

# Attractions in Sterically Stabilized Silica Dispersions

## I. Theory of Phase Separation

J. W. JANSEN, C. G. DE KRUIF, AND A. VRIJ

*Van't Hoff Laboratory for Physical and Colloid Chemistry, University of Utrecht,  
Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received September 2, 1985; accepted January 28, 1986

The presence of an attractive term in the interaction potential between colloidal particles will result in a phase separation (often a flocculation) on lowering the temperature. In this paper the attraction itself is assumed to increase on lowering the temperature in a manner similar to that observed in polymer solutions. A Van der Waals-like equation of state is introduced. For the osmotic pressure in this expression the Percus-Yevick (compressibility) relation is used. Phase diagrams are calculated by equating the thermodynamic potentials of solvent and colloidal particles in both phases. Both two and three component systems are dealt with. Polydispersity results in binodals which depend on initial concentration. © 1986 Academic Press, Inc.

### 1. INTRODUCTION

In order to study static and dynamic interactions in colloidal systems we synthesized at our laboratory a model colloid system of sterically stabilized silica particles dispersed in cyclohexane or chloroform. The interaction can be described as a so-called hard sphere potential as has been established experimentally by means of techniques such as light scattering (static and dynamic) and sedimentation (1–3). In dispersions encountered in industry, technology, and nature, the colloidal particles often exhibit attractions and/or soft repulsions. As a result their behavior at high concentrations is more complex than that of the hard sphere system. Our silica system is a very suitable basis for systematic research, because by changing the solvent or temperature we can vary the interaction potential from virtually hard sphere repulsive to moderately attractive.

The aim of this work is to investigate the effects of introducing a small attractive force between the particles. A thermodynamic theory is presented which predicts phase separation. The phase separation is a result of at-

tractions, which lead to a decrease in the free energy of the system when the dispersion separates into two phases: a dilute and a concentrated one. This separation can be compared with the condensation of a gas, in that colloidal particles are like (supra) gas molecules. In the case of colloidal particles the solvent is considered, at a given temperature, as a continuous background. The main difference between these two systems is that the interaction potential of gases does not change appreciably with temperature, whereas with sterically stabilized colloids the particle interactions are governed by the interactions of the stabilizing chains with the solvent and may be strongly temperature dependent.

The effects of attractions on the stability of dispersions have been studied by other investigators as well (4–8). Most of them have experimented with rather large particles (radius greater than 100 nm) stabilized with polymer chains. The resulting instability is often called flocculation. With such particles the change from strong repulsion to attraction in the dispersions occurs only within a very small temperature (or pressure) range. In other words:

the "liquid-gas" equilibrium can be measured only in an extremely short temperature range. The authors of Refs. (4-8) did not measure the equilibrium concentration in the dilute phase, but instead they measured the temperature at which on cooling (or heating) the dispersions become "unstable." Recently we reported on the phase separation of our silica particles dissolved in toluene (9). Independently Vincent and co-workers (10) have reported on the phase separation of particles similar to ours dissolved in short alkanes. They measured both upper and lower flocculation temperatures and constructed the phase diagram for temperature increase. The equilibrium of a microemulsion with its continuous phase has also been interpreted as a separation into a colloid-rich and a colloid-poor phase (11).

In our view the difference between flocculation and phase separation is only a gradual one. For example an attractive well of a few  $kT$  (depending on the width) gives a phase separation. When the temperature is lowered still further (in the case of instability on cooling) the attraction increases and nearly all collisions between two particles will result in an aggregate. This process can be called flocculation.

Our silica dispersions seem to be a suitable system for a study of phase separation. Because our particles have extremely short chains (octadecane) compared to polymers, the temperature range in which the interactions change from purely repulsive, via a "Boyle" temperature, to attractive extends over a few degrees.

In the following section the nature of the attractive forces between our silica particles is discussed. The phase diagram for a monodisperse colloidal system is shown in Section 3.1. The effects of polydispersity on phase separation are discussed in the last section. Experimental studies on phase separation induced by temperature variation is reported in the accompanying paper (Part II). Phase separation in colloidal silica dispersions brought about by adding nonadsorbing polymer molecules has been reported in an earlier article (12).

## 2. ORIGIN OF THE ATTRACTION

Phase separation of a colloidal system of particles into a dilute and a concentrated fluid phase will take place only if there is an attractive part in the interaction potential. (The so-called Kirkwood-Alder transition for hard spheres is a separation into an ordered and a disordered phase and is of a different kind.) Furthermore the attraction must be strong enough to exceed the entropic part in the (free) energy of mixing.

The apparent chain density on the particle surface of our silica spheres is very high (0.15-0.25 nm<sup>2</sup> per chain (13), which is equal or denser than the closest packing of aliphatic chains). Therefore the stabilizing layers of octadecyl chains can hardly interpenetrate. Because of this, the interaction potential between sterically stabilized silica spheres in apolar media will be steeply repulsive and can be modeled as a hard sphere repulsion. When interparticle distances are greater than this hard sphere diameter the calculation of the interaction potential should take all possible interactions into account. These interactions are the long-range London-Van der Waals attraction between the cores of the particles and the local interaction between the overlapping layers of the particles (this interaction can be repulsive or attractive). Because the particles are dissolved in apolar solvents possible charge interactions are considered to be ineffective (14).

The London-Van der Waals attraction between the particles can be calculated if the dielectric constants of both particle and solvent are known as a function of wavelength (15). The attractive potential in the Hamaker approximation is

$$V(r) = -\frac{A_H}{12} \left\{ \frac{4}{S^2 - 4} + \frac{4}{S^2} + 2 \ln \left( \frac{S^2 - 4}{S^2} \right) \right\} \quad [1]$$

where  $S$  is the ratio of the distance  $r$  between the core centers and the radius of the particle cores,  $A_H$  is the Hamaker constant. Because we do not know the exact structure of the silica core, which is not pure silica but probably

contains some silanol groups and some ethanol as well, we cannot calculate the Hamaker constant properly. For an estimate of the Hamaker constant we refer to the Appendix. When particles with a radius of 50 nm are dissolved in benzene the largest attractive potential possible is  $0.4kT$  (with  $S_0 = 2.06$ ), which would be too small to induce phase separation at normal temperatures. This is in contrast to what has been observed (16). Furthermore a Van der Waals attraction is hardly temperature dependent whereas the experiments show the contrary. The fact that colloidal crystals form upon sedimentation of particles with a radius of 150 nm (17) demonstrates also that in cyclohexane the Van der Waals attraction must be small. We think that such crystals will not form if an appreciable attraction is present.

It is difficult to calculate the interactions of the stabilizing chains. An attempt has been made by Lemaire *et al.* (18). They calculated the enthalpic part from the Lennard-Jones interaction potential between the  $\text{CH}_2$  groups of the chains and solvent. The entropic part is split into two: the first derives from the volume restriction of the chains when they try to overlap the hard spheres (repulsive) and the second derives from the mixing entropy of chains and solvent. The resulting interaction potential appears to be very sensitive to small differences in the molar volume of the solvent adsorbed in the layer and in the reference pure phase.

Because of these uncertainties we model the interaction potential as a square well with a width equal to a small part of the chain length (e.g., 0.5 nm) and a depth  $\epsilon$  which depends on the temperature  $T$ . This depth is chosen, as with polymers, to be

$$\epsilon = L \left( \frac{\theta}{T} - 1 \right) kT; (T \leq \theta) \quad [2]$$

where  $\theta$  is the theta temperature of the chain-solvent pair and  $L$  a factor proportional to the overlapping volume of the chains (this is also concluded in Ref. (18)). At a fixed interpenetration depth (= width of the well =  $\lambda$ ) this

volume is proportional to the diameter  $\sigma$  of the particles ( $V = (\pi/4)\lambda^2\sigma$ ). Different interaction potentials can be chosen but the results will be similar.

Using this interaction potential the osmotic pressure  $\Pi$  can be calculated as a function of the particle number density  $\rho$  (concentration) to the power of 2. For weak long-range attractions the attractive contribution to  $\Pi$  remains proportional to  $\rho^2$  even at high  $\rho$ . The total osmotic pressure is then given by the sum of the hard sphere contribution  $\Pi_{\text{HS}}$  and this attractive term (cf. the Van der Waals equation for imperfect gases). For short-range attractions the expression for  $\Pi$  will be more complicated since the attractions will also contribute to terms in the concentration higher than the second power. In this theoretical study we will assume an equation of the Van der Waals type, with an attractive term of the form  $\alpha\rho^2$

$$\Pi = \Pi_{\text{HS}} - \alpha\rho^2. \quad [3]$$

For small concentrations the osmotic pressure is given by

$$\frac{\Pi}{kT} = \rho(1 + B_2\rho + \dots) \quad [4]$$

with

$$B_2 = 2\pi \int_0^\infty (1 - e^{-V(r)/kT}) r^2 dr. \quad [5]$$

$V(r)$  is the interaction potential,  $r$  the distance between the centers of the particles, and  $k$  the Boltzmann constant ( $kT$  the thermal energy). For a square well the repulsive (hard sphere) part of the second virial coefficient  $B_2$  is

$$B_2(\text{rep}) = 2\pi \int_0^\sigma r^2 dr = \frac{2\pi}{3} \sigma^3 \quad [6]$$

where  $\sigma$  is the hard sphere diameter. The attractive part of  $B_2$  is given as

$$B_2(\text{att}) = 2\pi \int_\sigma^{\sigma+\lambda} (1 - e^{\tilde{e}}) r^2 dr \approx 2\pi \sigma^2 \lambda (1 - e^{\tilde{e}}) \quad [7]$$

where the last equality is valid when  $\lambda$  is small

compared to  $\sigma$ . For small attractions,  $\epsilon$  is small and  $B_2(\text{att})$  is given by

$$B_2(\text{att}) = -2\pi\sigma^2\lambda\tilde{\epsilon}; \tilde{\epsilon} = \epsilon/kT. \quad [8]$$

Rewriting the osmotic pressure (Eq. [3]) in dimensionless quantities we obtain

$$\frac{\Pi V_{\text{HS}}}{kT} = \frac{\Pi_{\text{HS}} V_{\text{HS}}}{kT} - \gamma\phi^2 \quad [9]$$

where  $V_{\text{HS}}$  is the volume of the hard sphere, and  $\phi$  the volume fraction  $\phi = \rho V_{\text{HS}}$  and  $\gamma = \alpha/(kTV_{\text{HS}})$ .  $\gamma$  becomes when  $\epsilon$  is small:

$$\gamma = 12\frac{\lambda}{\sigma}\epsilon = 12\frac{\lambda}{\sigma}L\left(\frac{\theta}{T} - 1\right)kT = A\left(\frac{\theta}{T} - 1\right). \quad [10]$$

Although this equality is in fact only consistent if  $\epsilon$  is small and  $\lambda$  is large, we use the relation between  $\gamma$  and  $T$  to describe the attraction.

### 3. PHASE SEPARATION

#### 3.1. Phase Separation in Monodisperse Systems

The condition for equilibrium is that the thermodynamic (chemical) potentials of all components present are constant in all phases. In the case of a monodisperse colloidal system the components are solvent [1] and colloidal particles [2]. For the thermodynamic potential of the solvent in this system one can write (19)

$$\mu_1 = \mu_1^0 - \Pi\bar{V}_1 \quad [11]$$

where  $\mu_1^0$  is the thermodynamic potential of the pure solvent,  $\bar{V}_1$  the partial molar volume of the solvent (assumed to be constant), and  $\Pi$  the osmotic pressure. It can be seen from Eq. [11] that the condition  $\mu_1^\alpha = \mu_1^\beta$  is equivalent to the condition that the osmotic pressures are the same  $\Pi^\alpha = \Pi^\beta$ . For the osmotic pressure we use Eq. [9]. Substituting for  $\Pi_{\text{HS}}$  the Percus-Yevick (compressibility) expression one obtains a function of the volume fraction  $\phi$  of the hard spheres:

$$\frac{\Pi V_{\text{HS}}}{kT} = \phi \frac{1 + \phi + \phi^2}{(1 - \phi)^3} - \gamma\phi^2. \quad [12]$$

The thermodynamic potential  $\mu_2$  (at constant  $\mu_1$ ) of the colloidal particles can be derived from Eq. [12] using the relation

$$\left(\frac{\partial\Pi}{\partial\phi}\right)_{T,\mu_1} = \frac{\phi}{V_{\text{HS}}} \left(\frac{\partial\mu_2}{\partial\phi}\right)_{T,\mu_1}. \quad [13]$$

One finds

$$\frac{(\mu_2)_{\mu_1}}{kT} = \frac{(\mu_2^0)_{\mu_1}}{kT} + \ln \frac{\phi}{1 - \phi} + \frac{\frac{5}{2} - \frac{1}{2}\phi + \phi^2}{(1 - \phi)^3} - 2\gamma\phi. \quad [14]$$

The thermodynamic potential  $\mu_2$  at constant pressure can also be found (19) using

$$\left(\frac{\partial\Pi}{\partial\phi}\right)_{T,\mu_1} = V_{\text{HS}}^{-1} \frac{\phi}{1 - \phi} \left(\frac{\partial\mu_2}{\partial\phi}\right)_{T,P} \quad [15]$$

and one gets

$$\frac{(\mu_2)_P}{kT} = \frac{(\mu_2^0)_P}{kT} + \ln \frac{\phi}{1 - \phi} + \frac{(3/2) + 3\phi}{(1 - \phi)^2} - 2\gamma\phi + \gamma\phi^2. \quad [16]$$

Equations [12] and [14] (or [12] and [16]) apply to both phases and equating the osmotic pressure and the thermodynamic potential in both phases gives two equations with two unknown volume fractions  $\phi'$  (dilute phase) and  $\phi''$  (concentrated phase). The same results are obtained using Eq. [14] or [16]. It is obvious that this will be the case, because the integrated difference between Eqs. [14] and [16] is proportional to the osmotic pressure.

We have calculated  $\phi'$  and  $\phi''$  as a function of  $\gamma$  ( $=A(\theta/T - 1)$ ). The results are shown in Fig. 1.

The spinodal (i.e., the curve where the stability changes from metastable to unstable) is given by

$$\frac{V_{\text{HS}}}{kT} \left(\frac{\partial\Pi}{\partial\phi}\right)_{T,\mu_1} = \frac{(1 + 2\phi)^2}{(1 - \phi)^4} - 2\gamma\phi = 0 \quad [17]$$

and is also drawn in Fig. 1. Finally the critical point is obtained by solving  $\partial\Pi/\partial\phi = 0$  and  $\partial^2\Pi/\partial\phi^2 = 0$  simultaneously. One finds  $\phi_{\text{crit}}$

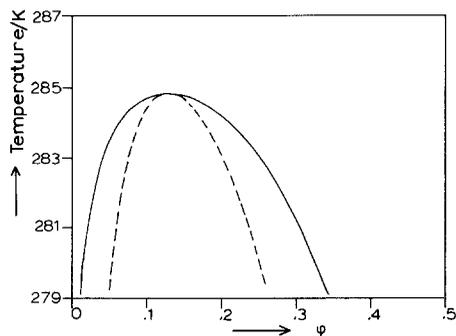


FIG. 1. Binodal (—) and spinodal (---) of a mono-disperse system.  $A = 200$  and  $\theta = 300$  K.

$= (\sqrt{73} - 7)/12 = 0.1287$  and  $\gamma_{crit} = 10.66$  (in Fig. 1,  $T_{crit} = 284.82$  K).

### 3.2. Phase Separation in Polydisperse Systems

In general, colloidal particles are not mono-disperse; instead they vary in size and vary in their interaction parameters and in internal properties (such as refractive index). Therefore experimentally one always measures a kind of average property. It is also possible that in a polydisperse system different phenomena arise, which did not exist in the monodisperse case.

In phase separation, polydispersity can mean polydispersity not only in the size of the particles but also in the attraction parameter  $\gamma$ . In principle these two aspects can be varied independently, but they are probably related (as is shown in Section 2). We again need to find the osmotic pressure and the thermodynamic potential of all kinds of particles.

The osmotic pressure of a polydisperse hard sphere system has been given by Hiroike *et al.* (20) (again using the Percus–Yevick compressibility approach). Together with the attractive part which is given by

$$\Pi(\text{att}) = - \sum_{i,j} \alpha_{ij} \rho_i \rho_j \quad [18]$$

we obtain for the total osmotic pressure (written in dimensionless form)

$$\Pi \frac{\pi}{6kT} = \eta_0 + 3\eta_1\eta_2 + 3\eta_2^3 - \sum_{i,j} \gamma_{ij} \phi_i \phi_j (\sigma_i \sigma_j)^{-3/2}. \quad [19]$$

Here  $\eta_k = \xi_k / (1 - \xi_3)$  and  $\xi_k = (\pi/6) \sum_i \rho_i \sigma_i^k = \sum_i \phi_i \sigma_i^{k-3}$ . The cross term  $\gamma_{ij}$  ( $i \neq j$ ) is written as the geometrical mean  $(\gamma_{ii} \gamma_{jj})^{1/2}$  but different choices are possible. The thermodynamic potential of particle  $i$  at constant  $\mu_i$  in a polydisperse hard sphere system is given in Ref. (21). Using Eq. [13] the attractive part of  $\mu_i$  is found as

$$\mu_i(\text{att}) = -2 \sum_j \alpha_{ij} \rho_j. \quad [20]$$

Rewriting the total thermodynamic potential  $\mu_i$  of spheres  $i$  in dimensionless quantities one obtains

$$\begin{aligned} \frac{\mu_i}{kT} = & \frac{\mu_i^0}{kT} + \ln \frac{\phi_i}{1 - \xi_3} + \sigma_i^3 \eta_0 + 3\sigma_i^2 \eta_1 + 3\sigma_i \eta_2 \\ & + 3\sigma_i^2 \eta_1 \eta_2 + \frac{9}{2} \sigma_i^2 \eta_2^2 + 3\sigma_i^3 \eta_2^3 - 2 \sum_j \gamma_{ij} \phi_j \left( \frac{\sigma_i}{\sigma_j} \right)^{3/2}. \end{aligned} \quad [21]$$

A further relation needed is the conservation of mass, i.e., the amount of particles  $i$  before and after separation is constant:

$$\phi_{i,t}(V' + V'') = \phi'_i V' + \phi''_i V''. \quad [22]$$

This is rewritten as

$$R = \frac{\phi_{i,t} - \phi'_i}{\phi''_i - \phi_{i,t}} \quad [23]$$

where  $R$  is the ratio of the volumes of the concentrated phase ( $V''$ ) and of the dilute phase ( $V'$ ) and  $\phi_{i,t}$  the initial volume fraction (before phase separation) of particles  $i$ . We now have  $2n + 1$  relations (i.e., Eq. [19] and  $n$  times Eqs. [21] and [23]) describing the phase equilibrium and with these we can in principle calculate all variables  $\phi'_i$ ,  $\phi''_i$ , and  $R$  at given volume fractions  $\phi_{i,t}$  and given system parameters  $\gamma_i$  and  $\sigma_i$ . From Eq. [23] it can be seen that the solutions of these equations must depend on the initial volume fractions  $\phi_{i,t}$ . This is in contrast to the monodisperse case where  $\phi''$  and  $\phi'$  are independent of  $\phi_t$ .

We have calculated some phase diagrams for a three component system (i.e., solvent and two kinds of particles). Table I lists the various sets of system parameters for which phase dia-

TABLE I  
Systems for Which Phase Diagrams  
Have Been Calculated

System number	Figure	$A_2/A_3$	$d_2/d_3$	$\phi_2/\phi_3$ (Initial)
1	2	0.8	1	1
2	3	0.6	1	1
3	4	0.8	0.8	1
4	5	0.6	0.6	1
5	6	0.6	0.6	0.216
6	7	$A_2 = 0$ $A_3 = 200$	1	1

Note. Except for system 6 the geometrical mean of  $A_2$  and  $A_3$  is taken to be 200.

grams have been calculated. The corresponding diagrams are shown in Figs. 2–7. System 6 consists of a mixture of hard spheres ( $A_2 = 0$ ) and attractive particles. In these figures the sum of the volume fractions of both particles in each phase is plotted, because this will be the experimentally obtained quantity. In the calculations the initial volume fractions of components 2 and 3 are chosen equal for all the systems, except for system 5 where equal number concentrations are chosen, so the ratio of the volume fractions is equal to the third power of the ratio of the diameters.

The calculations show that fractionation takes place and that this fractionation depends on the overall volume fraction and the tem-

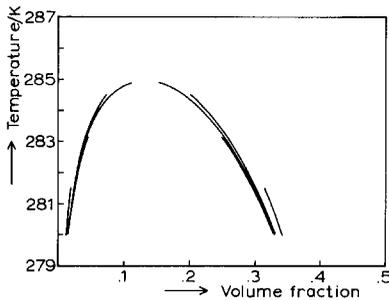


FIG. 2. Phase diagram for two particle system 1. Overall volume fractions 0.02, 0.08, 0.15, and 0.25 (high initial volume fractions are on the inside of the set of curves). Cloud-point curve and shadow curve are not plotted for clarity.

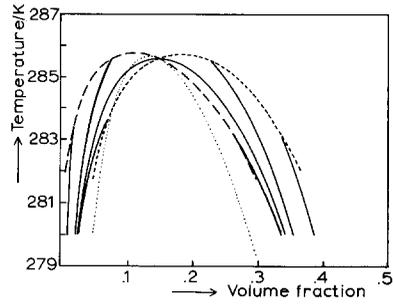


FIG. 3. Phase diagram for two particle system 2. Overall volume fractions 0.02, 0.08, 0.15 and 0.25 (high initial volume fractions are on the inside of the set of curves). (---) Cloud-point curve. (---) Shadow curve. (···) Spinodal curve.

perature. Fractionation is defined by the ratio of the volume fractions of particles 2 and 3, in the dilute phase. In the concentrated phase this ratio does not differ much from the original ratio (except in the case of volume fractions lower than about 0.05, where it is lower). For system 4 the fractionation is given as a function of  $T$  and  $\phi$  in Fig. 8. At low temperature the fractionation is greater than at high temperature. The fractionation does not depend very much on overall volume fraction, except for low overall volume fractions where it is smaller. When both particles have equal attraction parameters the smaller particles accumulate in the dilute phase. In this case the volume fraction of both phases do not depend much on overall volume fraction.

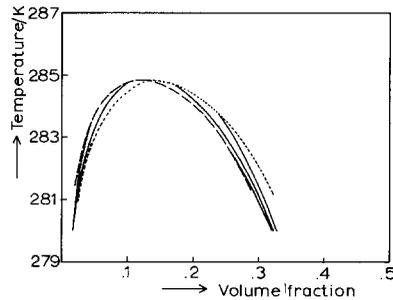


FIG. 4. Phase diagram for two particle system 3. Overall volume fractions 0.05, 0.10, and 0.25 (high initial volume fractions are on the inside of the set of curves). (---) Cloud-point curve. (---) Shadow curve.

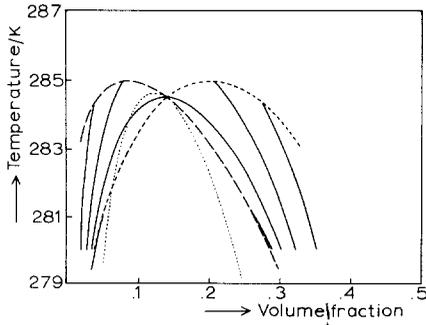


FIG. 5. Phase diagram for two particle system 4. Overall volume fractions 0.04, 0.08, 0.15, and 0.25 (high initial volume fractions are on the inside of the set of curves). (---) Cloud-point curve. (-·-) Shadow curve. (···) Spinodal curve.

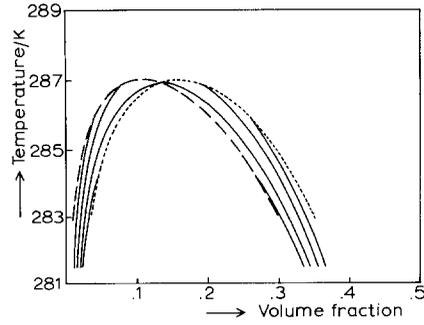


FIG. 6. Phase diagram for two particle system 5. Overall volume fractions 0.04, 0.08, 0.15, and 0.25 (high initial volume fractions are on the inside of the set of curves). (---) Cloud-point curve. (-·-) Shadow curve.

The spinodal for a polydisperse system is obtained from the condition that the amount of scattered light (at zero angle) reaches infinity. This is the case when the determinant  $\Delta$  is zero (22). For two kinds of particles  $\Delta$  is equal to (with constant  $\mu$ , and  $T$ )

$$\Delta = \left| \left( \frac{\partial \mu_i}{\partial \rho_j} \right) \right| = 0 \quad [24]$$

with  $i$  and  $j = 2, 3$ .  $(\partial \mu_i / \partial \rho_j)_\rho$  for hard spheres can be found in Ref. (23). When we add the attractive part  $(\partial \mu_i / \partial \phi_j)_\phi$  is written as

$$\begin{aligned} \left( \frac{\sigma_j}{\sigma_i} \right)^{3/2} \frac{1}{kT} \left( \frac{\partial \mu_i}{\partial \phi_j} \right)_\phi &= \frac{\delta_{ij}}{(\phi_i \phi_j)^{1/2}} + \frac{1}{1 - \xi_3} \left\{ \left( \frac{\sigma_i}{\sigma_j} \right)^3 \right. \\ &+ \left( \frac{\sigma_j}{\sigma_i} \right)^3 + (\sigma_i \sigma_j)^{3/2} \eta_0 + 3(\sigma_i \sigma_j)^{-1/2} [\sigma_i(1 + \sigma_i \eta_2) \\ &\times (1 + \sigma_j^2 \eta_1) + \sigma_j(1 + \sigma_j \eta_2)(1 + \sigma_i^2 \eta_1)] \\ &\left. + 9(\sigma_i \sigma_j)^{1/2} \eta_2(1 + \sigma_i \eta_2)(1 + \sigma_j \eta_2) \right\} - 2\gamma_{ij}. \quad [25] \end{aligned}$$

For systems 2 and 4 in Table I the spinodal is calculated and plotted in Figs. 3 and 5.

4. DISCUSSION

We have derived a set of equations which describes the phase separation of a colloidal dispersion into two phases each with a different concentration. As in the Van der Waals theory

pressure is divided into two terms. The first is a repulsive one of the hard sphere type, characterized by the hard sphere diameter only. The second term is an attractive one, the attractions being described by the parameter  $\gamma$ . This parameter is written as  $\gamma = A(\theta/T - 1)$ , where  $A$  is a measure of the overlap volume of interaction and depends on the chain density and solvent-chain pair.  $(\theta/T - 1)$  is a measure of the free energy per unit volume of overlap and depends on the chain type and solvent only. Attraction occurs when  $T < \theta$  and will lead to phase separation when the temperature is decreased still further. For a monodisperse colloidal system the critical temperature is given by  $T_c = \theta/(1 + \gamma_c/A)$ ;  $\gamma_c = 10.6$ .

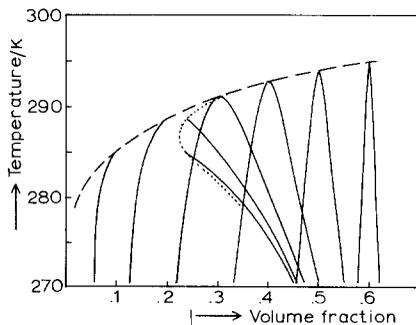


FIG. 7. Phase diagram for two particle system 6. Overall volume fractions 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 (from left to right). (---) Cloud-point curve. (-·-) Shadow curve.

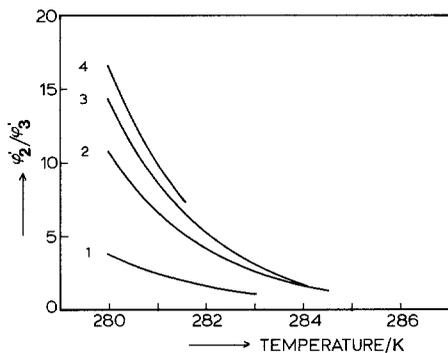


FIG. 8. Fractionation in the dilute phase of two particle 4 system as a function of temperature and initial volume fraction. (1)  $\phi_i = 0.04$ , (2)  $\phi_i = 0.08$ , (3)  $\phi_i = 0.15$ , and (4)  $\phi_i = 0.25$ .

With large particles the volume of overlap will be large and therefore  $A$  will be large.  $T_c$  will then be close to  $\theta$ . Of course the London-Van der Waals attraction will then become larger too, leading to an increase in  $T_c$  (possibly higher than  $\theta$ ).

The temperature range in which phase separation can be studied also depends on the value of  $A$  (Fig. 9). Therefore with large particles (and long chains) the concentration of the dilute phase can be measured only within a very short temperature range. In other words the temperature at which phase separation occurs is slightly dependent on concentration. This is found experimentally also (4-9). With smaller values of  $A$  one will observe a stronger dependence on volume fraction (Fig. 9). The values of  $A$  and  $\theta$  we used were chosen so as to obtain reasonable agreement with experiments (16).

In calculating the effects of polydispersity on phase separation we have taken only two kinds of particles into consideration, but the results will be similar when more particles (or in the extreme case a continuous distribution) are considered, but then the calculations will be more complicated.

To observe these effects, the polydispersity in attraction parameter  $\gamma$  must be greater than about 15% (i.e.,  $A_2/A_3 < 0.8$ ). The attraction parameter depends not only on size but also on the roughness of the particle surface.

Therefore polydispersity can play a role even with rather monodisperse (in size) systems.

The resulting binodals as a function of the initial volume fraction do not coincide. This phenomenon is also encountered in the phase separation of polydisperse polymers (24, 25). Furthermore it can be seen that the phase lines for the different overall volume fractions are not continuous, except those for the critical volume fraction. The phase lines end in two curves: the so-called cloud-point curve (CPC) and the shadow curve (SC). The meaning of these curves can be explained as follows. When a dispersion of a given volume fraction is cooled separation begins at a certain temperature. This temperature is the cloud-point temperature, so called because the turbidity increases sharply as a new phase starts to appear. This temperature as a function of the volume fraction of the initial dispersion is the cloud-point curve (CPC). At the cloud-point temperature a very small amount (zero volume) of another phase separates out. This phase has a well-defined particle volume fraction. The cloud-point temperature plotted against this volume fraction results in the shadow curve (SC). The SC is also called the coexistence curve of the CPC.

The CPC and the SC can also be interpreted as the limit of (physical) realistic solutions of Eqs. [19], [21], and [23]. Numerically the lines do not end at the CPC and the SC, but beyond these curves one of the volumes of the coexisting phases is negative ( $R$  is negative). This

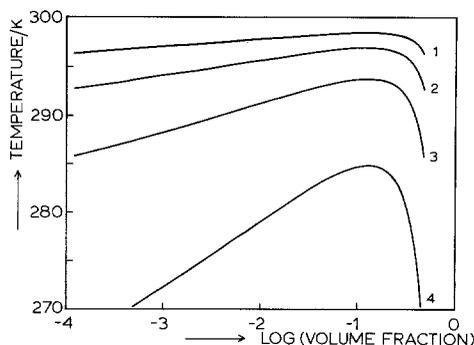


FIG. 9. Phase diagrams of monodisperse systems for various values of attraction parameter  $A$ . (1)  $A = 2000$ , (2)  $A = 1000$ , (3)  $A = 500$ , and (4)  $A = 200$ .  $\theta = 300$  K.

means that both phases (numerically) will have a volume fraction which is either smaller or greater than the original dispersion. This is clearly not possible. For a somewhat different approach to the three component phase diagrams we refer to Koningsveld *et al.* (24).

The SC can be found from phase separation experiments by extrapolating the volume fraction of the phase that separates to zero volume. This means for initial volume fractions lower than the critical volume fraction an extrapolation of the volume fraction of the concentrated phase  $\phi''$  to  $R$  is zero ( $R$  is the ratio of volumes of concentrated and dilute phase) and for initial volume fractions higher than the critical one an extrapolation of the volume fraction of the dilute phase  $\phi'$  to  $1/R$  is zero. These extrapolations need not be straight lines. Our calculations show that close to the critical volume fraction these extrapolations will result in the CPC only if temperatures are taken which are very close (0.001 K) to the cloud-point temperature.

The CPC and the SC intersect at the critical point (the two phases formed are identical). In this way the critical volume fraction can be found. The critical point can also be found analytically, but the formulas are quite complex and therefore not reproduced here.

It is important to note that with polydisperse systems the maximum of the CPC is not the same as the critical point.

## 5. CONCLUSIONS

The theory presented in this paper is derived using a Van der Waals-like approach to the interaction. With short-range attractions and when the attraction is large this approach does not give exact results. However, we think that even then the results are reasonably accurate. A better expression for the osmotic pressure of attractive particles may be found in further research.

The interaction between stabilizing polymer layers is described by polymer theory. Experiments are being performed with polymer (PIB) stabilized silica particles and the results of phase separation experiments will be published. The interaction between two overlap-

ping layers of short chains is also modeled using polymer theory. It is not certain whether this modeling is correct. This interaction therefore has to be studied in more detail. Phase separation experiments using silica particles coated with short (octadecane) chains will be described in a future article (16).

## APPENDIX

### AN ESTIMATE OF THE HAMAKER CONSTANT OF SILICA IN ORGANIC SOLVENTS

The Hamaker constant for two bodies of material 1 immersed in a liquid 2 can be obtained using (26):

$$A_{121} = \frac{3h}{8\pi^2} \int_0^\infty \left( \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^2 d\xi \quad [A1]$$

where  $\epsilon_\alpha = \epsilon_\alpha(i\xi)$  is the dielectric constant of material  $\alpha$  at imaginary frequency  $\xi$ ,  $h$  is the Planck constant. This is the Hamaker constant to be used in Eq. [1]. If both materials have only one absorption frequency,  $\epsilon_\alpha$  is given by

$$\epsilon_\alpha(i\xi) = 1 + \frac{\epsilon_{\alpha 0} - 1}{1 + (\xi/\nu_\alpha)^2} \quad [A2]$$

where  $\nu_\alpha$  is the absorption frequency and  $\epsilon_{\alpha 0}$  the static dielectric constant. Substitution of Eq. [A2] in [A1] results in (27)

$$A_{121} = \frac{3h(\nu_1\nu_2)^{1/2}}{64\bar{\epsilon}_0^{7/4}} \times \frac{X^2\bar{\epsilon}_0 + 2X\bar{\epsilon}_0^{1/2}\Delta\epsilon_0 + (\Delta\epsilon_0)^2(3 + 2Y)}{\{(Y - \sqrt{Y^2 - 1})^{1/2} + (Y + \sqrt{Y^2 - 1})^{1/2}\}^3} \quad [A3]$$

where

$$\bar{\epsilon}_0 = \frac{1}{2}(\epsilon_{10} + \epsilon_{20})$$

$$\Delta\epsilon_0 = \epsilon_{10} - \epsilon_{20}$$

$$X = \frac{\nu_1}{\nu_2}(\epsilon_{10} - 1) - \frac{\nu_2}{\nu_1}(\epsilon_{20} - 1)$$

$$Y = \frac{1}{4\bar{\epsilon}_0^{1/2}} \left\{ \frac{\nu_1}{\nu_2}(\epsilon_{10} + 1) + \frac{\nu_2}{\nu_1}(\epsilon_{20} + 1) \right\}.$$

The absorption frequency of silica can be found by extrapolation to zero of  $(n^2 + 2)/(n^2 - 1)$  (i.e., proportional to the inverse polarizability) as a function of the frequency to the

power of 2 (28). Unfortunately the refractive index  $n$  of the silica particles is only known in a short frequency interval. Therefore we use for  $\nu_1$  a value of fused silica (28)  $\nu_1 = 37.8 \times 10^{14} \text{ s}^{-1}$ . For  $\epsilon_{10}$  we use the square of the refractive index of our silica at zero frequency  $\epsilon_{10} = 2.04$ . In Table II values for  $\nu_2$  and  $\epsilon_{20}$  are listed for some organic solvents (28) together with the calculated Hamaker constant. These Hamaker constants are sensitive to uncertainties in  $\nu_1$ , so these values give a rough estimate only. In these calculations it was assumed that the layer around the particles has the same properties as the solvent.

The attractive term in Eq. [3] can be calculated by performing an integration over  $V(r)$  (29). The attractive parameter  $\gamma$  is then given as

$$\gamma = \frac{1}{4} A_{121} \frac{1}{kT} \left[ \frac{2}{3} \ln \frac{S_0 - 2}{S_0 + 2} - \frac{4}{3} S_0 - \frac{1}{3} S_0^3 \ln \frac{S_0^2 - 4}{S_0^2} \right] \quad [\text{A4}]$$

where  $S_0$  is the ratio of the hard sphere diameter and the radius of the silica core. The difference between the radius of the hard sphere and the silica core is about the chain length of the stabilizing chains, since the silica particle is densely covered with these chains. As an example of this calculation we take particles with a (core) radius of 50 nm and a chain length of about 1.5 nm, so  $S_0 = 2.06$ . With the Hamaker constant of silica in benzene we find  $\gamma = 0.42$ , which is far less than the critical  $\gamma$  ( $\approx 10.6$ ).

TABLE II

Values of  $\epsilon_{20}$  and  $\nu_2$  for Some Solvents (Ref. (26))  
Used for Calculating  $A_h$

Solvent	$\epsilon_{20}$	$\nu_2$ ( $10^{14} \text{ s}^{-1}$ )	$A_h$ ( $kT$ )
Cyclohexane	2.015	33.9	0.15
Benzene	2.274	25.4	0.60
<i>n</i> -Hexane	1.882	33.9	0.57
<i>n</i> -Octane	1.942	34.0	0.33
<i>n</i> -Decane	1.985	33.9	0.21

Note. For particles,  $\epsilon_{10} = 2.041$  and  $\nu_1 = 37.8 \times 10^{14} \text{ s}^{-1}$  is used.

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