

Vapor-Liquid Condensation in Charged Colloidal Suspensions

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Dilute aqueous polystyrene suspensions are found to exhibit a novel vapor-liquid condensation. Upon de-ionization, weakly interacting homogeneous suspensions below a critical particle concentration condense into a concentrated phase with liquidlike order and a dilute vapor phase. This phenomenon strongly suggests net attraction between particles at interparticle separation several times the particle diameter. The present results are understood on the basis of an effective interparticle model potential.

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The remarkable feature of electrostatically stabilized aqueous colloids is the appearance of crystalline, liquidlike, and even glassy structural ordering even at extremely low ($<1\%$) volume fractions [1]. Until now it was widely believed that the particles interact predominantly via a screened Coulomb repulsion [2-4]. It could explain many of the experimental results in charged colloids. A system of particles interacting via a purely repulsive potential when restricted to a finite volume is expected to remain homogeneous except for the fluid-solid transition. However, during the last decade, there have been several experimental observations [5-11] reported in dilute colloids which show that the suspension can be inhomogeneous under appropriate conditions, and hence these results cannot be understood on the basis of a repulsive potential alone. Recently, we reported a reentrant phase transition [12] in charged colloids where the suspension underwent phase separation only over a limited range of impurity ion concentration n_i and remained homogeneous otherwise. These results suggested the existence of a secondary minimum in the effective interparticle potential. An immediate consequence of a minimum in the pair potential is that the system must exhibit a vapor-liquid condensation under appropriate thermodynamic conditions.

In this Letter we report a novel phase transition in dilute aqueous polystyrene colloids which is analogous to vapor-liquid condensation in atomic systems. In a weakly interacting homogeneous suspension, when de-ionized, particles condense into a strongly interacting concentrated phase with liquidlike structural ordering which occupies a relatively smaller volume. The particle concentration in the remaining volume of the medium, which constitutes the dilute vapor phase, is several times smaller than that in the condensed phase. The occurrence of such a condensation strongly suggests the existence of attraction in the effective interparticle interaction at large interparticle separation. These results are explained on the basis of an effective interparticle model potential obtained in a recent formalism [13] of electrostatic interaction in colloidal suspensions, and are in good qualitative agreement with those of a recent Monte Carlo simulation [14] using this potential.

Monodisperse suspensions of polystyrene particles of

diameter $d=0.11\ \mu\text{m}$, obtained from M/s. Polysciences Inc., USA, are prepared by diluting the stock suspension, in de-ionized water, to the desired concentration. Suspensions thus prepared are homogeneous and have conductivity of the order of a few tens of μScm^{-1} . Suspensions with particle concentration n_p ranging over an order of magnitude [sample A_1 : 0.46, A_2 : 1.58, A_3 : 1.61, A_4 : 3.26, and A_5 : $4.11(\times 10^{12}\ \text{cm}^{-3})$] are investigated. Suspensions are taken in cylindrical cells of internal diameter of 1 cm. In order to de-ionize the suspensions, a mixed bed of ion exchange resin (cation: Ambercep 252; anion: Ambercep 900) is added to the suspensions. Structural ordering in the suspensions is investigated by measuring structure factor $S(Q)$ using an angle-resolved polarized light scattering setup described elsewhere [15]. Particle concentration in the suspension is obtained by the evaporation method [6] after the experiment is over.

Suspensions with n_p lower than $3 \times 10^{12}\ \text{cm}^{-3}$ exhibit a clear boundary between the concentrated phase and the dilute phase after the de-ionization equilibrium is reached (~ 10 days), whereas those with higher concentration

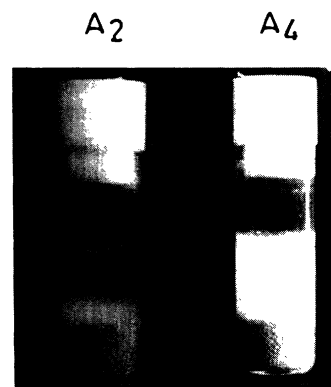


FIG. 1. Photograph of sample cells showing the suspensions A_2 and A_4 after reaching the de-ionization equilibrium. The dilute suspension A_2 exhibits the concentrated phase (lower part of the cell) macroscopically separated from the dilute phase (upper part of the cell). The concentrated suspension A_4 became homogeneous after an initial phase separation. Ion exchange resin is at the bottom of the cell.

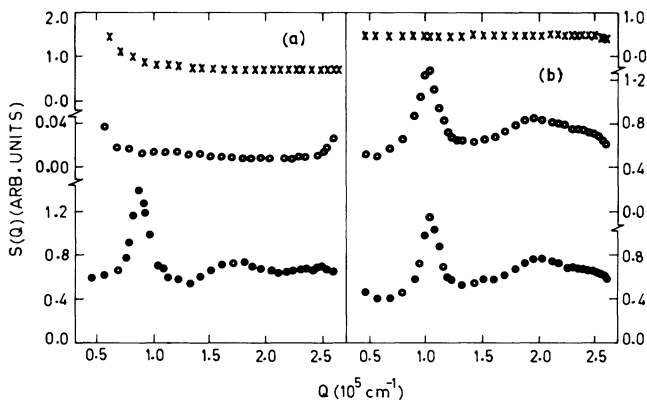


FIG. 2. Structure factor $S(Q)$ of suspensions at different heights for (a) sample A_2 and (b) sample A_4 . (●) Lower region of cell; (○) top region of cell. Note that $S(Q)$ for the top region of sample A_2 has extremely low magnitude and is also structureless. $S(Q)$'s of these suspensions before the addition of ion exchange resin are also shown (×) for comparison.

temporarily exhibit phase separation and eventually become homogeneous, consistent with the results reported earlier [12]. Figure 1 shows the suspensions A_2 and A_4 several days after the addition of ion exchange resin. If the suspensions A_1 to A_3 are made homogeneous by shaking, these become inhomogeneous again after a few days. However, when suspensions with $n_p > 3 \times 10^{12} \text{ cm}^{-3}$ are shaken, they remain homogeneous.

In order to investigate the structural ordering, the structure factor is measured in the concentrated as well as in the dilute phase. Figure 2 shows the structure factor for suspensions A_2 and A_4 . Note that in the suspension A_2 , the concentrated phase has a strong liquidlike order whereas the dilute phase has no structural ordering; i.e., it is gas or vaporlike. Suspensions A_1 and A_3 show similar behavior. On the other hand, the suspension A_4 , which appears homogeneous, exhibits strong liquidlike order extending over its full volume. Similar behavior is exhibited by sample A_5 .

In order to make a quantitative estimate of the extent of the difference of the particle concentrations in the concentrated and the dilute phases, scattered intensity $I(Q_0)$ at sufficiently large scattering vector ($Q_0 = 2.6 \times 10^5 \text{ cm}^{-1}$) is measured as a function of height in the suspension. At Q_0 the departure of $S(Q)$ from its asymptotic limit, due to structural correlations, is rather small. Figure 3 shows the dependence of $I(Q_0)$ on height for various suspensions. The boundary between the concentrated and the dilute phases causes the scattered intensity to reduce by typically 2 orders of magnitude. This shows that particle concentrations in the two phases are widely different. It is clear from these observations that the concentrated phase is basically a liquidlike condensed phase whereas the rest of the volume of the medium is occupied by an extremely dilute vaporlike phase. Thus, the present

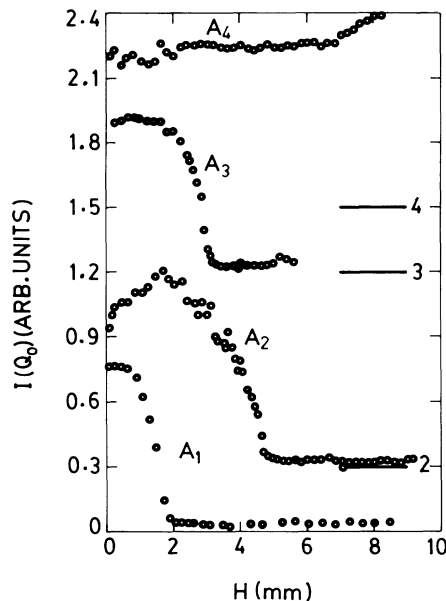


FIG. 3. Scattered intensity at a fixed scattering vector ($Q_0 = 2.6 \times 10^5 \text{ cm}^{-1}$) as a function of height in various suspensions. The decrease in the scattering beyond certain heights in the suspensions A_1 to A_3 is because of the boundary between the concentrated and the dilute phases. Horizontal lines marked 2 to 4 are the zeros of the ordinates for samples A_2 to A_4 .

results clearly demonstrate a vapor-liquid condensation in dilute charged colloids.

It is of interest to estimate the average nearest-neighbor (nn) distance d_{nn} or the particle concentration in the condensed phase. The position Q_{max} of the first peak in the structure factor can be used for this purpose. As suspensions at low volume fractions crystallize in the bcc structure, the liquidlike order is also assumed to have bcc-like local short-range order [6]. Then d_{nn} is $6^{1/2} \pi Q_{max}^{-1}$ and is shown in Fig. 4. The average interparticle separation R_a [for bcc-like coordination, $R_a = 3^{1/2} (4n_p)^{-1/3}$] expected for a homogeneous dispersion

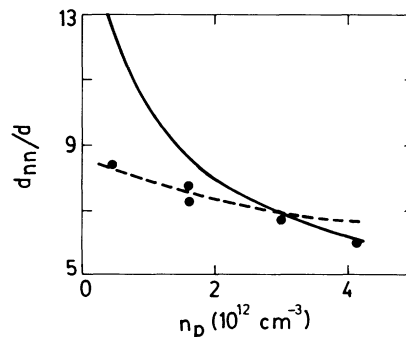


FIG. 4. Estimated nn distance from Q_{max} of $S(Q)$ as a function of particle concentration (●). R_a and R_m are also shown as solid and dashed curves, respectively.

is also shown as a continuous curve. Note that d_{nn} is significantly smaller than R_a for suspensions exhibiting condensation. This implies that the particle concentration in the condensed phase is several times higher than the average concentration n_p . On the other hand, for the suspensions which become homogeneous (A_4 and A_5) $d_{nn} \approx R_a$, as expected.

A vapor-liquid condensation can occur, in principle, if there exists a sufficiently deep potential minimum in the effective interaction potential at a distance smaller than R_a . One has to also understand why concentrated suspensions A_4 and A_5 remain homogeneous. According to the recent theory [13] of electrostatic interaction in charged colloids, the effective interparticle potential $W(r)$ has the form

$$W(r) = B[(A/r) - K] \exp(-Kr),$$

where $A = 2 + Kd \coth(Kd/2)$ and $B = 2[eZ \sinh(Kd/2)/Kd]^2/\epsilon$. The first term is repulsive and dominates at small r whereas the second term is attractive and leads to a secondary minimum whose position and depth depends on inverse Debye screening length K given as $K^2 = 4\pi e^2(n_p Z + n_i)/\epsilon k_B T$. Ze is the charge on the particle, ϵ the dielectric constant of water, k_B the Boltzmann constant, and T the temperature (298 K). The position R_m of the potential minimum is given as $R_m = A + [A(A + 4)]^{1/2}/2K$. The dependence of R_m on n_p is also shown, as the dashed curve in Fig. 4, for $Z = 500$ [2] and $n_i = 3 \times 10^{15} \text{ cm}^{-3}$ [16]. Note that $R_m < R_a$ for $n_p < 2.9 \times 10^{12} \text{ cm}^{-3}$ and note the excellent agreement between d_{nn} and R_m for the suspensions A_1 to A_3 . It may be pointed out that Monte Carlo simulations of dilute colloids using the model potential $W(r)$ also predict a vapor-liquid condensation [14] similar to that reported here. Further, as $R_m > R_a$ for $n_p > 2.9 \times 10^{12} \text{ cm}^{-3}$, concentrated suspensions are not expected to exhibit vapor-liquid condensation in agreement with the present observations. Also note that d_{nn} is close to R_a rather than R_m . It is worth mentioning that the present measurements are carried out as a function of n_p after reaching de-ionization equilibrium and are complementary to those reported earlier [12], where measurements were made on a suspension of given n_p during the evolution of the de-ionization process. One can also compare the vapor-liquid transition in atomic systems with that in colloids. In atomic systems, as a result of lowering the temperature, when thermal energy $k_B T$ becomes lower than the depth of the potential minimum, this transition takes place [17]. In colloids one can change the well depth of the secondary minimum of $W(r)$ relative to $k_B T$ at a given temperature simply by changing n_i . It is straightforward to show [13] from Eq. (1) that for $Kd > 2.4$, $W(R_m)/k_B T$ increases as n_i reduces. Hence reducing n_i is analogous to reducing the equivalent temperature $T^* = k_B T/W(R_m)$. Occurrence of the vapor-liquid transition in charged colloids upon de-ionization is thus un-

derstandable.

As mentioned earlier, there are a number of other experimental observations which cannot be understood on the basis of the screened Coulomb potential even if van der Waals attraction is also taken into account. Some of these are as follows: (a) The measured particle concentration in the ordered phase is always significantly higher than the average n_p [5,6]. (b) Ordered regions are found to coexist with disordered regions with widely different particle concentrations [7,8]. (c) Stable voids are observed in ordered suspensions [9,10]. (d) Isolated stable bound pairs of particles are observed with equilibrium separation being several times the particle diameter [11]. All these observations also support the presence of a secondary minimum in the effective interparticle potential. It may further be pointed out that many of the experimental results, which were earlier understood on the basis of the screened Coulomb or the DLVO [3] potential, e.g., the structure factor of liquidlike ordered suspensions [16], the liquid-solid transition [18], and the elastic constants of colloidal crystals [19], have also been explained using $W(r)$. Thus $W(r)$ appears to be a good model potential for explaining wide-ranging phenomena in charged colloids. It may be mentioned that the theoretical formalism developed to obtain the effective pair potential [13] uses the linearized Poisson-Boltzmann equation and adiabatic approximation for the motion of counterions. The statistical mechanics of the counterions in the Gibbs ensemble leads to the attractive term in $W(r)$. Although the approximations in the formalism and their implications have been examined in the past [20,21], an *ab initio* calculation of the exact interparticle interaction from first principles would greatly improve the current understanding of the subject.

To conclude, the present experiments have clearly demonstrated the occurrence of a vapor-liquid condensation in dilute charged colloids. The nearest-neighbor distance in the condensed phase is in excellent agreement with the position of the minimum of an effective interparticle potential. These results can be considered to be direct evidence for an attractive component in the effective interaction potential which dominates at large r , and hence the widely used repulsive screened Coulomb potential needs reconsideration. Apart from the implications on the current understanding of the interparticle interactions in charged colloids, the present results also open the possibility of observing corresponding critical phenomena in these systems.

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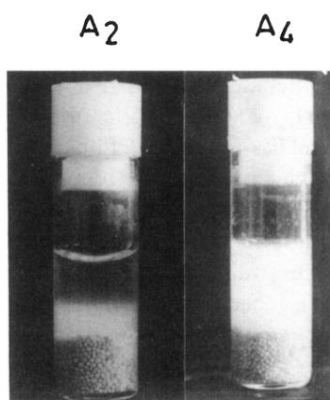


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