Phase behavior of colloidal rod-sphere mixtures

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We investigate the depletion induced phase separation in mixed suspensions of colloidal spheres with diameter σ and colloidal rods with length L and diameter D. Using an extension of the free volume method developed by one of us [H.N.W. Lekkerkerker and A. Stroobants, Physica A **195**, 387 (1993)], we calculate the phase diagrams for $L \leq \sigma$ and various L/D ratios. For long thin rods, the volume fractions of rods needed to induce phase separation scale as $D^2/L\sigma$. Good agreement with recent experimental results is obtained. © *1999 American Institute of Physics.* [S0021-9606(99)50333-4]

I. INTRODUCTION

In the last 25 years a large interest has developed for phase separation processes induced by entropic interactions. Already in 1954, Asakura and Oosawa[1] showed that the addition of nonadsorbing polymer to a dispersion of colloidal particles will lead to an effective attractive interaction. This result was independently recovered and further elaborated by Vrij[2] in 1976. The attractive interaction, which is called depletion interaction, is the origin of the rich phase behavior displayed by colloid–polymer mixtures.

The depletion interaction can be explained in terms of purely repulsive interactions between the polymers and the colloidal particles. Each colloidal particle is surrounded by a shell with a thickness of the order of the radius of gyration of a polymer molecule in which the center of the polymer cannot penetrate. This excluded region is called the depletion zone. When two colloidal particles approach each other such that their respective depletion zones start to overlap, the available volume for the polymer increases. This extra volume in turn causes the total entropy to increase and the free energy to decrease. This in turn implies that the colloidal particles experience an effective attraction.

In the last two decades significant progress has been made in understanding the phase behavior of colloid–polymer mixtures. This progress has been achieved by extensive experimental work on a variety of (model) systems,[3–9] the development of theoretical concepts and tools[10,11] and computer simulations.[12,13] For various systems, the phase diagrams have now been determined experimentally, showing colloidal gas–liquid, colloidal gas–solid and colloidal fluid–solid phase equilibria. At the same time quenches deeper in the two phase region of the phase diagram show a transition of equilibrium states to nonequilibrium states.[14,15] This is illustrative for the rich phase behavior displayed by colloid–polymer mixtures.

The depletion interaction mechanism is not limited to colloid–polymer mixtures. Using the same entropy argument as for colloid–polymer mixtures, mixtures of different size and/or shape are expected to exhibit similar phase behavior. In case of binary mixtures of large and small colloidal hard spheres, the depletion potential is to lowest order in the density given by[1,16]

$$W(h) = -\frac{3}{2} k_B T \phi^R \frac{\sigma_l}{\sigma_s} \left(1 - \frac{h}{\sigma_s}\right)^2. \qquad (1)$$

Here, $k_B T$ is the thermal energy, ϕ^R is the volume fraction of the small spheres in a reservoir in osmotic equilibrium with the mixture of large and small colloidal spheres, σ_l the diameter of the large spheres, σ_s the diameter of the small spheres, and h the distance between the surfaces of the two large spheres. Guided by simulation results,[17] which indicate that the critical temperature for narrow ranged potentials corresponds to $k_B T_c / \epsilon \simeq 0.4$, we estimate that an attraction between 2 and 3 $k_B T$ will lead to phase separation. Equation (1) then implies that for a size ratio $\sigma_l / \sigma_s = 10$ the depletion interaction will cause phase separation when the volume fraction of small spheres is about 17%. Indeed, in mixtures of large and small spheres, phase transitions have been predicted[18,19] observed experimentally[20–23] and by simulations[24–26] around this volume fraction of small spheres.

An even more interesting colloidal mixture from a depletion interaction point of view is that of colloidal spheres and colloidal rods. This was already recognized by Asakura and Oosawa who mentioned rodlike macromolecules as highly efficient depletion agents in their 1958 paper.[27] Auvray[28] derived an expression for the depletion interaction potential due to thin rods in the Derjaguin approximation. More recently Mao *et al.*[29] calculated the depletion interaction of rods of length L and diameter D up to third order in the density of the rods. In the limit that the length L of the rodlike particles is much smaller than the diameter σ of the colloidal spheres, the depletion potential to the lowest order in density is given by

$$W(h) = -\frac{1}{3} k_B T \phi^R \frac{L\sigma}{D^2} \left(1 - \frac{h}{L}\right)^3, \qquad (2)$$

where ϕ^R is now the volume fraction of the rods in a reservoir in osmotic equilibrium with the mixture of colloidal spheres and rods, and σ the diameter of the spheres. From
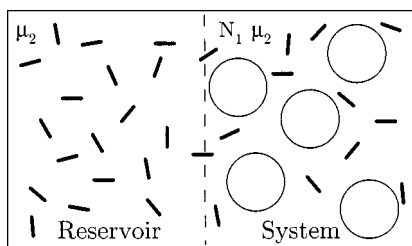
FIG. 1. Osmotic equilibrium model. Two compartments are in osmotic equilibrium through a semipermeable membrane. The left compartment (reservoir) contains the rods at chemical potential μ_2. The right compartment (system) contains N_1 spheres in a volume V at temperature T and $\langle N_2 \rangle$ rods at chemical potential μ_2.

Eq. (2) we estimate that for the case $L/\sigma = 0.2$ and $L/D = 20$ a minimum of the depletion interaction of $-2.5 k_B T$ is obtained when the volume fraction ϕ of rods is only about 0.4%. Without the Derjaguin approximation, a calculation to first order in the density gives a slightly higher volume fraction of rods for which demixing is expected to occur.[30] Clearly, rodlike particles are efficient depletion agents; very low concentrations of rods are predicted to lead to phase separation.

Although the theoretical considerations above indicate that rods constitute interesting depletion agents, so far few experimental results have been reported on the phase transitions of colloidal mixtures involving rods. Adams et al.[31] have studied mixtures of the rodlike fd virus ($L = 880$ nm, $D = 7$ nm) and polystyrene spheres ranging from 20 to 300 nm. In these mixtures, at relatively high concentrations of rods, various new and exciting phases have been found. Recently we have investigated phase separation in a mixture of silica coated boehmite rods ($L = 230$ nm, $D = 10$ nm) and silica spheres ($\sigma = 740$ nm) suspended in dimethyl formamide.[32] The formation of colloidal crystals was observed for sphere concentrations as low as 1% and rod concentrations of 0.3%.

A few years ago Bolhuis and Frenkel[13] presented simulation results and theoretical calculations for the phase behavior of mixtures of spheres and infinitely thin rods. Here we present a theory which takes into account the finite thickness of the rods and thus allow for direct comparison with experimental results. This theory is based on an extension of the free volume model[18,19] for the phase behavior of asymmetric binary hard-sphere mixtures.

II. THEORY

The thermodynamic formalism for the phase behavior of a mixture of colloidal hard spheres (component 1) and colloidal hard rods (component 2) presented here is based on the semigrand potential. Consider the osmotic equilibrium system illustrated in Fig. 1. A reservoir with rods at chemical potential μ_2 is in osmotic equilibrium with a system of N_1 spheres in a volume V at temperature T. The semigrand potential $\Omega(N_1, V, T, \mu_2)$ for this system can be written as

$$\Omega(N_1, V, T, \mu_2) = F(N_1, V, T) + \int_{-\infty}^{\mu_2} \left(\frac{\partial \Omega}{\partial \mu_2} \right)_{N_1, V, T} d\mu_2$$

$$= F(N_1, V, T) - \int_{-\infty}^{\mu_2} N_2 d\mu_2, \tag{3}$$

where $F(N_1, V, T)$ is the Helmholtz free energy for the pure hard sphere system.

In the limit $\rho_2^R \to 0$ (and hence $\rho_2 \to 0$) the chemical potential of the rods in the reservoir is given by

$$\mu_2 = \text{const} + k_B T \ln(\rho_2^R). \tag{4}$$

According to Widom's particle insertion principle,[36] the chemical potential in the system in the limit $\rho_2 \to 0$ is equal to $\mu_2 = \text{const} + k_B T \ln(\rho_2 V / \langle V_{\text{free}} \rangle_0)$. Since the chemical potentials in the reservoir and system are equal, it follows that

$$N_2 = \rho_2^R \langle V_{\text{free}} \rangle_0. \tag{5}$$

Here $\langle V_{\text{free}} \rangle_0$ is the free volume available for the rods in the system. Equation (5) is exactly valid in the limit $\rho_2^R \to 0$, but higher order terms will play a role for finite ρ_2^R. Nevertheless we will use Eq. (5) as an approximation for N_2 for all densities ρ_2^R. Substituting Eq. (5) in Eq. (3) and using the Gibbs–Duhem relation

$$d\Pi = \rho_2^R d\mu_2, \tag{6}$$

we obtain

$$\Omega = F - \Pi f V, \tag{7}$$

where Π is the osmotic pressure of the rods in the reservoir and $f = \langle V_{\text{free}} \rangle_0 / V$ is the free volume fraction. As a model for the rods we take spherocylinders (consisting of cylinders with length L and diameter D and capped with two hemispheres). For the osmotic pressure Π of the spherocylinders in the reservoir we use the scaled particle expression,[33–35]

$$\frac{\Pi v_2}{k_B T} = \frac{\phi_2^R}{1 - \phi_2^R} + C_2 \left(\frac{\phi_2^R}{1 - \phi_2^R} \right)^2 + C_3 \left(\frac{\phi_2^R}{1 - \phi_2^R} \right)^3, \tag{8}$$

where $v_2 = (\pi/4) L D^2 + (\pi/6) D^3$ is the volume of a spherocylinder, $C_2 = 3\gamma(\gamma + 1)/(3\gamma - 1)$ and $C_3 = 12\gamma^3/(3\gamma - 1)^2$ with $\gamma = (L/D) + 1$. An expression for f can be obtained realizing that according to Widom's particle insertion method[36]

$$\mu^{\text{ex}} = -k_B T \ln f, \tag{9}$$

where μ^{ex} is the excess chemical potential of a test hard rod in a sea of hard spheres. Using the scaled particle expression for the excess chemical potential for rods with a volume fraction approaching zero in a sea of spheres[35,37] one obtains

$$f = (1 - \phi_1) \exp\left[-\left(A \left(\frac{\phi_1}{1 - \phi_1} \right) + B \left(\frac{\phi_1}{1 - \phi_1} \right)^2 + C \left(\frac{\phi_1}{1 - \phi_1} \right)^3 \right) \right]. \tag{10}$$

Here $\phi_1 = (N_1/V)[(\pi/6)\sigma^3]$ is the volume fraction of the large spheres and the coefficients A, B, and C take the form,

$$A = 3q + 3q^2 + q^3 + 1.5r + 3qr + 1.5q^2r,$$

$$B = 4.5q^2 + 3q^3 + 4.5qr + 4.5q^2r, \tag{11}$$

$$C = 3q^3 + 4.5q^2r$$

with $r = L/\sigma$ and $q = D/\sigma$.

From Eq. (7) we obtain using standard thermodynamical relationships the expressions for the pressure and chemical potential,

$$\mu_1 = \left(\frac{\partial \Omega}{\partial N_1} \right)_{\mu_2, V, T} = \mu_1^0 - \Pi \frac{df}{d\phi_1}, \tag{12}$$

$$P = - \left(\frac{\partial \Omega}{\partial V} \right)_{\mu_2, N_1, T} = P^0 + \Pi \left(f - \phi_1 \frac{df}{d\phi_1} \right). \tag{13}$$

Here P^0 and μ_1^0 denote the pressure and chemical potential of the pure hard sphere system. The phase diagram is obtained by solving the coexistence conditions,

$$\mu_1' = \mu_1'', \tag{14}$$

$$P' = P'', \tag{15}$$

where prime and double prime denote the coexisting phases.

In order to perform the actual calculations, explicit expressions for P^0 and μ_1^0 are needed for both the fluid and the solid phase. For the fluid phase we use the well-known Carnahan–Starling expressions,[38]

$$\frac{P^0 v_1}{k_B T} = \frac{\phi_1(1 + \phi_1 + \phi_1^2 - \phi_1^3)}{(1 - \phi_1)^3}, \tag{16}$$

$$\frac{\mu_1^0}{k_B T} = \ln \phi_1 + \frac{\phi_1(8 - 9\phi_1 + 3\phi_1^2)}{(1 - \phi_1)^3}, \tag{17}$$

where v_1 is the volume of a sphere. The pressure and chemical potential of the hard sphere crystal were obtained starting from a free volume equation of state for hard spheres based on the work of Wood[39] and Salsburg and Wood,[40]

$$\frac{P^0 v_1}{k_B T} = \frac{3\phi_1}{1 - (\phi_1/\phi_{cp})}. \tag{18}$$

This simple equation of state gives results, which agree very well with the computer simulations for the pressure of hard sphere crystals of Alder, Hoover, and Young.[41] Using this equation of state and the excess free energy for a hard sphere solid at $\phi_1 = 0.5759$ obtained by Frenkel and Ladd[42,43] using the Monte Carlo Einstein-crystal method, we obtain for the chemical potential,

$$\frac{\mu_1^0}{k_B T} = 2.1306 + 3 \ln \left(\frac{\phi_1}{1 - (\phi_1/\phi_{cp})} \right) + \frac{3}{1 - (\phi_1/\phi_{cp})}, \tag{19}$$

where $\phi_{cp} = \pi\sqrt{2}/6$ is the closed packed density. Using the simple expressions (16)–(19) for the pressure and chemical potential of the pure hard sphere system, the fluid solid transition is found to occur for coexisting densities of $\phi_{\text{fluid}} = 0.492$ and $\phi_{\text{crystal}} = 0.542$. This should be compared with the computer simulation results $\phi_{\text{fluid}} = 0.494$ and $\phi_{\text{crystal}} = 0.545$ for the coexisting densities obtained by Hoover and Ree.[44]
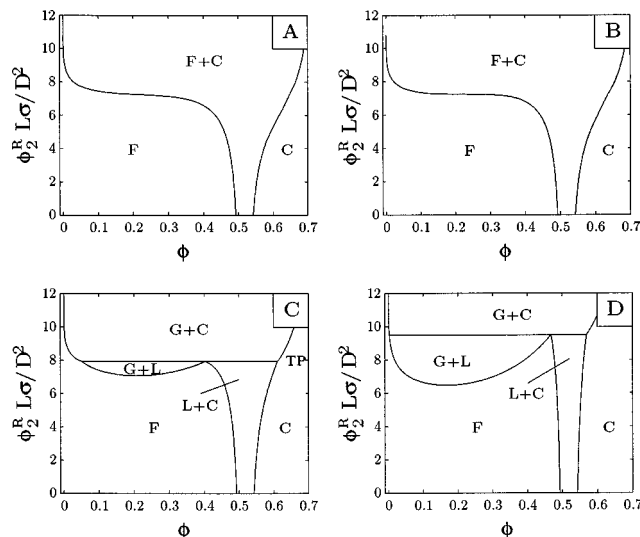

FIG. 2. Phase diagram of the mixture of colloidal spheres and hard colloidal rods in the field–density representation. The aspect ratio L/D of the spherocylinders is fixed at 20. A: $r = 0.2$, B: $r = 0.29$, C: $r = 0.5$, D: $r = 1.0$.

The semigrand potential in Eq. (7) which is central to our theory is simple but approximate. The approximate character stems from the fact that we have used Eq. (5) for the number density of component 2 in the system. As already indicated Eq. (5) is only exact in the limit $\rho_2^R \to 0$. We have however combined in the thermodynamic integration [Eq. (3)] this first order result in ρ_2^R with the full expression for the chemical potential μ_2 introducing terms to all order in ρ_2^R in the semigrand potential. Clearly this implies that the terms of order $O((\rho_2^R)^2)$ and higher are only approximate.[26] It is difficult to assess the consequences of this nonsystematic procedure on the resultant phase diagrams. Comparing phase diagrams[19] obtained by this procedure[18] with computer simulation results agreement is fair. On a more fundamental level we expect that $N_2^{\text{exact}} \geq \rho_2^R \langle V_{\text{free}} \rangle_0$ and hence the semigrand potential Ω given by Eq. (7) represents an upper bound to the exact semigrand potential.

III. RESULTS AND DISCUSSION

In Figs. 2 and 3 we present phase diagrams for rod-sphere mixtures calculated by the method presented in the preceding section, for L/σ ranging from 0.2 to 1.0 and L/D fixed at $L/D = 20$ in the field–density and density–density representation,[45] respectively. Guided by the expression for the depletion interaction between two spheres in a sea of thin rods [Eq. (2)], we have scaled the volume fractions of rods by multiplication with $L\sigma/D^2$.

For $L/\sigma \leq 0.29$ simple fluid–solid coexistence is found while for $L/\sigma > 0.29$ a region of three phase coexistence (gas–liquid–crystal) bounded by three distinct two phase regions (gas–liquid, liquid–crystal and gas–crystal) is found. The same global features for the phase diagram were first predicted[10,11] and experimentally confirmed[7,8] for colloid polymer mixtures.

We now consider the effect of the aspect ratio L/D on the phase diagram. For the purpose of discussion we introduce a characteristic volume fraction of rods ϕ_2^* required to
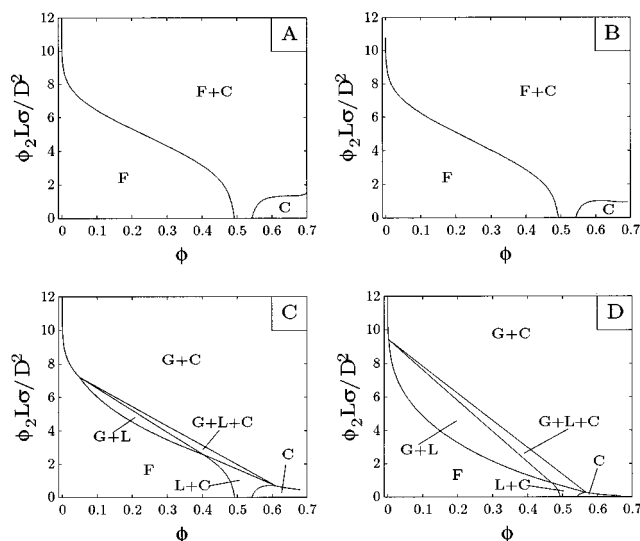
FIG. 3. Phase diagram of the mixture of colloidal spheres and hard colloidal rods in the density–density representation. The aspect ratio L/D of the spherocylinders is fixed at 20. A: $r=0.2$, B: $r=0.29$, C: $r=0.5$, D: $r=1.0$.

induce phase separation. For systems with $L/\sigma < 0.29$ this volume fraction is defined, somewhat arbitrary, as the volume fraction ϕ_2^R where the phase transition takes place at $\phi = 0.2$. For $L/\sigma > 0.29$ we take ϕ_2^* as ϕ_2^R at the critical point. In Fig. 4, we plot for $L/\sigma = 0.2$ and $L/\sigma = 1.0$ the scaled volume fraction $\phi_2^*(L\sigma/D^2)$ for L/D ranging from 10 to 250. From this figure it is clear that whereas the value of ϕ_2^* decreases with increasing L/D, the scaled value $\phi_2^*(L\sigma/D^2)$ increases slightly with increasing L/D. The limiting value for $L/D \to \infty$ depends on L/σ. While for $L/D = 20$ there is still a small but significant difference with the results of Bolhuis and Frenkel for infinitely thin rods,[13] for $L/D = 100$ our results approach theirs very closely. Comparing $\phi_2^* \sim 9(D^2/L\sigma)$ to the volume fraction of rods at which the isotropic–nematic phase transition occurs $\phi_{I-N} \sim 3.3(D/L)$[46] and taking into account that $D \ll L \leqslant \sigma$ (and hence $D \ll \sigma$) we conclude that $\phi_2^* \ll \phi_{I-N}$.

The scaling of the characteristic volume fraction of rods with $D^2/L\sigma$ implies very low volume fractions of rods needed to induce phase separation which is in agreement with our recent experimental results.[32] We studied the phase
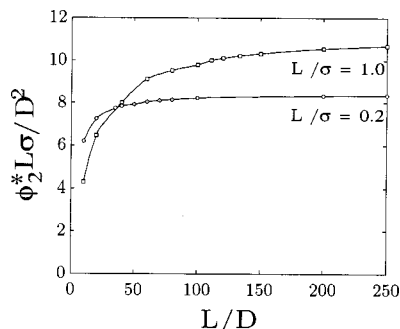
separation in a mixture of silica coated boehmite rods ($L = 230$ nm, $D = 10$ nm and silica spheres $\sigma = 740$ nm) suspended in dimethylformamide. The experiments were performed in a small window in the phase diagram. The sphere volume fraction was varied between $\phi_1 = 0.01$ and $\phi_1 = 0.05$ and the rod volume fraction was varied between $\phi_2 = 0.0025$ and $\phi_2 = 0.006$. We found in this range of sphere volume fractions that the phase transitions occur above $\phi_2 \sim 0.003$ whereas the predictions from theory give values around $\phi_2 \sim 0.005$. Clearly the theory, although not quantitatively correct, provides a good guide for the experimental concentrations where phase separation is to be expected.

The theoretical work presented here together with the experimental work[31,32] indicate that rod–sphere mixtures show interesting and rich phase behavior at low and high rod concentrations. However, to obtain a detailed and quantitative insight in the phase behavior of these mixtures, it is necessary to further map the phase diagram experimentally, theoretically and by computer simulation.

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FIG. 4. The characteristic transition density as a function of L/D for $r = 0.2$ (circles) and $r = 1$ (squares).

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