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Equilibrium Phase Diagram of Suspensions of Electrically Stabilized Colloidal Particles

Joachim Kaldasch, Jozua Laven,* and Hans N. Stein

Laboratory of Colloid Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

A second-order perturbation theory based on statistical thermodynamics is employed to calculate the phase diagram of suspensions of charge-stabilized, monodisperse, spherical, colloidal particles that are assumed to interact by a standard DLVO potential. Taking into account van der Waals forces, the phase diagram consists of an ordered colloidal crystal, a disordered fluid phase, and a liquid phase that is formed by particles flocculated into the secondary minimum.

1. Introduction

Colloidal particles may repel each other, either electrostatically (by electric charges on their surfaces) or sterically (by polymers attached to their surfaces and protruding into the continuous phase). The effective interaction potential, due to double layers surrounding the colloidal particles in an electrolyte solution, can be represented by a screened coulombic potential. For the spherical particles investigated here we will use a Debye interaction potential. Thus, the present treatment neglects deviations from the Boltzmann distribution of the ions around the particles, e.g., by hydrated ions on the surface or chemisorption.

The coulombic potential can be progressively screened at constant surface potential by subsequent addition of electrolyte, and under these conditions, the van der Waals attraction becomes important. The resulting interaction potential can be described by the standard DLVO theory.[1−3] A "primary" minimum of the potential close to the particle surface may be separated from a "secondary" minimum at larger distances by a coulombic barrier as depicted in Figure 1.

Dilute suspensions form a random distribution of electrostatically stabilized colloidal particles ("fluid phase"). However, at higher volume fractions a colloidal crystal may be more favorable. Two ordered crystal phases, a body-centered cubic lattice (bcc) and a face-centered cubic lattice (fcc), have been found in a number of experimental[4−6] and theoretical[7−9] investigations. The bcc crystal was only found at very low ionic strengths. The transition line between them has been calculated by using a density functional approach.[10−12]
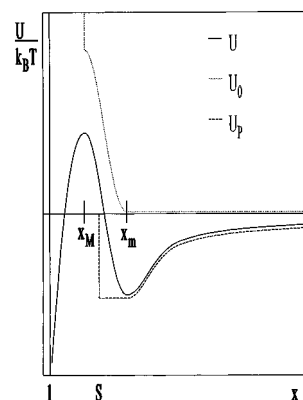

Figure 1. Total two-particle interaction potential (solid line) $U(x)/k_BT$ scaled by the thermal energy as a function of the center-to-center distance x. The theoretical potential can be separation into a repulsive potential $U_0(x)$ which can be transformed into an effective hard-sphere potential with diameter S and an attractive perturbation $U_p(x)$.

Victor and Hansen[13] theoretically predicted that on increasing the ionic strength a reversible "liquid−vapor" spinodal decomposition appears in a flocculated phase ("liquid") and a low-density phase of nonflocculated particles ("vapor"). This flocculation essentially is aggregation at the secondary minimum. It is reversible and occurs as long as irreversible coagulation is prevented by a coulombic barrier.

The limitation of the approach by Victor and Hansen, however, is that they calculated the spinodal lines of the liquid−vapor transition disregarding the presence of the colloid crystal phase. Including the crystal phase allows one to determine the phase diagram also at high volume fractions and low Debye screening parameters. Our approach can lead to qualitatively different results if compared to those of Victor and Hansen. The expected liquid−vapor spinodal decomposition disappears, for example, with low attractive forces. Their analysis had been confined to a first-order perturbation approach.

The objective of this paper is to improve the approximations made by Victor and Hansen. For that purpose we start from the interaction potential introduced by Victor and Hansen[13] for electrostatically stabilized colloidal particles, which consists of a superposition of a repulsive hard-sphere potential and an attractive per-

* Corresponding author.
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turbation. Using this interaction potential, we apply a second-order perturbation approach to determine the free energy of the colloidal fluid and the crystal phase based on statistical thermodynamics as developed originally by Weeks et al.[14] and used, e.g., by Gast et al.[15] for predicting the phase diagram of nonaqueous, colloidal suspensions in the presence of nonadsorbing polymers. By comparing the free energies of the fluid and crystal phases, the coordinates of the coexistence lines in the phase diagram can be determined. Employing a numerical scheme, we will calculate the coexistence lines as a function of the salt concentration for different temperatures, surface potentials, and particle sizes.

2. Theory

2.1. Interaction Potential. We consider a suspension of N charged, monodisperse, colloidal spheres. The spheres are surrounded by counterions and additional electrolyte, forming an electrical double layer around them. The total DLVO potential energy $\tilde{U}(r)$ is the sum of the electric repulsion of the double layers and the van der Waals attraction between two colloidal particles:

$$\tilde{U}(r) = \tilde{U}_R(r) + \tilde{U}_A(r) \tag{1}$$

where r is the center-to-center distance between the colloidal particles.

In the linear superposition approximation the electrostatic term has been calculated from the Poisson–Boltzmann theory[1,16] to be:

$$\tilde{U}_R(r) = \frac{16\pi\epsilon_0\epsilon_r\sigma_0^2}{e_0^2}\left[k_B T \tanh\left(\frac{e_0\Psi_0}{4k_B T}\right)\right]^2\frac{\exp(-\kappa_0(r-\sigma_0))}{r} \tag{2}$$

where Ψ_0 is the surface potential of a colloidal particle, σ_0 is its diameter, ϵ_0 is the permittivity of vacuum, ϵ_r is the relative dielectric constant of the solvent, e_0 is the elementary charge, k_B is Boltzmann's constant, T is the temperature, and κ_0^{-1} is the "Debye screening length" of the ions.

The "Debye screening parameter" κ_0 can be written as:

$$\kappa_0 = \sqrt{\frac{2e_0^2z^2C}{\epsilon_0\epsilon_r k_B T}} \tag{3}$$

where C is the added salt concentration of a z,z electrolyte based on the liquid volume.

For not too large surface potentials (less than $\Psi_0 \approx 25$ mV), the hyperbolic tangent in eq 2 can be linearized and the potential reduces to

$$\tilde{U}_R(r) = \pi\epsilon_0\epsilon_r\sigma_0^2\Psi_0^2\frac{\exp(-\kappa_0(r-\sigma_0))}{r} \tag{4}$$

This coulombic potential scaled by the thermal energy $k_B T$ takes the form

$$U_R(x) = \frac{T_R}{T}\frac{\exp(-\kappa(x-1))}{x} \tag{5}$$

where we introduced $x = r/\sigma_0$ as the reduced center-to-

center distance, $\kappa = \kappa_0\sigma_0$ is the reduced Debye reciprocal length and

$$T_R = \frac{\pi\epsilon_0\epsilon_r\sigma_0\Psi_0^2}{k_B} \tag{6}$$

The van der Waals attraction energy between spherical particles is of the form[13]

$$U_A(x) = -\frac{Ah(x)}{12} \tag{7}$$

where A is Hamaker's constant and

$$h(x) = \frac{1}{x^2-1} + \frac{1}{x^2} + 2\ln\left(1-\frac{1}{x^2}\right) \tag{8}$$

Thus, the total potential scaled by the thermal energy becomes

$$U(x) = \frac{1}{T}\left(T_R\frac{\exp(-\kappa(x-1))}{x} - T_A\frac{h(x)}{12}\right) \tag{9}$$

with $T_A = A/k_B$. The interaction potential may exhibit a positive maximum at $x_M > 1$ and has a secondary minimum at x_m where $x_m > x_M$ (Figure 1). The secondary minimum in $U(x)$ becomes more pronounced either on increasing the van der Waals attraction or on screening the coulombic repulsion by increasing the concentration of salt. This leads to flocculation into the secondary minimum, if the thermal energy is the only energy of motion of the dispersed particles. Coagulation into the primary minimum will be prevented as long as the coulombic barrier $U(x_M)$ is substantially larger than the thermal energy $k_B T$. Victor and Hansen assumed, somewhat arbitrarily, that the suspension is charge-stabilized if

$$U(x_M) > 10 \tag{10}$$

Their results with respect to the phase diagram of such suspensions are rather insensitive to the precise value of the assumed potential barrier.

In order to calculate the thermodynamic properties of charge-stabilized colloidal particles, we make use of the perturbation theory developed by Gast et al.[15] based on a hard-sphere reference state. For that purpose the total potential is transformed into an effective hard-sphere part and an attractive perturbation.

2.2. Separation of the Potential. The total potential is attractive for large distances and repulsive for small distances. According to Victor and Hansen, this can be written as:

$$U(x) = U_0(x) + W(x) \tag{11}$$

while U_0 and W are

$$U_0(x) = \infty; \quad x < x_M$$

$$U_0(x) = U(x) - U(x_m); \quad x_M < x < x_m$$

$$U_0(x) = 0; \quad x > x_m \tag{12}$$

and

$$W(x) = U(x_m); \quad x < x_m$$

$$W(x) = U(x); \quad x > x_m \tag{13}$$

Here x_m is the distance at the secondary minimum, and

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x_M is the distance at the maximum of the repulsion. Note that the model of Victor and Hansen deviates from the approach of Weeks et al. in that $U_0(x < x_M)$ in eq 12 was set to infinity. This approach is justified because the high coulombic barrier will practically prevent particles from getting as close as x_M and coagulation is negligible, provided the condition of eq 10 is satisfied.

Summarizing, the system of colloidal particles is considered to interact by the purely repulsive potential $U_0(x)$ as the reference system, while the attractive component $W(x)$ will be looked upon as a perturbation.

2.3. Effective Hard-Sphere Diameter. Victor and Hansen accounted for the soft repulsive interaction $U_0(x)$ between particles with a diameter σ_0 by employing a hard-sphere interaction between particles with an effective diameter σ. For that purpose they calculated the Barker–Henderson parameter S,[17] defined by $S = \sigma/\sigma_0$. Its value can be derived from a functional Taylor expansion of the Helmholtz free energy in powers of the difference between the Boltzmann factors associated with the reference system (e^{-U_0}) and the equivalent hard-sphere fluid. The leading term in this expansion is

$$S = \frac{\sigma}{\sigma_0} = x_M + \int_{x_M}^{x_m}[1 - \exp(-U_0(x))]\,\mathrm{d}x \quad (14)$$

Because $S \geq 1$, the volume fraction of the particles in the equivalent hard-sphere system Φ will be larger than the true volume fraction Φ^0: $\Phi = S^3\Phi^0$ with

$$\Phi^0 = \frac{\pi\rho\sigma_0^{\,3}}{6} \quad (15)$$

where $\rho = N/V$ is the number density.

2.4. Perturbation Theory. The basic idea of the perturbation approach is to write the potential energy of a two-particle system as the sum of two terms:

$$U(x) = U_{HS}(x) + U_p(x) \quad (16)$$

in which $U_{HS}(x)$ is the potential energy of the unperturbed effective hard-sphere reference system:

$$U_{HS}(x) = \infty; \quad x < S$$

$$U_{HS}(x) = 0; \quad x \geq S \quad (17)$$

and where $U_p(x)$ is the attractive perturbation potential, which has the form:

$$U_p(x) = 0; \quad x < S$$

$$U_p(x) = U(x_m); \quad S \leq x < x_m$$

$$U_p(x) = W(x) = \frac{1}{T}\left(\frac{T_R\exp(-\kappa(x-1))}{x} - \frac{T_A h(x)}{12}\right);$$
$$x \geq x_m \quad (18)$$

The potential U_p is shown in Figure 1. Note that the attractive potential is kept constant in the region $S \leq x < x_m$.

According to Zwanzig[18] and Barker and Henderson,[17] the Helmholtz free energy of a thermodynamic system of particles with an attractive two-particle interaction potential can be written as a perturbation expansion in $1/k_B T$ (high-temperature expansion). Because the high-

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temperature case is equivalent to the hard-sphere system, the expansion of the Helmholtz free energy including an approximated second order term takes the form:

$$\frac{F}{Nk_B T} = \frac{F_{HS}}{Nk_B T} + \frac{\rho}{2}\int_0^\infty U_p(r)\,g_{HS}(r)\,4\pi r^2\,\mathrm{d}r -$$
$$\frac{\rho}{4}\left(\frac{\partial\rho}{\partial p}\right)_{HS} k_B T\int_0^\infty (U_p(r))^2 g_{HS}(r)\,4\pi r^2\,\mathrm{d}r \quad (19)$$

where F_{HS} is the free energy of the hard-sphere system, g_{HS} is the hard-sphere pair distribution function, and

$$\left(\frac{\partial\rho}{\partial p}\right)_{HS} k_B T = \frac{1}{Z_{HS} + \Phi\dfrac{\partial Z_{HS}}{\partial\Phi}} \quad (20)$$

while Z_{HS} is the hard-sphere equation of state. This equation is valid for both colloidal fluids and colloidal crystals.

The thermodynamic relationships between the Helmholtz free energy, the Gibbs free energy G, and the osmotic pressure p as used by us are given by

$$\frac{G}{k_B T} = \frac{\partial}{\partial\rho}\left(\frac{\rho F}{k_B T}\right)_{p,T} \quad (21)$$

and

$$\frac{p}{k_B T} = \frac{\rho G}{k_B T} - \frac{\rho F}{k_B T} \quad (22)$$

Note that the screened coulombic interaction potential is also a function of the density. The intersection of the curves of the Gibbs free energies of the colloidal fluid and the crystal phase determines the coexistence pressure and thus the coexistence densities of these phases.

3. Numerical Procedure

The volume fraction dependent Barker–Henderson parameter S is obtained by numerical integration of eq 14. For the numerical integration of the contributions to the Helmholtz free energy of the crystal and fluid phases, eq 19 was modified by rescaling r with the effective diameter σ. The equations of state and the correlation functions of the hard-sphere reference system for both the fluid and crystal phases were taken as summarized in ref 15.

The Gibbs free energies are obtained by numerical differentiation of eq 19 according to eq 21. The intersection of the fluid and the solid Gibbs free energies $G/(k_B T)$ as plotted versus the pressure determines the coexistence pressure p' of the transition.

Substituting the pressure p' in eq 22 gives the coexistence densities of the fluid and solid phases. Plotting the coexisting volume fractions for varying salt concentrations maps out the phase diagram. The independent parameter set of a given particle–solvent system consists of the surface potential, the particle diameter, the temperature, the dielectric constant of the solvent, the Hamaker constant, and the concentration of added electrolyte. These parameters are combined into three independent parameters that determine the phase diagram: T_A, T_R, and κ. To test the proper functioning of the computer program, one of the phase diagrams as calculated by Gast et al.[15] was evaluated. Their original result was reproduced well.

4. Results and Discussion

A number of phase diagrams have been calculated for electrically stabilized particles in water as a function of

Table 1

T_R/K	Ψ_0/mV	T_R/K	Ψ_0/mV
60 000	19.2	70 000	20.8
65 000	20	75 000	21.6

Table 2

T_A/K	$A/10^{-20}$ J	T_A/K	$A/10^{-20}$ J
1800	2.5	4000	5.5
3500	4.9	4500	6.2
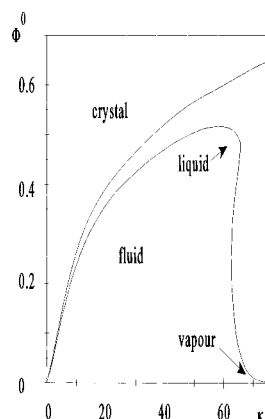
Figure 2. Phase diagram of electrically stabilized colloidal particles for the parameter values $T_R = 70\ 000$ K and $T_A = 4000$ K.

Figure 3. Phase diagram of electrically stabilized colloidal particles for the parameter values $T_R = 60\ 000$ K and $T_A = 1800$ K.

Figure 4. Phase diagram of electrically stabilized colloidal particles for the parameter values $T_R = 70\ 000$ K combined with various values of T_A.

the dimensionless Debye screening parameter $\kappa = \kappa_0\sigma_0$. In order to compare our formalism with the results of Victor and Hansen,[13] we have chosen identical values of the parameters T_A and T_R, as summarized in Tables 1 and 2. These tables also give the corresponding values of the surface potential and the Hamaker constant. We restricted our calculations to polystyrene particles with a diameter $\sigma_0 = 1\ \mu$m, dispersed in water ($\epsilon_r = 80.37$) surrounded by monovalent ions.

In Figure 2 the phase diagram of a latex suspension with $T_A = 4000$ K and $T_R = 70\ 000$ K is displayed. For low salt concentrations the fluid−crystal transition starts at the origin. The coexistence lines rise monotonically in the volume fraction with increasing the screening. The further increase of the screening lets the transition finally occur at almost the values of the fcc−fluid transition of hard spheres ($\Phi^0_{\text{fluid}} = 0.49$; $\Phi_{\text{solid}}^0 = 0.54$). This result is in agreement with the theoretical[16] and experimental[19−21] investigations. On further increasing the screening parameter κ, the fluid becomes unstable against flocculation. It decomposes into a liquid (flocculated structure) and a vapor phase. At $\Phi^0 = 0.47$ and $\kappa = 66$ we arrive at a triple point, where the liquid, gas, and solid (crystal) phases are in thermodynamic equilibrium. The spinodal decomposition into a flocculated liquid and a gas phase as predicted by us is shifted by nearly a factor of 2 to lower values of the dimensionless Debye screening length κ if compared with the results of Victor and Hansen on the basis of their first-order perturbation theory. This deviation can be devoted to the main differences between our approach and that of Victor and Hansen: (i) we acknowledge the occurrence of a crystal phase and (ii) our perturbation approach is of second order.

In Figure 3 the attractive and repulsive forces were decreased by applying the parameter set $T_A = 1800$ K and $T_R = 60\ 000$ K. Disregarding the crystal phase, the
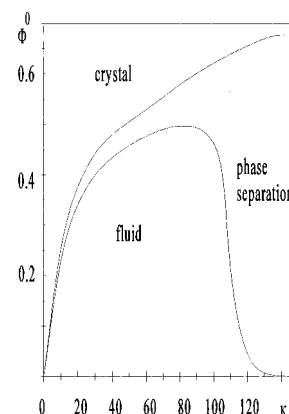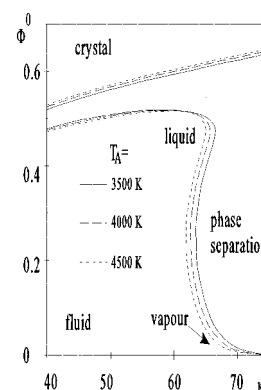
approach by Victor and Hansen expected for this parameter set a phase separation into a liquid and a gas phase. However, the liquid phase, made up of aggregated colloidal particles, disappears, and a phase separation takes place in a fluid and a crystal phase. Similar results have been obtained recently by Mederos and Navascues,[22] while they applied a density functional theory. In agreement with our investigations, they found that the liquid phase will only appear in the case of a fairly large attractive potential. Tejero et al.[23,24] systematically investigated colloidal suspensions with a double-Yukawa pair potential, and found that the liquid phase occurs only for long-range attractive forces and disappears for intermediate-range attractions.

In order to study the influence of the attractive and repulsive forces of the interaction potential on the phase diagram, the parameters T_A and T_R were varied. Figure 4 shows the dependence of the phase diagram on the attractive forces. Keeping $T_R = 70\ 000$ K, values of T_A of 4500, 4000, and 3500 K are investigated. On increasing the attraction, the critical point also shifts to slightly lower values of Φ^0 and κ. The triple point shifts to slightly larger values of Φ^0 and lower values of κ. On increasing the attraction, the fluid−crystal coexistence region broadens. This is in agreement with calculations of other investigators[15,24,25] with interaction potentials using a constant effective diameter and varying attractive potentials.

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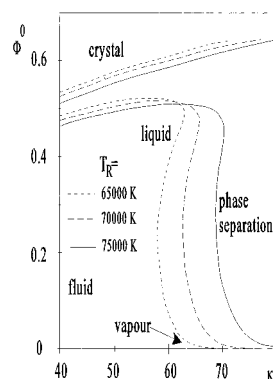(21) Takano, K.; Hachisu, S. *J. Colloid Interface Sci.* **1978**, *66*, 130.

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Figure 5. Phase diagram of electrically stabilized colloidal particles for the parameter values $T_A = 4000$ K combined with various values of T_R.

In Figure 5 the attractive interaction is kept constant at $T_A = 4000$ K, while values of T_R of 65 000, 70 000, and 75 000 K are investigated. On increasing the repulsion temperature T_R, the critical and triple points shift to larger values of κ and will coincide eventually. With increasing repulsion the liquid phase becomes less pronounced. The fluid−crystal coexistence lines shift to lower values of the volume fraction on increasing the repulsion, because the effective diameter of the colloidal particles is increased.

5. Conclusion

In order to calculate the phase diagram of electrically stabilized colloidal suspensions, we applied a second-order perturbation theory[15] in the attractive perturbation potential. For that purpose we approximated the two-particle interaction potential by a repulsive effective hard-sphere potential and an attractive perturbation potential. The numerical calculations showed that a flocculation transition into a colloidal fluid occurs accompanied by the appearance of a triple point, where fluid, crystal, and liquid phases are in equilibrium. Applying a higher order perturbation approach than that used by Victor and Hansen[13] and taking into account the possibility of the occurrence of a crystal phase lead to a substantial shift of the predicted critical point to lower values of the Debye screening parameter. For small attractive forces the liquid phase disappears.