Whereas MC simulations showed dense phase in the form of droplets which coexisted with rare phase in the form of single particles and small clusters. Though, the simulations showed existence of small particle clusters in the gas phase, observation of such

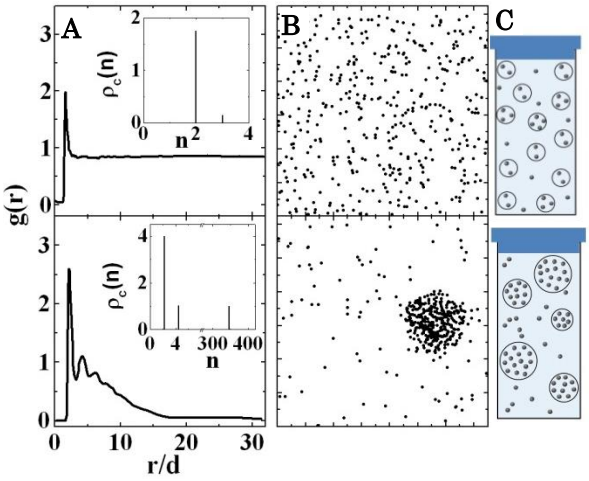

Fig. 3 MC simulation results under microgravity showing gas-liquid transition in aqueous charged colloidal suspension with suspension parameters: ϕ = 0.0009, σ = 0.21 μC/cm^2, d=110 nm; (A) $g(r)$ vs r showing gas-like disorder at C_s= 221 μM (top panel). $g(r)$ shows gas-liquid coexistence at C_s = 43 μM. Cluster size distribution $\rho_c(n)$ vs n for the corresponding values of C_s are shown as insets. (B) Projection of coordinates of particles in MC cell in XY-plane. Top panel show homogeneous distribution of particles. Bottom panel show big droplet with liquid - like order coexisting with single particles and small size clusters. (C) Schematic picture depicting distribution of clusters under microgravity conditions in samples with gas-like disorder (top) and in a gas-liquid coexistence state.

droplets with short-range correlations are possible only in space experiments and are shown schematically in **Fig 3(C)**.

3.2 Gas-solid and Re-entrant solid-liquid transitions

There have been several reports of stable voids coexisting with ordered/disordered regions and also interparticle separation estimated through scattering studies being smaller than l obtained from the volume fraction [2), 6), 7), 15)]. Through systematic light scattering and CLSM studies, Tata *et. al* have confirmed these observations to be gas-solid coexistence [2), 6), 7)]. Gas-solid coexistence was observed in the form of voids (rare phase with very few particles) as the minority phase and the ordered/disordered dense phase as the majority phase. When void fraction is small suspension appeared homogeneous to the unaided eye. At low volume fraction ϕ = 0.0005, deionized suspension showed macroscopic phase separation (**Fig. 4**) with dense phase being at the bottom of the cell having iridescence and a rare phase at the top. $S(q)$ measured in the rare region showed gas-like disorder (**Fig. 4**) and crystalline order in the dense phase. When void (gas) phase becomes majority, the dense phase (minority phase) initially appear as ordered clusters during the phase separation. Under gravity, these clusters sediment down, leading to macroscopic phase separation as shown in **Fig. 4**. MC simulations as function of σ have revealed that a homogenous colloidal crystal becomes inhomogeneous in the form of voids with dense ordered regions or voids with glass-like disordered dense regions beyond a critical charge density[2,10,11)]. For volume fractions below 0.01, MC simulations with high values of σ and C_s showed gas-like disorder (**Fig. 5(A)**: $g(r)$ shows a single peak with peak position at R_m) with small size stable clusters. Upon lowering the salt concentration MC simulations showed $g(r)$ with long-range spatial correlations decaying as function of r (see **Fig. 5A** bottom panel). The projection of particles in the MC cell showed ordered clusters coexisting single particles (see inset in the bottom panel). Existence of such stable clusters can only be observed in space experiments. Since the density of these dense phase clusters is more than the density of the solvent, clusters settle down due to gravity and coalesce, leading to a macroscopic phase separation as shown in **Fig. 5**.

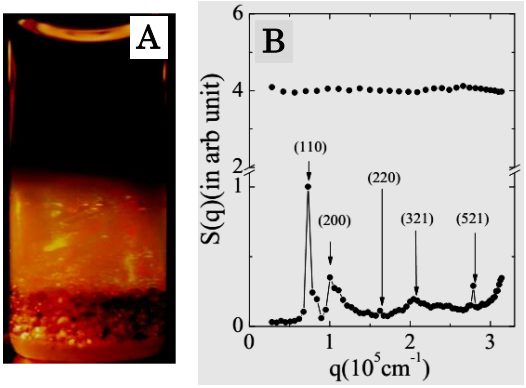

Fig. 4 Gas-solid coexistence in deionised aqueous suspension of polystyrene particles with ϕ = 0.0005, σ = 0.41 μC/cm^2, d=104 nm. A: Photograph of the sample showing a macroscopic phase separation in the form of dense phase, showing iridescence (at the bottom), coexisting with a rare phase (at the top). B: $S(q)$ vs q measured in the rare phase (top curve) shows gas-like disorder and that measured in the dense phase (bottom curve) shows bcc crystalline order.

Yamanaka and co-workers [5), 16)] have reported a re-entrant solid-liquid transition (also known as re-entrant order-disorder transition) by varying σ on deionized charged colloidal suspensions of silica and polystyrene particles. Initially a homogenous disordered (liquid-like ordered) deionized suspension undergoes crystallization upon increasing σ of the particles. This crystalline order (solid phase) once again disorders on further increase of σ. The occurrence of a re-entrant transition with increase in σ is unique to charged colloids. The occurrence of re-entrant order-disorder transition and the underlying phase transition was understood by Mohanty *et. al* [12)] by performing MC simulations with SI potential as function of σ. MC simulations showed re-entrant order-disorder transition.

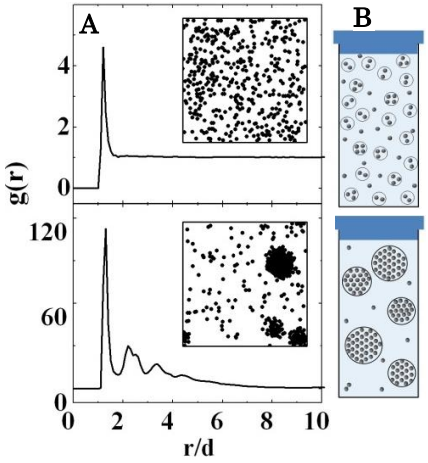

Fig. 5 MC simulation results under microgravity showing gas-solid transition in highly charged colloidal suspension with suspension parameters: ϕ = 0.005, σ =0.5 μC/cm^2, d=120 nm; (A) $g(r)$ vs r showing gas-like disorder at C_s=1000 μM (top panel). Upon lowering the salt concentration to 550 μM, g(r) shows gas-solid coexistence by exhibiting decay as function of r with long-range structural correlations. Inset shows projection of coordinates of particles in MC cell in *XY*- plane. Top panel shows homogeneous distribution of particles. Bottom panel shows gas-solid coexistence by exhibiting ordered clusters coexisting with single particles. (B) Schematic picture depicting distribution of clusters under microgravity conditions: Top panel shows small particle clusters and bottom panel shows large size ordered clusters coexisting with single particles.

However, the reentered state is reported to be inhomogeneous (gas-solid coexistence) and disordered. Since silica colloids offer continuous tunability of surface charge density, microgravity experiments on large size silica particles as function of σ are expected to provide deeper insight into the colloidal interactions responsible for the re-entrant transition.

3.3 Measurement of effective pair-potential

Above mentioned puzzling observations in bulk suspensions as well as measurements of effective pair-potential $U(r)$ under confined conditions[17–19] in dilute suspensions, have motivated Tata *et. al* [14] to measure $U(r)$ of like-charged colloids under confinement-free as well as microgravity conditions. Confinement-free condition was created by investigating bulk suspensions using a confocal laser scanning microscope (CLSM) as it allows to image particles far away from cover-slip thus avoiding the influence of charged walls. Microgravity conditions were created by dispersing 600nm diameter polystyrene particles in a density-matched fluid (50:50 H_2O-D_2O mixture). For very dilute suspensions, the pair-correlation function $g(r)$ is directly related to $U(r)$ by

$$g(r) = \exp[-U(r)/k_BT] \qquad (4)$$

Hence, $U(r)$ can be obtained by measuring $g(r)$. Tata *et. al* have measured $U(r)$ using CLSM on deionised dilute charged polystyrene colloidal suspensions of same diameter but having two different effective surface charge densities σ = 2.7 μC/cm^2 and σ = 0.3 μC/cm^2 [14]. Bound pairs and small size cluster (3 to 5 particles) (**Fig. 6**) stable over several seconds were observed. Observation of these clusters constitutes direct evidence for the existence of long-range attraction between like charged particles with neutralizing charges being monovalent counterions. The measured pair-correlation function $g(r)$ was inverted using Eq. (4) to determine $U(r)$ and is shown in **Fig. 6**. $U(r)$ clearly shows a potential minimum at more than two particle diameters with well depths larger than k_BT, providing direct evidence for the existence of long-range attraction between like-charged polystyrene spheres in the $U(r)$ of like charged colloids with monovalent counterions.

Measured experimental $U(r)$ data was found to fit to Eq. (3) where the constants A, B represent the strength of repulsive and attractive components of the interaction, respectively and κ^{-1} represents the range of interaction. The fit to Eq. (3) is shown in **Fig. 6.** We could fit $U(r)$ data to Eq. (3) by taking A, B and κ as independent variables. The values of the constants A, B and κ, obtained from the fit (A = 1.79 ± 0.55 × 10^{-21} J·m, B = 1.37 ± 0.42 × 10^{-15} J, κ = 6.75 ± 0.2 μm^{-1}) are higher for sample with σ = 2.7 μC/cm^2 as compared to that (A = 9.91 ± 1.9 × 10^{-23} J·m, B = 7.5 ± 1.6 × 10^{-17} J, κ = 4.87 ± 0.14 μm^{-1}) for sample with lower σ = 0.3 μC/cm^2. Notice from Eq. (3) that constants A, B and κ are not independent. Hence the good fit of $U(r)$ data to SI potential does not constitute as an experimental measurement of SI potential.

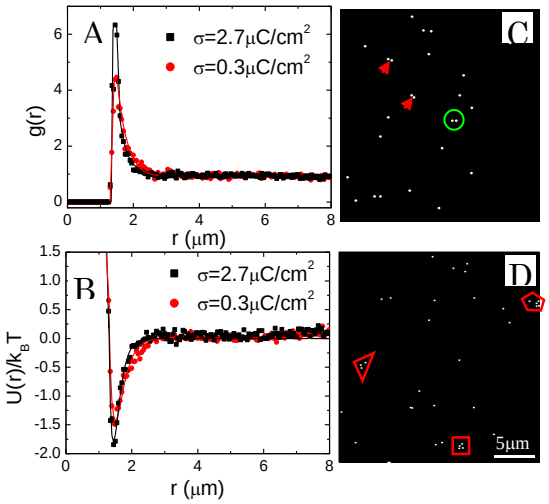

Fig. 6 (A) Experimental $g(r)$ and (B) the corresponding effective pair-potential $U(r)$ determined using Eq. (4) for very dilute (ϕ=0.0001) deionized suspensions of 600nm diameter polystyrene particles with two different effective charge densities. $U(r)$ shows an attractive minimum at ~2d with well depths more than 1.5k_BT. Lines drawn through $g(r)$ data are guide to the eye. The lines drawn through $U(r)$ data are fit to the SI potential (see text for fit parameters). Confocal images (C) and (D) show bound pairs and small size (3, 4 and 5) clusters of polystyrene. The images are recorded at a depth of 150 μm from the cover-slip using a 40x/0.55 objective.

4. Conclusions

Monodisperse charge stabilized colloids serve as ideal model condensed matter system to study the rich phase behaviour arising due to electrostatic interactions. It was widely believed that screened Coulomb repulsive pair-potential given by DLVO theory is responsible for the ordering phenomena and associated fluid - solid transition observed in charged colloids. However, experimental observations such as gas-liquid, gas-solid and re-entrant transitions observed as function of salt concentration and surface charge density, constitute evidence for existence of long-range attraction between like-charged colloids with monovalent counterions. MC simulations based on Sogami-Ise potential is shown to qualitatively predict most of the experimental observations. However, MC simulations which simulate microgravity conditions, predicted (i) existence of small clusters (< 5 particle clusters) at finite salt concentration where suspensions showed gas-like disorder, (ii) existence of large size droplets in suspensions with low salt and medium charge density particles and (iii) strongly bound ordered/disordered (glass-like) clusters in deionized suspensions of highly charged colloids. Due to gravitational influence, one

observes macroscopic phase separation in the form of gas-liquid and gas-solid coexistence in dilute charged colloids.

Observation of stable bound pairs along with the observation of an attractive minimum at several micrometres in the measured $U(r)$, constitute direct evidence for the existence of long-range attractive interaction between like charged particles with monovalent counterions. These observations in highly charged large size polystyrene was possible because polystyrene offer density matching in 50:50 H_2O-D_2O mixture thus simulating microgravity conditions in the lab. There is great need to establish existence of long-range attractive interaction with monovalent counterions in other charged colloidal systems. Aqueous suspensions of silica or titania particles with large Pècklet number ($P_e > 1$) are the right choice as they offer the tunabiity of surface charge density by chemical methods. Microgravity experiments in space are a must as there are no suitable solvent for density matching these particles without altering the surface chemistry. A suitable apparatus based on the Kikuchi-Kossel diffraction method and digital video imaging for performing some of the above mentioned experiments in space has been built in Kyoto Sangyo University with the support of JAXA [20].

It is widely believed that polyvalency of counterions is a must for attraction to exist between like-charged macroions in an aqueous medium [21–24]. However, we have shown here that like-charge attraction is possible with monovalent counterions. Mean field approach based on linearized Poisson-Boltzmann equation is not adequate in the limit of high charge densities where counterion-counterion correlations and nonlinear effects are important. We believe the results of proposed space experiments not only provide direct evidence for counterion mediated long-range attractive interaction but also paves the way for *ab-initio* simulations and theoretical studies towards understanding the origin and mechanism for the long-range attractive interaction between like charged colloids with monovalent counterions.

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