

ORDER-DISORDER TRANSITION IN IONIC COLLOIDAL DISPERSIONS

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Abstract: Phase diagram of the order-disorder transition in electrostatically stabilized colloidal silica dispersions were determined as a function of the effective surface charge density (σ_e), particle volume fraction and salt concentration. It was found that the disordered dispersion first became ordered, and thereafter reentered into the disordered state, with increasing σ_e . This reentrant transition is not explainable in terms of widely accepted concept based on Yukawa-type pair potential and charge-renormalization model.

Introduction

The ionic colloidal systems undergo the order-disorder transition with varying magnitude of an electrostatic interparticle interaction. Major experimental variables which determine the interaction are the effective surface charge density of the particles σ_e , the particle volume fraction ϕ , and the salt concentration C_s [1]. The phase diagram of the transition has extensively been studied [1-4]. Usually, ϕ and C_s have been adopted as variables, and the charge dependence was examined only in recent studies by Palberg *et al.* [3] and by ourselves [4]. In both studies, the C_s value at the transition point, which was determined at a fixed ϕ and at relatively small σ_e 's, increased with σ_e .

In the present study, we report a three dimensional phase diagram of the order-disorder transition as a function of σ_e , ϕ and C_s [5]. We investigated much broader charge conditions than in the previous studies, and found that the disordered state became ordered and thereafter reentered into the disordered state with increasing σ_e .

Experimental

Aqueous dispersions of colloidal silica particles (KE-P10W, Nippon Shokubai Co., Tokyo; a diameter = $0.12 \pm 0.01 \mu\text{m}$) were used after thorough purification by dialysis and ion-exchange method. The value of σ_e was continuously varied by tuning the degree of dissociation of weakly acidic silanol groups on the particle surfaces with additions of NaOH [4-6]. All the experiments were performed at $\text{pH} < 8$, that is, under conditions where the concentrations of excess NaOH were less than $1 \mu\text{M}$. The values of σ_e at various analytical

(bare) charge densities σ_u , were determined by conductometry [5], which will be discussed later (Fig. 2A).

Phase diagram

Figure 1 is the phase diagram, which was constructed by observing iridescence from the ordered structure [5]. C_s values were estimated from the sum of concentrations of coexisting NaCl, ionic species in the water used ($2\mu M$) and excess NaOH, if any. The region whose C_s is smaller than that at the phase boundary (shown by rectangles) corresponds to the ordered state.

With increasing ϕ at fixed σ_e 's, the C_s at the boundary increased monotonously as reported previously [1, 2]. On increasing σ_e , the phase boundary first shifted towards higher C_s due to an augmented electrostatic interaction. However, with further increase in σ_e , a maximum was observed at around $\sigma_e = 0.4 - 0.5 \mu C cm^{-2}$, at least for $\phi \geq 2 \times 10^{-2}$, after which C_s at the boundary decreased. In other words, there existed a reentrant disordered state in high σ_e region.

The phase diagram was further examined by applying an ultra-small-angle x-ray scattering method, which confirmed the presence of the reentrant disordered state [5]. The reentrant transition was also observed for ionic polymer latex systems having various charge densities [5].

On the reentrant order-disorder transition

The interaction between charged colloidal particles has often been claimed to be explainable in terms of a pair potential of the Yukawa form $U_Y(r) = A [(Ze)^2 / 4\pi\epsilon] \exp(-\kappa r)/r$. Here r is the interparticle distance, Z the charge number, e the elementary charge, ϵ the dielectric constant of the medium, $1/\kappa$ the Debye screening length defined as $\kappa^2 = 4\pi e^2 [C_C + 2C_s] / \epsilon k_B T$ (C_C is the concentration of counterion), $A = [\exp(\kappa a)/(1 + \kappa a)]^2$ a geometrical factor, and a the particle radius [1]. Robbins *et al.* [7] have reported a numerical simulation study on the phase diagram for systems interacting *via* Yukawa potential.

$U_Y(r)$ is derived from the linearized Poisson-Boltzman (P-B) equation under Debye-Hückel (D-H) approximation [1]. In practice, especially at low salt conditions examined here, the D-H

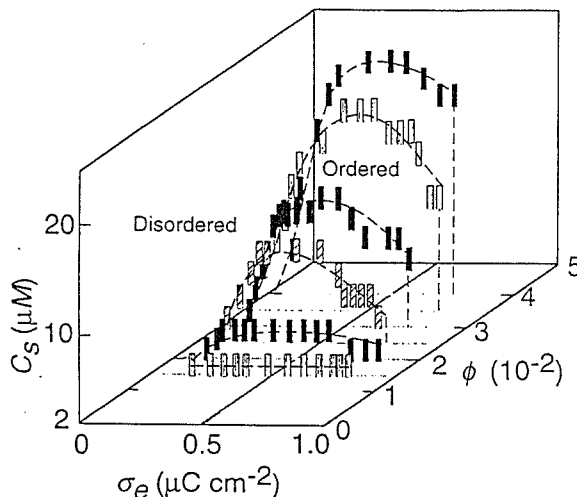


Fig. 1 Phase diagram for the order-disorder transition of aqueous dispersion of KE-P10W silica particles (diameter = $0.12\mu m$) as a function of the effective charge density σ_e , the particle volume fraction ϕ , and the salt concentration C_s . The order-disorder phase boundary was shown by rectangles.

approximation is not valid. Even then, it has been considered that the use of $U_Y(r)$ was justified, if one introduces a renormalized charge density, σ^* , proposed by Alexander *et al.* [8]. In fact, it has been reported that the observed phase diagrams showed a close agreement with that by Robbins *et al.* by using σ^* [2,3]. Furthermore, Palberg *et al.* [3] reported that the renormalized charge was close to the effective charge determined by their conductivity measurements. We note that these conclusions have been drawn for relatively small charge particles ($\sigma_a < 0.63 \mu\text{Ccm}^{-2}$ in Ref. [3]).

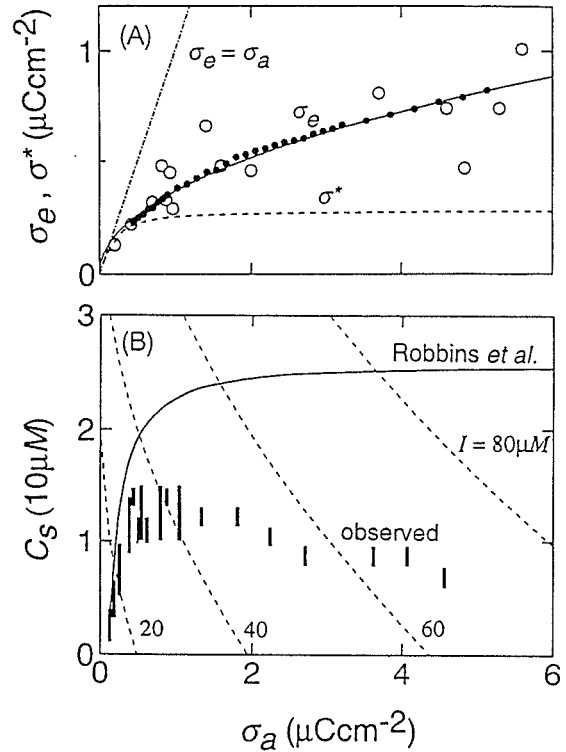
Figure 2A demonstrates a comparison between σ_e determined in the present study ($\phi = 2 \times 10^{-2}$) and σ^* calculated by the method in Ref. [8] (broken curve). The value of σ_e was close to σ^* at small σ_a 's, as reported in the previous studies. At higher σ_a 's, however, the σ^* value leveled off, while σ_e kept increasing. The observed σ_e was well described by an empirical relationship determined for latices,

Fig.2 (A) Relationship between σ_e and σ_a for the silica dispersions ($\phi = 2 \times 10^{-2}$). The full curve is an empirical relationship, $\ln \sigma_e = 0.49 \ln \sigma_a - 1.0$, determined from the data for latex particles[6]. The double-dashed curve represents $\sigma_e = \sigma_a$. The renormalized charge density, σ^* (broken curve) was also shown for comparison.

(B) Comparison between observed phase boundary (rectangles) and the numerical simulation results by Robbins *et al.* with σ^* ($\phi = 3 \times 10^{-2}$). Broken lines show isoionic lines at $I = 20, 40, 60$ and $80 \mu\text{M}$'s.

In Fig. 2B, the experimental phase boundary and that determined by the method of Robbins *et al.* with σ^* are shown as functions of σ_a ($\phi = 3 \times 10^{-2}$). At small σ_a 's, the predicted boundary (full curve) was close to the observed one, as reported in the previous studies. However, at higher σ_a 's, C_s at the boundary became constant, due to the saturation of σ^* . Thus the reentrant transition was not in accord with the theoretical treatment based on the Yukawa potential and charge renormalization concept.

When σ_e was used instead of σ^* , C_s of the boundary increased with σ_a under the conditions examined here, and showed a maximum at around $\sigma_a = 6 \mu\text{Ccm}^{-2}$, resulting from increases in both σ_e and C_c with increasing σ_a . The ionic strength of the dispersion, I ($\equiv C_s + (1/2) C_c$), increases with σ_a . Since κ is proportional to $I^{1/2}$, the screening effect



becomes more pronounced at higher σ_a 's, resulting in a reentrant order to disorder transition. Conditions where I was constant (*isoionic lines*), which is a measure of the screening effect, are also shown in Fig.2B. Thus, when σ_e was coupled with $U_V(r)$, the reentrant transition is expected because of the screening effect. However, the predicted maximum position ($\sigma_a \sim 6\mu\text{Ccm}^{-2}$) was much higher than the observed one ($\sim 1\mu\text{Ccm}^{-2}$).

The above mentioned discrepancy might be partly attributed to, *e.g.*, neglect of the many-particle interaction in the theory, which appears to be more significant in strongly interacting systems like the present one. In our opinion, the Yukawa potential, in which only Coulombic repulsion between two particles is assumed, does not duly account for the phase behavior in low-salt dispersions: Recent experimental results suggest the presence of interparticle *net* attraction in ionic colloidal systems in low-salt conditions. For example, spontaneous formation of void structures [9], where vapor and liquid states are coexisting, seems to be difficult to explain without assuming a *net* attraction. We like to point out that the void structure was favored for highly charged particles [10], for which the reentrant disordered states was observed here. Further studies are needed to discuss the observed reentrant transition in more detail. However, in the present stage, we may reasonably conclude that the argument in terms of Yukawa potential and the charge-renormalization model is not applicable for highly charged colloidal systems.

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