

Charge and salt-driven reentrant order–disorder and gas–solid transitions in charged colloids

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Abstract

Monte Carlo simulations have been performed for aqueous charged colloidal suspensions as a function of effective charge density (σ) on the particles and salt concentration C_s . We vary the effective charge density in our simulations over a range where a reentrant solid–liquid transition in suspensions of silica and polymer latex particles has been reported by Yamanaka et al. (Phys. Rev. Lett. 80 (1998) 5806). We show that at low ionic strengths a homogeneous liquid-like ordered suspension undergoes crystallization upon increasing σ . Further increase in σ resulted once again in a disordered state, which is in agreement with experimental observations. In addition to this reentrant order–disorder transition, we observe an inhomogeneous-to-homogeneous transition in our simulations when salt is added to the disordered inhomogeneous state. This inhomogeneous-to-homogeneous disordered transition is analogous to the solid–gas transition of atomic systems and has not yet been observed in charged colloids. The reported experimental observations on charged colloidal suspensions are discussed in the light of present simulation results.

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1. Introduction

Monodisperse charge-stabilized colloidal suspensions are studied with great interest because they exhibit a variety of structural orderings analogous to that occur in atomic systems [1,2]. Unlike those in atomic systems, the range and strength of the effective interparticle interactions among the constituent particles are tunable over a wide range in colloidal systems. Hence, different structural orderings can be realized with ease in these systems at ambient conditions. Though the most dominant interparticle interaction among like-charged particles in a charge-stabilized colloidal suspension is screened Coulomb repulsion, experimental observations in bulk suspensions such as reentrant transition [3,4], vapor–liquid transition [4,5], stable voids coexisting with ordered or disordered regions [6–9] have served as evidence for the existence of a long-range attractive component in the effective interparticle interaction of like-charged colloids [10]. A purely repulsive pair-potential given by the

Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [11] cannot explain the inhomogeneous nature or the phase separation observed in like-charged colloidal suspensions. The DLVO theory is advanced by Sogami and Ise by considering the counterion-mediated attraction and regarding the macroionic part as a one-component system [12]. The effective pair-potential $U(r)$ [12] obtained from the Gibbs free energy is found to have a long-range attractive term in addition to the usual screened Coulomb repulsive term given by DLVO theory. Tata et al.'s computer simulations using this $U(r)$ could explain the above mentioned experimental observations satisfactorily [1,4,13–16].

Recently there have been several alternative theories [17–19] to explain the observed phase separation in charged colloids. These theories, which are also known as “volume term theories” [17,18], have strong similarity in approach but differ in technical details and are extensions of the Debye–Hückel theory for asymmetric electrolytes. These theories consider the total Helmholtz free energy of the system that arises from Coulomb interaction between all species in the system. The outcome of all these theories is that pair potentials between colloidal particles can remain repulsive

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as a function of interparticle distance r , yet a gas–liquid or gas–solid phase separation can occur due to volume terms which are responsible for the spinodal instability. Recently Schmitz and Bhuiyan [20] brought out the connection between volume term theories and the long-range attractive term that is present in the Sogami–Ise potential $U(r)$. It is shown that Sogami–Ise theory includes volume terms and the attractive term in $U(r)$ arises from the electrostatic interactions that are present in volume term theories. Further, the criticism of Sogami–Ise theory by Overbeek [21] and Woodward [22] has been countered by Smalley [23] and Schmitz [24]. Hence, we use $U(r)$ as the model potential in our MC simulations.

The objective of this paper is twofold. (1) Carry out simulations as a function of σ for volume fractions and salt concentrations, which are the same as that used in experiments of Yamanaka et al. [25], and look for the reentrant solid–liquid phase behavior observed by them. The reentered disordered state observed at high values of σ is known to be inhomogeneous but the nature of the underlying phase transition has not been identified. (2) Identify conditions under which the reentered inhomogeneous disordered state will transform to a homogeneous state. Toward this end we perform a detailed MC study over a wide range of salt concentrations, as C_s is known to alter the position R_m of the minimum as well as the depth U_m of $U(r)$. Our simulations as a function of σ show the reentrant order–disorder transition in agreement with experimental observations and we go on to predict an inhomogeneous-to-homogeneous transition as a function of C_s , which has yet to be observed in charged colloidal suspensions.

The details of MC simulations are given in Section 2. The effect of charge density on the phase behavior of suspensions with different volume fractions at low salt concentrations is discussed in Section 3, where the suspensions exhibit a reentrant solid–liquid transition. Section 4 includes the results on the influence of salt concentration on the reentered disordered state. Comparison of our simulation results with the results of reported experiments is presented in Section 5. A brief summary with conclusions are given in Section 6.

2. Details of simulation

Monte Carlo (MC) simulations are carried out using the Metropolis algorithm with periodic boundary conditions for a canonical ensemble (constant N , V , T where N , V , and T are, respectively, the number of particles, the volume, and the temperature). Particles of diameter d ($= 120$ nm) are assumed to interact via a pair potential $U(r)$ having the functional form

$$U(r) = 2 \frac{(Ze)^2}{\epsilon} \left(\frac{\sinh(\kappa d/2)}{\kappa d} \right)^2 \left(\frac{A}{r} - \kappa \right) \exp(-\kappa r), \quad (1)$$

where $A = 2 + \kappa d \coth(\kappa d/2)$ and the inverse Debye screening length κ is given as

$$\kappa^2 = 4\pi e^2 (n_p Z + C_s) / (\epsilon k_B T). \quad (2)$$

Ze is the effective charge on the particle (related to the surface charge density by $\sigma = Ze/\pi d^2$), C_s the salt concentration, T the temperature (298 K), ϵ the dielectric constant of water, and k_B the Boltzmann constant. The position of the potential minimum R_m is given as $R_m = \{A + [A(A + 4)]^{1/2}\}/2\kappa$ and its depth by $U_m = U(R_m)$. Both R_m and U_m depend on σ and C_s . For the required volume fraction ϕ ($= n_p \pi d^3/6$), the length l of the MC cell is fixed from the relation $l^3 = N/n_p$. By performing simulations with different numbers of particles, N , we found in our earlier simulations [4,14,16] that the results are the same within the statistical error for $N \geq 432$. Hence N is fixed at 432.

The results presented in this paper correspond to $\phi = 0.005$ and 0.03 . At these volume fractions the deionized suspensions are known to crystallize into a body-centered cubic (bcc) ordering [26]; hence we have chosen particles placed on a bcc lattice as the initial configuration in all our simulations. We monitor the total interaction energy U_T and the first peak height of the structure factor $S_{\max}$ to identify thermal equilibrium unambiguously [27,28]. Most of the simulations away from the transition (e.g., freezing) took approximately 8×10^5 configurations to reach equilibrium, while those close to the transition needed nearly 6×10^6 configurations. An MC Step (MCS) is defined as N attempted moves during which, on average, each particle gets a chance to move. The step size to move the particles during MC evolution process is chosen in such a way that the trial acceptance ratio is always around 50%. After equilibrium is reached the pair-correlation function $g(r)$, the coordinate-averaged pair-correlation function $g_c(r)$, and $S_{\max}$ are calculated using procedures reported earlier [28,29]. $g_c(r)$ is obtained by averaging the coordinates of the particles over a sufficiently large number of configurations [29]. Since $g_c(r)$ is free from thermal broadening and helps in identifying the crystal structure unambiguously. Further, for suspensions which exhibit solid-like behavior, $g_c(r)$ shows sharper peaks than the corresponding $g(r)$. The mean square displacement $\langle r^2(t) \rangle$ for a chosen particle is defined as $\langle r^2(m) \rangle = \langle |\mathbf{r}_i(m+n) - \mathbf{r}_i(n)|^2 \rangle$, where $\mathbf{r}_i(m)$ is the position of the i th particle after m MCS and $\langle \dots \rangle$ denotes the configurational average over the initial configurations n . Cluster size and its distribution are calculated as described in our earlier work [14]. The total fraction of particles participating in the clustering F_c , defined as the ratio of the total number of particles that participate in the clustering to the total number of particles N , has also been obtained for suspensions which exhibited inhomogeneous nature (phase separation). We identify the nature of suspension whether it is homogeneous or inhomogeneous by calculating the ratio d_s/d_0 , where d_0 ($= \sqrt{3}/2[1/n_p]^{1/3}$) is the average interparticle separation calculated from the particle concentration n_p and assuming a bcc-like coordination in the liquid-like

order and d_s is the average interparticle distance estimated from the first peak position in $g(r)$. For a homogeneous suspension $d_s/d_0 = 1$ and for an inhomogeneous suspension $d_s/d_0 < 1$.

3. Effect of charge density

We have carried out MC simulations for two volume fractions, $\phi = 0.005$ and $\phi = 0.03$, as a function of charge density on the particles, keeping the salt concentration at 2 μM . These parameters are same as that used by Yamanaka et al. [25] in their experiments. The charge density used in the present simulations correspond to the effective charge estimated experimentally by Yamanaka et al. [25].

It may be mentioned here that the Sogami–Ise potential is derived under the Debye–Hückel approximation and that this approximation is violated for high values of the bare charge (also referred as analytical charge). For highly charged (bare charge) macroions the electrostatic energy of a macroion near its surface largely exceeds the thermal energy $k_B T$. Hence, linearization of the Poisson–Boltzmann equation is not possible. However, the Poisson–Boltzmann equation can be reduced to the Debye–Hückel equation by using the concept of effective charge [30,31]. Here, one considers the macroion and the microions (counterions) which have accumulated in the immediate vicinity of the macroion due to high electrostatic coupling with the macroion as a single entity. Then the dressed colloidal particle (macroion along with the captive microions) can be considered to have an effective charge Z , which is much lower (in absolute value) than the bare charge on the particle. The Debye–Hückel approximation is valid for the dressed colloidal system. Though the theoretical methods for computing effective charges for highly charged colloidal systems [32] are still evolving, the concept of charge renormalization is now well accepted. Several properties of charged colloids are calculated using effective charge and compared with those measured experimentally. Hence, we believe that the Sogami–Ise potential is applicable to describe the reentrant order–disorder transition observed as a function of effective charge.

Figure 1 shows the pair-correlation functions and projections of the corresponding MC cell onto an xy -plane for suspensions with $\phi = 0.005$ and $\sigma = 0.1, 0.23$, and $0.5 \mu\text{C}/\text{cm}^2$. For low values of σ ($= 0.1 \mu\text{C}/\text{cm}^2$), $g(r)$ and $g_c(r)$ showed decay as a function of r , the corresponding particle positions (Fig. 1B) showed disorder, and the ratio d_s/d_0 is found to be one (see Table 1). These observations suggest the suspension at this value of σ is homogeneous and liquid-like ordered. On the other hand, for suspension with $\sigma = 0.27 \mu\text{C}/\text{cm}^2$ we find that $g(r)$ does not decay with r and the positions of sharp peaks in $g_c(r)$ clearly indicate that the ordering is bcc. The projection of particles in the MC cell shows perfect ordering and the calculated d_s/d_0 is found to be one confirming the bcc ordered crystalline structure is homogeneous. At high values of σ ($= 0.5 \mu\text{C}/\text{cm}^2$),

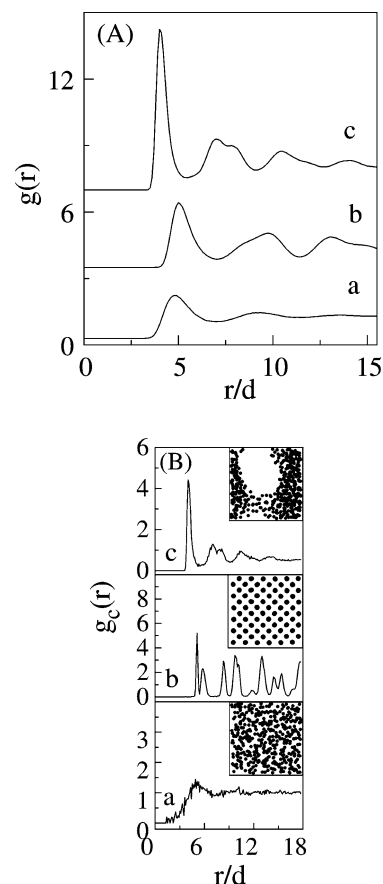


Fig. 1. (A) $g(r)$ vs r for different charge densities at a salt concentration of 2 μM and $\phi = 0.005$. Curves *a*, *b*, and *c* correspond to $\sigma = 0.1, 0.23$, and $0.50 \mu\text{C}/\text{cm}^2$, respectively. (B) $g_c(r)$ vs r for charge densities the same as in (A); the corresponding insets show projection of time-averaged particle coordinates in the MC cell.

$g(r)$ and $g_c(r)$ are found to decay as a function of r once again. Further, we observe the first peak in $g(r)$ shifted to smaller r implying $d_s/d_0 < 1$. These observations suggest that suspension is inhomogeneous and disordered. The corresponding projected particles in the MC cell also confirm this and show particle-free regions (voids) coexisting with disordered dense regions. Since the $g_c(r)$ shows sharper features than the corresponding $g(r)$, the dense disordered region is identified to be solid-like (amorphous).

In order to identify the values of σ at which the homogeneous liquid (HL) freezes into a homogeneous crystalline (HC) order and then to an inhomogeneous disordered (also referred as a phase separated (PS)) state, the structural parameter S_{max} is calculated as a function of σ and is shown in Fig. 2. The sudden increase in S_{max} at $\sigma = 0.23 \mu\text{C}/\text{cm}^2$ (Fig. 2) corresponds to the freezing transition and the sudden drop in S_{max} at $\sigma = 0.33 \mu\text{C}/\text{cm}^2$ corresponds to the transition from the homogeneous crystalline state to a phase-separated (gas–solid coexistence) state. Simulations for suspension with $\phi = 0.03$ showed similar phase behavior except that the corresponding transitions have been found to occur at lower values of σ (see Table 1).

Table 1

Inverse Debye screening length (κ), position of the potential minimum (R_m), depth of the potential well (U_m), average interparticle separation (d_0), and average interparticle separation d_s calculated from first peak position of $g(r)$ for different values of σ corresponding to two suspensions with widely differing volume fractions

ϕ	σ ($\mu\text{C}/\text{cm}^2$)	κd	R_m/d	$U_m/k_B T$	d_0/d	d_s/d_0	State
0.005	0.065	0.667	7.350	−0.088	5.143	1.0	HL
0.005	0.100	0.718	6.841	−0.221	5.143	1.0	HL
0.005	0.150	0.786	6.270	−0.539	5.143	1.0	HL
0.005	0.200	0.848	5.837	−1.023	5.143	1.0	HL
0.005	0.230	0.883	5.600	−1.399	5.143	1.0	HC
0.005	0.273	0.930	5.340	−2.050	5.143	1.0	HC
0.005	0.300	0.960	5.190	−2.547	5.143	1.0	HC
0.005	0.410	1.070	4.690	−5.173	5.143	0.9	PS
0.005	0.500	1.152	4.383	−8.119	5.143	0.8	PS
0.030	0.060	1.021	4.890	−0.107	2.830	1.0	HL
0.030	0.150	1.462	3.542	−0.850	2.830	1.0	HC
0.030	0.200	1.660	3.100	−1.608	2.830	1.0	HC
0.030	0.273	1.900	2.841	−3.142	2.830	1.0	HC
0.030	0.300	1.990	2.744	−3.853	2.830	1.0	PS
0.030	0.410	2.300	2.460	−7.348	2.830	0.9	PS
0.030	0.500	2.530	2.300	−10.90	2.830	0.8	PS

The abbreviations HL, HC, and PS represent the homogeneous liquid, homogeneous crystalline, and phase-separated states, respectively.

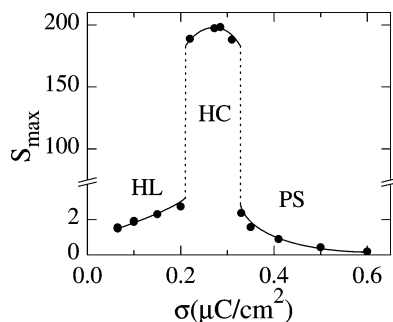


Fig. 2. Structural parameter $S_{\max}$ as a function of σ for a suspension with $C_s = 2.0 \mu\text{M}$ and $\phi = 0.005$. The line drawn through the points is a guide to the eye.

These observations are understood from the dependence of $U(r)$ on σ . At low charge density the suspensions remain homogeneous because the particles which are at a distance d_0 will always experience screened Coulomb repulsive interaction as $d_0 < R_m$ (see curve *a* of Fig. 3). The structural ordering in the homogeneous state depends upon the strength of $U(r)$ at $r = d_0$. As the charge density on the particles is increased the strength of repulsive interaction increases. This results in freezing into a homogeneous crystalline state. Since R_m decreases monotonically with increase in σ , particles which are at separation of d_0 will experience attraction when $R_m \leq d_0$ (see curve *b*). Due to strong attraction the particles condense into a solid-like dense phase leaving some particles in the rare phase (gas-like) which appear as voids when the fraction of the volume occupied by the rare phase is smaller than that of the dense phase. Thus the occurrence of freezing of a homogeneous liquid into a homogeneous crystalline state at lower values of σ and the system reentering into a disordered inhomogeneous phase (gas–solid coexistence) at higher values of σ are understandable.

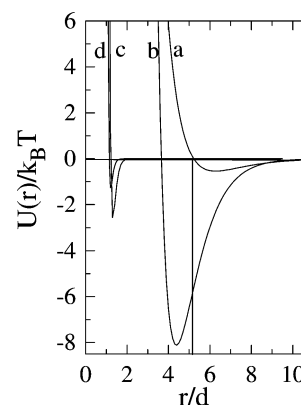


Fig. 3. Pair potential $U(r)/k_B T$ for different suspension parameters with $\phi = 0.005$. Curves *a* and *b* correspond to $\sigma = 0.15$ and $0.5 \mu\text{C}/\text{cm}^2$, respectively, and $C_s = 2.0 \mu\text{M}$. Curves *c* and *d* correspond to $C_s = 550.0$ and $1000 \mu\text{M}$, respectively, and $\sigma = 0.15 \mu\text{C}/\text{cm}^2$. The vertical line corresponds to the average interparticle separation d_0 .

4. Effect of salt on inhomogeneous disordered phase

There have been reports of theoretical [16,29,33,34] and experimental investigations [2,26,35] on the effect of C_s on melting/freezing of a homogeneous colloidal suspension. However, the conditions under which an inhomogeneous disordered state, which occurs in highly charged colloids, becomes homogeneous are not known. When the well depth $U_m < k_B T$, the attraction between particles becomes weak, hence the suspension can remain homogeneous. It can be seen from Fig. 3 (curve *d*) that the well depth U_m decreases to values smaller than $k_B T$ at high salt concentrations. So we performed MC simulations over a wide range of salt concentrations, keeping the other suspension parameters fixed, and results are summarized in Table 2. Figure 4 shows the effect of increasing salt concentration on the disordered dense phase which coexisted with voids at $C_s = 2 \mu\text{M}$ (Fig. 1c).

Table 2

Inverse Debye screening length (κ), position of the potential minimum (R_m), depth of the potential well (U_m), and the ratio of dense phase concentration n_d to homogeneous particle concentration n_p for different values of C_s for suspensions with volume fractions $\phi = 0.005$ and 0.03 exhibiting inhomogeneous and homogeneous states

ϕ	σ ($\mu\text{C}/\text{cm}^2$)	C_s (μM)	κd	R_m/d	$U_m/k_B T$	n_d/n_p	State
0.005	0.5	10	1.607	3.270	−9.909	3.890	PS
0.005	0.5	20	2.037	2.700	−10.76	6.980	PS
0.005	0.5	50	2.975	2.070	−10.50	15.33	PS
0.005	0.5	100	4.086	1.740	−8.541	27.11	PS
0.005	0.5	200	5.688	1.520	−5.757	39.04	PS
0.005	0.5	300	6.930	1.422	−4.267	49.71	PS
0.005	0.5	350	7.474	1.390	−3.774	53.19	PS
0.005	0.5	400	7.980	1.360	−3.382	55.96	PS
0.005	0.5	500	8.908	1.328	−2.803	60.72	PS
0.005	0.5	550	9.340	1.313	−2.583	63.54	PS
0.005	0.5	600	9.743	1.300	−2.395	1.000	HG
0.005	0.5	700	10.521	1.278	−2.095	1.000	HG
0.005	0.5	800	11.241	1.261	−1.860	1.000	HG
0.005	0.5	900	11.918	1.246	−1.670	1.000	HG
0.005	0.5	1000	12.558	1.234	−1.524	1.000	HG
0.030	0.3	10	2.285	2.474	−3.933	1.500	PS
0.030	0.3	50	3.389	1.915	−3.548	3.230	PS
0.030	0.3	100	4.395	1.680	−2.858	4.782	PS
0.030	0.3	150	5.211	1.565	−2.335	5.916	PS
0.030	0.3	200	5.915	1.495	−1.958	6.786	PS
0.030	0.3	250	6.544	1.446	−1.680	7.500	PS
0.030	0.3	300	7.117	1.410	−1.471	1.000	HG
0.030	0.3	400	8.145	1.358	−1.176	1.000	HG
0.030	0.3	500	9.055	1.323	−0.980	1.000	HG
0.030	0.3	600	9.883	1.296	−0.841	1.000	HG

The abbreviations PS and HG represent the phase-separated state and a homogeneous gas state, respectively.

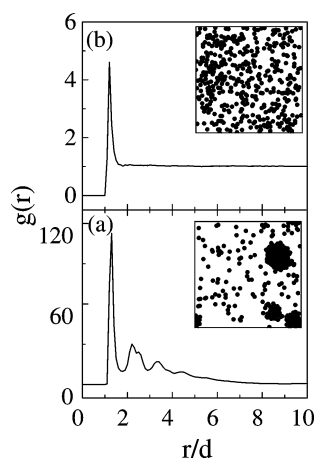


Fig. 4. $g(r)$ vs r at two different salt concentrations: (a) $C_s = 550.0 \mu\text{M}$ and (b) $C_s = 1000.0 \mu\text{M}$. Insets show the projection of particles in the MC cells corresponding to the two values of C_s . Other parameters of the suspension are $\phi = 0.005$, $\sigma = 0.5 \mu\text{C}/\text{cm}^2$.

For low values of C_s , $g(r)$ shows a decay, but the structural correlations persist to the full length of the MC cell (Fig. 1c) suggesting that the disordered dense phase is connected. The fraction of volume occupied by the voids is found to be smaller than that occupied by the dense phase. Hence the voids constitute the minority phase at low values of C_s . The particle positions in the MC cell (see Fig. 1c) confirm this. When the salt concentration is increased we observe struc-

tural correlations in $g(r)$ (Fig. 4a) to extend up to a few times the diameter of the particle. The first peak height is also found to be very high and the first peak position matches exactly with R_m . These observations imply the formation of dense phase clusters with R_m as the average distance between particles within the cluster. The other sharp peaks appearing at distances beyond the first peak correspond to short-range ordering of particles within the clusters (intra-cluster ordering).

Since the clustering occurs at large values of C_s , the ordering of particles within a cluster could be liquid-like or solid-like (amorphous). In order to distinguish between the two types of ordering we have calculated $g_c(r)$, $g(r)$, and the mean square displacement $\langle r^2(t) \rangle$ of particle within the cluster. We compare the behavior of these quantities with that corresponding to a vapor–liquid coexistence state. This vapor–liquid coexistence states obtained by performing simulations for suspension parameters at which a vapor–liquid coexistence has been reported [1,4,5]. It can be seen from Fig. 5 that the peaks in $g_c(r)$ (curve a) corresponding to $C_s = 550 \mu\text{M}$ are much sharper, with increased peak height as compared to the corresponding $g(r)$ (Fig. 4a), whereas the $g_c(r)$ corresponding to the vapor–liquid coexistence (dotted curve in Fig. 5) is much lower in peak height and also poorer in features as compared to the corresponding $g(r)$ (inset of Fig. 5). The mean square displacement of particles inside the cluster corresponding to $C_s = 550 \mu\text{M}$ shows a saturation behavior as a function of MC time and undergo much

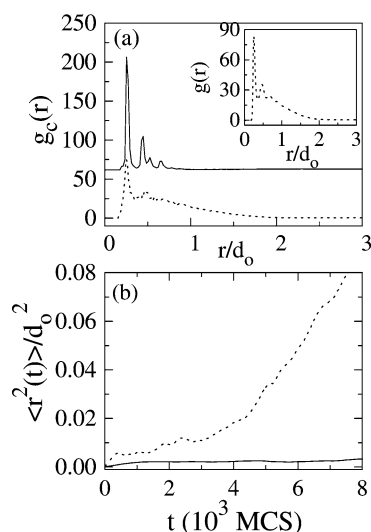


Fig. 5. (a) $g_c(r)$ vs r for suspensions exhibiting gas–solid (full curve: $\phi = 0.005$, $\sigma = 0.5 \mu\text{C}/\text{cm}^2$) and vapor–liquid (dotted line: $\phi = 9.02 \times 10^{-3}$, $\sigma = 0.21 \mu\text{C}/\text{cm}^2$, $C_s = 40.8 \mu\text{M}$, $d = 0.109 \mu\text{m}$) coexistence. $g(r)$ vs r for the vapor–liquid coexistence is shown as an inset. (b) Mean square displacement $\langle r^2(t) \rangle$ vs t (in units of 1000 MCS) for particles within a solid-like (full curve) and liquid-like (dashed curve) clusters.

smaller displacement as compared to that of particle within a liquid-like ordered cluster. These observations unambiguously suggest that the clusters formed at higher values of C_s for highly charged colloids are solid-like. These clusters can be observed either in the scattering or microscopy experiments provided the density of the solvent is matched with the density of colloidal particles. Tata et al. have observed the coexistence of voids with dense phase disordered regions [8,9] and existence of clusters under density matched conditions [9] in highly charged polychlorostyrene sulfonate particles (PCSS) dispersed in an aqueous medium. Density matching for PCSS particles has been achieved by redispersing them in 60% glycerol aqueous solution.

Simulations at a salt concentration of 1000 μM showed only a single peak in $g(r)$ (see Fig. 4b) at $r = R_m$. The corresponding projection of particles in the MC cell (see inset of Fig. 4b) do not show clustering and are distributed uniformly. These observations suggest that the suspension with $C_s = 1000 \mu\text{M}$ is homogeneous and noninteracting (gas-like). Thus we observe for $C_s \leq 550 \mu\text{M}$ an inhomogeneous state in the form of dense phase clusters having solid-like ordering and a homogeneous gas-like disordered state at $C_s = 1000 \mu\text{M}$. Hence the inhomogeneous (PS)-to-homogeneous (HG) transition is expected to occur in between these salt concentrations. We identify this transition by monitoring the total fraction of particles participating in the clustering F_c (Fig. 6a) and the first peak height g_{max} of $g(r)$ (Fig. 6b). Note the sudden change in both of these parameters around $C_s = 570 \mu\text{M}$ as C_s is increased. This change is associated with the inhomogeneous (PS) to homogeneous (HG) transition or in other words transition from a gas–solid coexistence to a gas phase. The large values of g_{max} in the inhomogeneous state arise due to scal-

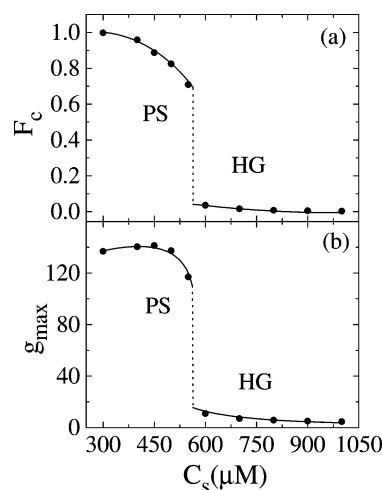


Fig. 6. Quantities (a) F_c and (b) g_{max} as functions of C_s used for the identification of the transition from an inhomogeneous disordered state to a homogeneous gas phase. Other parameters of the suspension are the same as in Fig. 4.

ing of $g(r)$ with respect to particle concentration n_p . The dense phase concentration n_d is estimated from the first peak position ($\cong R_m$) of $g(r)$ and is found to be several times higher than n_p (see Table 2). In the case of suspension with $\phi = 0.03$ the transition is found to occur at $C_s = 270 \mu\text{M}$ which is lower than $C_s = 570 \mu\text{M}$ for $\phi = 0.005$. Suspensions of higher volume fraction undergo PS to HG transition at lower values of C_s . This is due to increased screening of particles in suspensions of higher volume fraction as compared to that in suspensions with lower ϕ .

5. Comparison with experiments

It is important to compare our simulation results with those observed experimentally. Our simulations as a function of σ revealed the existence of the three phases viz., a homogeneous liquid (HL) at low σ , a homogeneous crystalline (HC) state at intermediate values of σ , and an inhomogeneous disordered state (PS) at high values of σ . Further, we showed that the homogeneous liquid freezes into a homogeneous crystalline state at about $\sigma \geq 0.22 \mu\text{C}/\text{cm}^2$ and disorders once again at about $\sigma \geq 0.33 \mu\text{C}/\text{cm}^2$. Yamanaka et al. [25] have reported freezing of a homogeneous liquid-like ordered aqueous suspension of charged particles with $\phi = 0.005$ into a homogeneous crystalline state for charge densities beyond $0.24 \mu\text{C}/\text{cm}^2$. The suspension is found to disorder once again when σ is increased beyond $0.40 \mu\text{C}/\text{cm}^2$. This reentered disordered state is identified to be inhomogeneous from the scattering measurements. The measured average interparticle separation d_{exp} is found to be less than d_0 [25,36], which implies the non-space-filling nature of the suspension at high charge densities. Thus present simulations are in good agreement with the experimental observations. Further, our simulations at higher volume fraction have revealed that the values of σ at which the

HL-to-HC transition and the HC-to-PS transition occur are lower than that in suspensions of lower ϕ . This result is also in agreement with experimental observations [25].

Present simulations on the reentrant inhomogeneous disordered state as a function of salt concentration revealed that the inhomogeneous state undergoes a transition to the homogeneous gas phase beyond a critical salt concentration. This gas–solid transition, which can be observed in highly charged colloids by varying the salt concentration, has not yet been investigated experimentally. Further, we notice from these simulations the absence of vapor–liquid coexistence for highly charged colloids. In this context, it is worth mentioning the result from MC simulations on a system of hard sphere particles with an attractive Yukawa interaction by Hagen and Frankel [37]. They showed the disappearance of vapor–liquid coexistence when the range of the attractive part of the Yukawa potential was less than approximately one-sixth of the hard-core diameter. In the present simulations the range of attractive and repulsive parts of $U(r)$ have been varied by changing σ and C_s . The range of attraction is found to be smaller for suspensions of high-charge-density particles as compared to the suspensions of low-charge-density particles. Hence, one can observe a vapor–liquid coexistence in suspension of low-charge-density particles [4,5] but not in suspensions of highly charged particles.

Schmitz in his recent work [38] concludes that neither the DLVO nor the Sogami–Ise potential can explain the reentrant transition, based on the following observations. The well depth $U_m/k_B T$ when plotted as a function of C_s shows a minimum (see Fig. 3 of Ref. [38]) but does not show a minimum when plotted as a function of effective charge Z . According to Schmitz, the lack of a minimum in the profile of $U_m/k_B T$ versus charge on the particle indicates that the Sogami–Ise potential does not describe the reentrant order–disorder transition observed by Yamanaka et al. [25]. A minimum in the profiles of $U_m/k_B T$ vs C_s or $U_m/k_B T$ vs Z is not necessary for understanding the reentrant transitions observed as a function of C_s by Tata et al. [4] and for describing the reentrant order–disorder transition observed as a function of Z by Yamanaka et al. [25]. This is explained below.

Free energy calculations using $U(r)$ as a function of C_s [4] have revealed that at high values of C_s the configurational entropy of the colloidal particles dominates over the interaction energy. Hence, the suspension at high values of C_s exhibits a homogeneous disordered (gas-like) phase. At low values of C_s , the suspension once again becomes homogeneous (liquid-like ordered) because the colloidal particles experience screened Coulomb repulsive interaction as a result of $R_m > d_0$. For intermediate values of C_s , $R_m < d_0$, and $|U_m/k_B T| \sim 1$; hence, particles experience an attractive interaction and undergo gas–liquid condensation.

In a deionized highly charged colloidal system, the reentrant disordered (gas–solid coexistence) state occurs at high values of effective charge because $R_m < d_0$ and well depths are very large (i.e., $|U_m/k_B T| > 1$; see Table 1 and curve *b* of Fig. 3). Because of this the particles experience strong at-

traction and the suspension exhibits gas–solid coexistence. Upon addition of salt the well depths become shallower ($|U_m/k_B T| \leq 1$; see curve *d* of Fig. 3 and Table 2), resulting in a homogeneous gas-like disordered phase. Thus highly charged particles always exhibit a disordered state, which could be either a gas–solid coexistence (for low values of C_s) or a homogeneous gas phase (for high values of C_s). Experimental evidence exists for occurrence of gas–solid coexistence in a deionized highly charged colloidal latex system [7,8]. We would like to mention here that the USAXS results (see Fig. 2 of Yamanaka et al. [25]) correspond to $C_s = 10 \mu\text{M}$; hence the attraction is weaker than for a suspension with low salt. This results in a smoother second peak (instead of a split second peak as observed by Tata et al. [8]), resulting in interpreting the USAXS profile (curve *c*, Fig. 2 of Yamanaka et al. [25]) as liquid-like ordered.

Thus our MC simulations using the Sogami–Ise potential unambiguously describe the occurrence of a reentrant order–disorder transition. Since the DLVO potential is purely repulsive at all interparticle distances it cannot describe the reentrant phenomenon observed in charged colloids. Since the Sogami–Ise potential can be obtained from volume term theories [20], these theories are also expected to provide a qualitative explanation for the observed reentrant transition. However, calculations using volume term theories [17–19] close to the experimental conditions of Yamanaka et al. [25] do not exist.

Schmitz proposes an “Orbital model of colloidal cluster,” which uses the methods of juxtaposition of potential fields and Brownian dynamics (BD) simulations [38] to understand the reentrant order–disorder transition. His calculations deal with equilibrium distribution of microions for a fixed macroion configuration and do not allow macroions to move. A reentrant order–disorder transition was observed by performing USAXS experiments on silica colloids by varying the charge on the particle. USAXS experiments probe the spatial ordering of macroions over length scales on the order of hundreds of nanometers, whereas Schmitz’s simulations probe length scales on the order of tens of nanometers. Further, the magnitude of the bare charge on the particles used in his simulations is four orders of magnitude lower than the measured analytical charge on the colloidal particle. Hence, Schmitz’s orbital model cannot provide information about the equilibrium spatial distribution, in other words ordering, of macroions. Orbital model which incorporates the motion of macroions along with microions and calculations using such a model as a function of bare charge close to experimental conditions are expected to provide a more realistic description of reentrant order–disorder than the so-called mean field theories.

6. Conclusions

MC simulations using a pair potential with a long-range attractive term show a homogeneous liquid, a homogeneous

crystal, and a disordered inhomogeneous phase as the charge density is varied, suggesting a reentrant order–disorder transition, which is in agreement with the observed experimental results. The reentered inhomogeneous phase is identified as the gas–solid coexistence state and occurs due to strong attraction experienced by the highly charged particles. Suspensions exhibit homogeneous liquid-like and homogeneous crystalline orders at lower values of σ due to the dominant screened Coulomb repulsion at average interparticle separation. The inhomogeneous disordered state undergoes a transition to a homogeneous gas state upon increasing the salt concentration. This transition is analogous to the gas–solid transition observed in atomic and colloid-polymer mixtures as a function of temperature and free polymer, respectively [39]. We believe that our prediction of a gas–solid transition driven by the salt concentration would motivate experimentalists to investigate highly charged colloids in search of this transition as well as for detailed phase diagrams with gas–liquid or gas–solid coexisting phases.

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