

Phase Behaviour of Rod-like Colloid + Flexible Polymer Mixtures (*).

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Summary. — The effect of non-adsorbing, flexible polymer on the isotropic-nematic transition in dispersions of rod-like colloids is investigated. A widening of the biphasic gap is observed, in combination with a marked polymer partitioning between the coexisting phases. Under certain conditions, areas of isotropic-isotropic-nematic or isotropic-nematic-nematic three-phase coexistence appear in the phase diagram of rod-polymer mixtures.

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1. – Introduction.

The addition of non-adsorbing polymer molecules to a suspension of colloidal particles may lead to phase separation into a colloid-rich and a colloid-poor phase. An explanation for this phenomenon which is of fundamental interest and considerable biological and technological importance was first advanced by Asakura and Oosawa [1, 2]. They pointed out that exclusion of the non-adsorbing polymer from the region between two colloidal particles when their surface-surface separation becomes smaller than the diameter of a free polymer coil gives rise to an attractive force due to the imbalance in osmotic pressure. The resulting interaction has been termed depletion interaction [3, 4].

One of the possible effects of this interaction, which was in fact already observed over two centuries ago, is the significantly increased sedimentation rate of red blood cells in the case of various illnesses [5]. The increased sedimentation rate is caused by the spontaneous face-to-face aggregation of the red blood cells to form rouleaux-long

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cylindrically shaped objects resembling piles of coins. There are good reasons to believe that the aggregation of the red blood cells is induced by the depletion mechanism associated with the increased concentrations of protein molecules in the blood (particularly fibrinogen and globulines) in the case of illness[6]. Other phenomena of technological and biological interest caused by the polymer-induced depletion interaction that were already studied over half a century ago include the concentration of rubber latex particles by creaming[7-9] and the isolation and purification of virus particles[10].

Following the pioneering work of Asakura and Oosawa[1,2] a considerable amount of work has been done to refine the treatment of the depletion interaction[3,4,11-15] and to calculate and observe the accompanying phase separation[16-44]. These studies were almost exclusively directed towards suspensions of spherical colloidal particles. Some attention however has been given to the phase separation induced by non-adsorbing polymer in suspensions of rod-like colloidal particles, namely the precipitation of rod-like virus particles by polyethylene glycol[45-48]. The aim of this work was the isolation and purification of viruses.

Closely related to the polymer-induced phase separation in colloidal dispersions is the phase separation observed in solutions containing a rigid rod-like polymer and a flexible randomly coiled polymer[49-55]. Flory[56] gave a theory for the phase behaviour of the latter kind of system assuming that the ternary solution is an athermal system with only excluded-volume interactions between the coils and the rods. This means that the phase transition is due to an entropy effect like the phase transitions caused by the depletion interaction. The theory of Flory predicts an isotropic-nematic phase transition to occur with a marked partitioning of the rods and coils between the isotropic and nematic phase. The coils are predicted to be almost totally excluded from the nematic phase and the concentration of the rods is predicted to be much lower in the isotropic phase than in the nematic phase. The experimentally observed phase behaviour of most ternary rod-coil-solvent systems studied so far appears to follow the theory set forth by Flory quite well[49,50,52-54]. However in some cases[51,55] the observed phase diagrams do not closely resemble those predicted by the Flory theory. For example Marsano *et al.*[51] observed in addition to biphasic isotropic-anisotropic equilibria, also biphasic isotropic-isotropic equilibria at low polymer concentration. The large difference between the experimental and theoretical phase diagram predicted by Flory[56] is attributed by Marsano *et al.*[51] to the incompatibility of the rods and coils in the system studied by them.

Recently in our laboratory, in addition to a biphasic isotropic-nematic equilibrium, a three-phase isotropic-isotropic-nematic region was observed in the phase diagram[57] of a colloidal suspension of sterically stabilized rod-like colloidal boehmite particles[58] and polystyrene in orthodichlorobenzene. Such a triphasic equilibrium is reminiscent of the three-phase isotropic-isotropic-solid equilibria recently observed in suspensions of spherical colloidal particles and non-adsorbing polymers[37,43]. The existence of such a three-phase region in the phase diagram was predicted by us[42].

Given the analogy of the phase behaviour of suspensions consisting of spherical colloidal particles and non-adsorbing polymer molecules and suspensions consisting of rod-like colloidal particles and non-adsorbing polymer with the role of the crystal phase in the former replaced by the nematic liquid crystal phase in the latter, it appeared worthwhile to extend the simple theory for spherical particles presented

in[42] to rod-like particles. Some work in this direction was recently published by Warren[59] who treated rod + coil mixtures on the second virial coefficient level. This limits the treatment to very long rods and very low polymer concentrations in order to ensure that the second virial contribution dominates the higher virial contributions. Under these conditions Warren found a widening of the biphasic isotropic-nematic gap and a partitioning of the flexible polymer towards the isotropic phase. Like Warren we also start from the method presented in[42] for calculating the effect of the depletion interaction on the phase behaviour but the treatment given here is not limited to the second virial level and therefore free of the restrictions of being only valid for very long rods and very low polymer concentrations.

2. - Theory.

2.1. *Model.* - The model used in this work is the same as in[42]. The polymer molecules are treated as freely interpenetrable coils of diameter σ , whose centres of mass cannot approach the (non-adsorbing) surface of the colloidal particles closer than a distance $\sigma/2$. As the polymer coils do not feel each other the pure polymer solution will behave thermodynamically ideally. The colloidal particles themselves are modelled as hard spherocylinders consisting of cylinders of diameter D and length L capped with two hemispheres. Like in[42] we use as independent thermodynamic variables to describe the colloid + polymer mixture the number of colloidal particles N_C , the chemical potential of the polymer molecules μ_p and the volume V . This means that we consider the colloidal dispersion in osmotic equilibrium with a reservoir containing a pure polymer solution characterized by a chemical potential μ_p . The osmotic pressure exerted by the polymer in the reservoir will be denoted by Π_p^r .

In the presence of the polymer molecules the effective interaction (potential of mean force[60-62]) between the colloidal particles can be written as[63]

$$(1) \quad W(\mathbf{r}_C, \mathbf{u}_C; \mu_p) = U(\mathbf{r}_C, \mathbf{u}_C) - \Pi_p^r(\mu_p) V_{\text{free}}(\mathbf{r}_C, \mathbf{u}_C).$$

Here U is the colloid-colloid interaction in the absence of polymer and V_{free} is the volume available for the polymer coils. Both the colloid-colloid interaction in the polymer-free dispersion and the available volume depend on the colloidal particle positions and orientations collectively denoted by the position vector \mathbf{r}_C and the orientation (unit) vector \mathbf{u}_C .

As mentioned above the colloidal particles are modelled as hard spherocylinders thus

$$(2) \quad \begin{cases} U(\mathbf{r}_C, \mathbf{u}_C) = 0 & \text{in case of no particle overlap,} \\ U(\mathbf{r}_C, \mathbf{u}_C) = \infty & \text{in case of particle overlap.} \end{cases}$$

The volume available to the polymer coils V_{free} is the volume outside the excluded volume which consists of the colloidal particles surrounded by a shell of thickness half the polymer diameter $\sigma/2$ (see fig. 1).

Approximating V_{free} by its average value in the colloidal dispersion in the absence of polymer molecules, the semi-grand potential for the system under consideration can be written as

$$(3) \quad \Omega(N_C, V, T, \mu_p, [f]) = F_C(N_C, V, T, [f]) - \Pi_p^r \langle V_{\text{free}} \rangle_0.$$

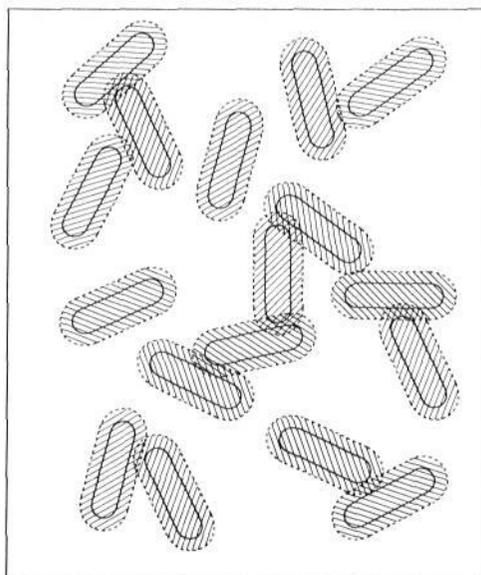


Fig. 1. - Illustration of V_{free} , the available volume. V_{free} is the unshaded volume.

Here F_C is the Helmholtz free energy of N_C colloidal rods in a volume V at a temperature T and $\langle V_{\text{free}} \rangle_0$ is the average free volume in the absence of polymer. Further $f(\mathbf{u})$ is the orientation distribution function which gives the probability of finding a rod with an orientation characterized by the unit vector \mathbf{u} . This distribution function must be normalized

$$(4) \quad \int f(\mathbf{u}) d\Omega = 1,$$

where $d\Omega$ is the element of solid angle surrounding the direction \mathbf{u} .

In order to assess the influence of added polymer on the phase behaviour of the dispersion of rod-like particles, the Helmholtz free energy F_C of the pure rod system and the free-volume fraction

$$(5) \quad \nu = \frac{\langle V_{\text{free}} \rangle_0}{V}$$

have to be known as a function of the density, in the isotropic as well as in the nematic phase.

2.2. Free energy. - Onsager's theory for the isotropic-nematic phase transition [61] provides an expression for the free energy of a rod system up to the second virial contribution. This free-energy expression is accurate for systems of slender rigid hard rods with $L/D \gg 1$ (and in fact it is an exact theory for $L/D \rightarrow \infty$) as in the case of large axial ratios, the third and higher virial contributions become small compared to the second virial contribution [64]. Adding polymer, however, induces an effective attraction between the rods which (strongly) lowers the second virial coefficient. Moreover even a weak inter-rod attraction that does not affect significantly the second virial coefficient may have a considerable influence on the third virial

coefficient [65]. Consequently if one does not want to limit the treatment to very long rods and very low polymer concentrations it is imperative to use for the Helmholtz free energy of the pure colloidal dispersion an expression which includes, be it necessarily only approximately, contributions beyond the second virial contribution. Such an expression is provided by the Scaled Particle Theory (SPT) [66]:

$$(6) \quad \frac{F_C}{N_C kT} = \text{const} + \ln n_C - \ln(1 - \phi_C) + \sigma[f] + H_2 \frac{\phi_C}{1 - \phi_C} + \frac{1}{2} H_3 \left(\frac{\phi_C}{1 - \phi_C} \right)^2,$$

where n_C is the colloidal-particle number density

$$(7) \quad n_C = \frac{N_C}{V}$$

and ϕ_C is the colloidal-particle volume fraction

$$(8) \quad \phi_C = n_C \left(\frac{\pi}{6} D^3 + \frac{\pi}{4} D^2 L \right).$$

The coefficients H_2 and H_3 are given by the expressions

$$(9) \quad H_2 = 3 + \frac{3(\gamma - 1)^2}{(3\gamma - 1)} \rho[f]$$

and

$$(10) \quad H_3 = \frac{12\gamma(2\gamma - 1)}{(3\gamma - 1)^2} + \frac{12\gamma(\gamma - 1)^2}{(3\gamma - 1)^2} \rho[f],$$

where γ is the overall length-to-diameter ratio of the spherocylinders

$$(11) \quad \gamma = \frac{L + D}{D}.$$

The quantities $\sigma[f]$ and $\rho[f]$ depend on the orientation distribution function f :

$$(12) \quad \sigma[f] = \int f(\mathbf{u}) \ln [4\pi f(\mathbf{u})] d\Omega$$

and

$$(13) \quad \rho[f] = \frac{4}{\pi} \iint |\sin \Phi| f(\mathbf{u}) f(\mathbf{u}') d\Omega d\Omega',$$

where Φ is the angle between two spherocylinders.

2'3. Free volume. – In order to calculate the free volume accessible to a polymer coil with diameter σ in a sea of N_C spherocylinders we write the chemical potential μ_p of the polymer molecules in the dispersion in the form

$$(14) \quad \mu_p = \text{const} + kT \ln \frac{N_p}{V} + W'.$$

Here W' stands for the reversible work required to introduce the polymer molecule in the dispersion of rod-like colloidal particles. According to Widom's particle insertion method [67] the chemical potential of the polymer molecules can also be written in the form

$$(15) \quad \mu_p = \begin{cases} \text{const} + kT \ln \frac{N_p}{\langle V_{\text{free}} \rangle_0}, \\ \text{const} + kT \ln \frac{N_p}{V} - kT \ln \nu. \end{cases}$$

Combining eqs. (14) and (15) we find that

$$(16) \quad \nu = \frac{\langle V_{\text{free}} \rangle_0}{V} = \exp \left[-\frac{W'}{kT} \right].$$

This is an exact relationship. In order to obtain a concrete result we use the scaled particle theory [66, 68-70] to calculate W' (see appendix for details). This leads to the following (approximate) result for the free-volume fraction:

$$(17) \quad \nu = (1 - \phi_C) \exp \left[- \left\{ A \left(\frac{\phi_C}{1 - \phi_C} \right) + B \left(\frac{\phi_C}{1 - \phi_C} \right)^2 + C \left(\frac{\phi_C}{1 - \phi_C} \right)^3 \right\} \right],$$

where

$$\begin{aligned} A &= \frac{6\gamma}{3\gamma - 1} q + \frac{3(\gamma + 1)}{3\gamma - 1} q^2 + \frac{2}{3\gamma - 1} q^3, \\ B &= \frac{1}{2} \left(\frac{6\gamma}{3\gamma - 1} \right)^2 q^2 + \left(\frac{6}{3\gamma - 1} + \frac{6(\gamma - 1)^2}{3\gamma - 1} \rho[f] \right) q^3, \\ C &= \frac{2}{3\gamma - 1} \left(\frac{12\gamma(2\gamma - 1)}{(3\gamma - 1)^2} + \frac{12\gamma(\gamma - 1)^2}{(3\gamma - 1)^2} \rho[f] \right) q^3. \end{aligned}$$

In these expressions γ is the overall length-to-diameter ratio of the spherocylinders (eq. (11)) and q is the ratio of the polymer diameter and the colloid diameter

$$(18) \quad q = \sigma/D.$$

It is instructive to compare the SPT result for the free-volume fraction obtained here with the expression obtained by Warren [59] from a geometric calculation

$$(19) \quad \nu = 1 - k_1 \phi_C + \frac{1}{2} k_2 \phi_C^2,$$

where

$$k_1 = (1 + q)^3$$

and

$$k_2 = \frac{16}{3\pi} q^3 \left(1 + \frac{5}{8} q - \frac{3}{160} q^2 + \dots \right).$$

This result is exact to order ϕ_C^2 in the limit $L/D \rightarrow \infty$. Expanding the SPT result, eq. (17), to order ϕ_C^2 and taking the limit $L/D \rightarrow \infty$, we obtain

$$(20) \quad v = 1 - (1 + q)^3 \phi_C + \left[\left(2 - \frac{2}{3} \rho[f] \right) q^3 + \frac{1}{2} q^4 \right] \phi_C^2 .$$

Whereas eqs. (19) and (20) show agreement as far as the term of order ϕ_C is concerned, there is no such agreement for the ϕ_C^2 term. In addition to a quantitative difference there is also a significant qualitative difference. The geometric calculation shows that up to order ϕ_C^2 the free volume is independent of the orientation distribution function of the rods, whereas the SPT result does display a dependence on it. This means that in this case SPT already deviates from the exact result on the level of the ϕ_C^2 term. Nevertheless SPT provides a practical route to obtain an expression for the free-volume fraction beyond ϕ_C^2 . In the case of colloidal spheres the agreement between the SPT result [42] (which is now exact to order ϕ_C^2) and computer simulations [71] is quite good for colloidal-particle volume fractions up to 0.5.

3. - Calculations.

To treat the phase behaviour of rod + polymer mixtures we must first minimize the semi-grand-canonical potential Ω with respect to the orientation distribution function f . This can be done formally considering Ω as a function of f while taking into account the normalization condition (4) by subtracting $\lambda \int f(\mathbf{u}) d\Omega$ (λ being a Lagrange undetermined multiplier) and then minimizing the resulting expression. An alternative route is to choose a (normalized) trial function with one or more variational parameters and then minimize the free energy with respect to these parameters. Here we shall use a Gaussian distribution function [72]:

$$(21) \quad f(\theta) \sim \begin{cases} \frac{\alpha}{4\pi} \exp \left[-\frac{1}{2} \alpha \theta^2 \right], & 0 \leq \theta \leq \frac{\pi}{2}, \\ \frac{\alpha}{4\pi} \exp \left[-\frac{1}{2} \alpha (\pi - \theta)^2 \right], & \frac{\pi}{2} \leq \theta \leq \pi. \end{cases}$$

This function only depends on the polar angle θ because of the uniaxial symmetry of a nematic phase. Using the Gaussian distribution one obtains to leading order (large α) [72]

$$(22) \quad \sigma(\alpha) \sim \ln(\alpha) - 1,$$

$$(23) \quad \rho(\alpha) \sim \frac{4}{\sqrt{\pi\alpha}}.$$

Substitution of eqs. (22) and (23) in the Helmholtz free energy (6) and the free-volume fraction (17) leads to an analytic expression for the grand potential (3) which depends on a single variational parameter and hence is easily minimized.

To locate the phase transitions in the system we must solve the coexistence conditions equating the chemical potential and osmotic pressure in the coexisting phases. In the formalism used here the chemical potential of the polymer molecules is

already set (by the reservoir) at a given value throughout the system and therefore the coexistence conditions take the form

$$(24) \quad \mu_C(\phi'_C, [f'], \mu_p) = \mu_C(\phi''_C, [f''], \mu_p),$$

$$(25) \quad \Pi(\phi'_C, [f'], \mu_p) = \Pi(\phi''_C, [f''], \mu_p).$$

Here ϕ'_C and ϕ''_C are the colloid volume fractions in the coexisting phases and f' and f'' are the distributions that minimize Ω . The expressions for μ_C and Π are obtained from Ω using the standard relationships

$$(26) \quad \mu_C = \left(\frac{\partial \Omega}{\partial N_C} \right)_{V, \mu_p} = \mu_C^0 - \Pi_p^r \frac{dv}{dn_C},$$

$$(27) \quad \Pi = - \left(\frac{\partial \Omega}{\partial V} \right)_{N_C, \mu_p} = \Pi^0 + \Pi_p^r \left(v - n_C \frac{dv}{dn_C} \right).$$

Here μ_C^0 and Π^0 denote the chemical potential of the colloidal particles and osmotic pressure for the pure colloidal dispersion. Using the SPT expression (6) for the Helmholtz free energy of the pure colloidal dispersion one obtains

$$(28) \quad \mu_C^0 = \text{const} + \ln n_C - \ln(1 - \phi_C) + (1 + 2\Pi_2) \frac{\phi_C}{1 - \phi_C} + \\ + \left(\Pi_2 + \frac{3}{2}\Pi_3 \right) \left(\frac{\phi_C}{1 - \phi_C} \right)^2 + \Pi_3 \left(\frac{\phi_C}{1 - \phi_C} \right)^3,$$

$$(29) \quad \frac{\Pi^0}{n_C kT} = \frac{1}{1 - \phi_C} + \Pi_2 \frac{\phi_C}{(1 - \phi_C)^2} + \Pi_3 \frac{\phi_C^2}{(1 - \phi_C)^3}.$$

The procedure of solving (24) and (25) was repeated for a wide range of «geometries» determined by the length-to-width ratio L/D of the rod-like colloidal particles and the ratio of the polymer diameter and colloid diameter σ/D . For each $\{L/D, \sigma/D\}$ -combination the phase equilibria were evaluated for different values of the imposed polymer activity characterized by μ_p (or equivalently the Π_p^r value). The case $\Pi_p^r = 0$ corresponds to the limit of the pure colloidal dispersion.

4. - Results.

Depending on the length-to-width ratio of the rod-like particles and the ratio of the polymer diameter and rod diameter we find three types of phase behaviour.

a) A phase diagram with two isotropic phases («dilute» and «concentrated» the equivalent of vapour and liquid) and a nematic phase. This phase behaviour is predicted to occur for mixtures of relatively short rods and large polymers.

b) A phase diagram with an isotropic and a nematic phase. This phase behaviour is predicted to occur for rods with intermediate length-to-width ratios and polymers with intermediate polymer-to-rod diameter ratios.

c) A phase diagram with one isotropic phase and two nematic phases differing

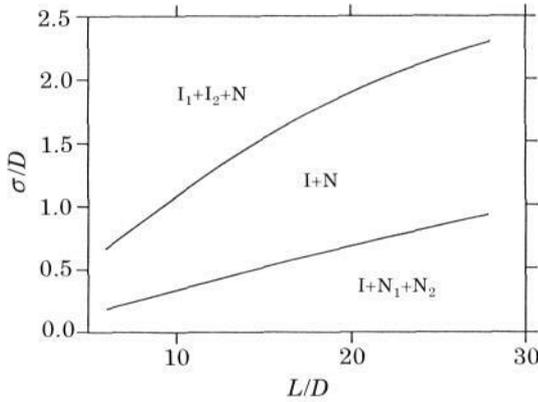


Fig. 2. – Dependence of the type of phase behaviour of rod-like colloid + flexible polymer mixtures on the size parameters of the colloid and polymer. $I_1 + I_2 + N$: phase diagram with two isotropic phases and a nematic phase, $I + N$ phase diagram with an isotropic and a nematic phase, $I + N_1 + N_2$ phase diagram with one isotropic and two nematic phases.

in concentration. This phase behaviour is predicted to occur for long rod-like particles and relatively small polymer molecules.

The occurrence of the three different regimes as a function of the geometrical parameters L/D and σ/D is shown in fig. 2.

The three types of phase behaviour are illustrated in fig. 3 in a representation showing colloid volume fraction ϕ_C against polymer volume fraction in the reservoir ϕ_p^r .

Experimentally one controls the polymer concentration in the system rather than the polymer concentration in the reservoir. Using the relation

$$(30) \quad n_p = \frac{N_p}{V} = - \frac{1}{V} \left(\frac{\partial \Omega}{\partial \mu_p} \right)_{N_C, V} = v \frac{\partial H_p^r}{\partial \mu_p} = v n_p^r$$

phase diagrams in the experimentally accessible (ϕ_p, ϕ_C) -plane can be obtained from the results in the (ϕ_p^r, ϕ_C) -plane by simply multiplying with $v(\phi_C)$.

The resulting phase diagrams are shown in fig. 4. Note that in the (ϕ_p, ϕ_C) -representation the triple lines present in the (ϕ_p^r, ϕ_C) -representation expand into three-phase regions bounded by three distinct two-phase regions. In fig. 3 and 4 tie lines are indicated in the two-phase regions. Because of mass conservation they are straight and the relative volumes of each phase can be obtained by the usual lever rule[73]. In the three-phase regions of fig. 4 the compositions of the phases are given by the vertices of the triangle and the phase volumes by an area rule[74].

5. – Discussion.

Obviously the approach taken in this work is highly idealised and it is not expected that the theory will provide quantitatively agreement with experiment. Nevertheless it is hoped that this work will serve as a guide to predict trends in the phase behaviour upon changing the relative sizes of the rods and the polymers. Some

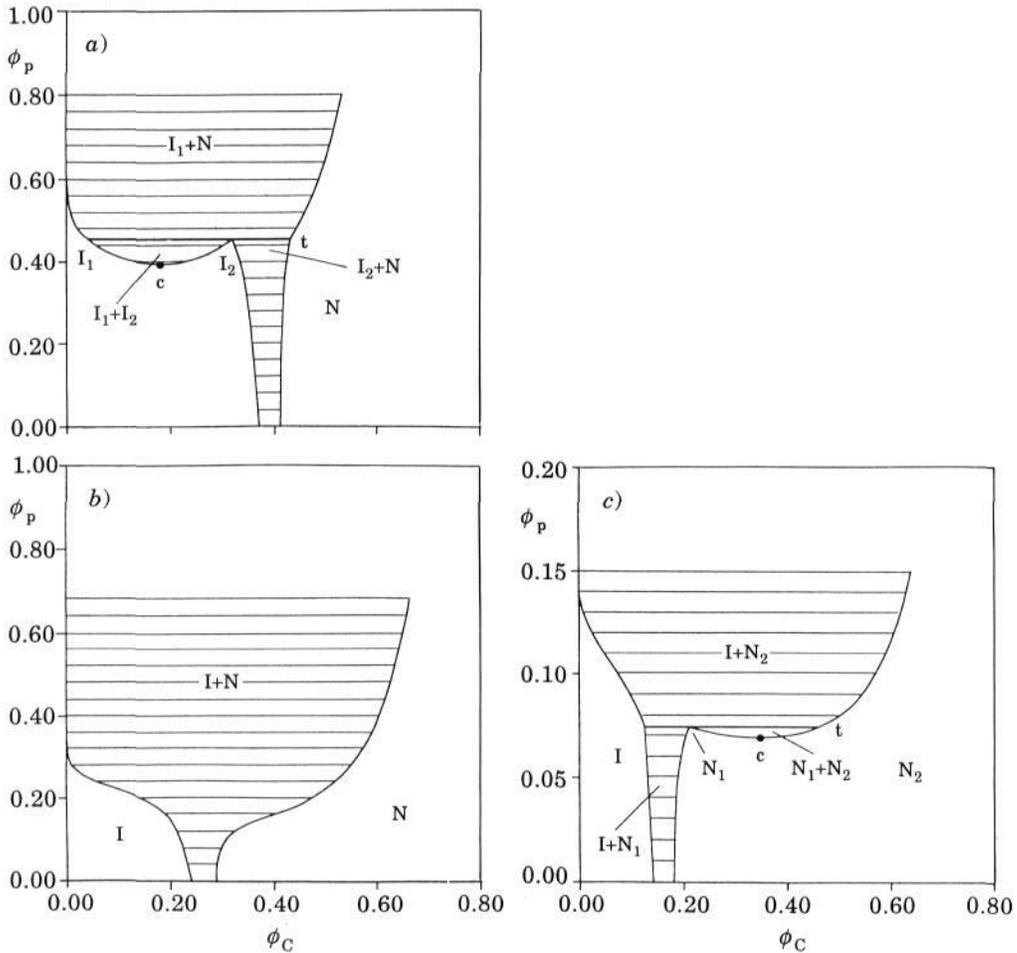


Fig. 3. - Phase diagrams for rod-like colloid + flexible polymer mixtures showing colloid volume fraction ϕ_C against polymer coil volume fraction in the reservoir ϕ_p^r . a) $L/D = 5$, $\sigma/D = 0.80$; b) $L/D = 10$, $\sigma/D = 0.65$; c) $L/D = 20$, $\sigma/D = 0.50$. The lines are shown in the two-phase regions. The critical point (c) and triple line (bold line marked t) are also indicated. I and N refer to isotropic and nematic phases, respectively.

success in this direction was obtained from the experiments that were performed by Buijtenhuis *et al.* [57] on mixtures of sterically stabilized rod-like colloidal boehmite particles and flexible polymer (polystyrene, polydimethylsiloxane) in a good solvent (orthodichlorobenzene, cyclohexane). For colloids with sufficiently large L/D ratios ($\gamma \cong 27$) just an isotropic and a nematic phase were obtained, whereas for small L/D ratio ($\gamma \cong 6.4$) a three-phase equilibrium consisting of two isotropic phases («dilute» and «concentrated») and a nematic phase was observed.

In connection we note that the mirror image three-phase equilibrium, *i.e.* two nematic phases and an isotropic phase predicted by the present theory will be difficult to realize experimentally. First of all according to the calculations the more concentrated nematic phase will appear at colloid volume fractions above the concentration where the dispersion experimentally is observed to turn into a

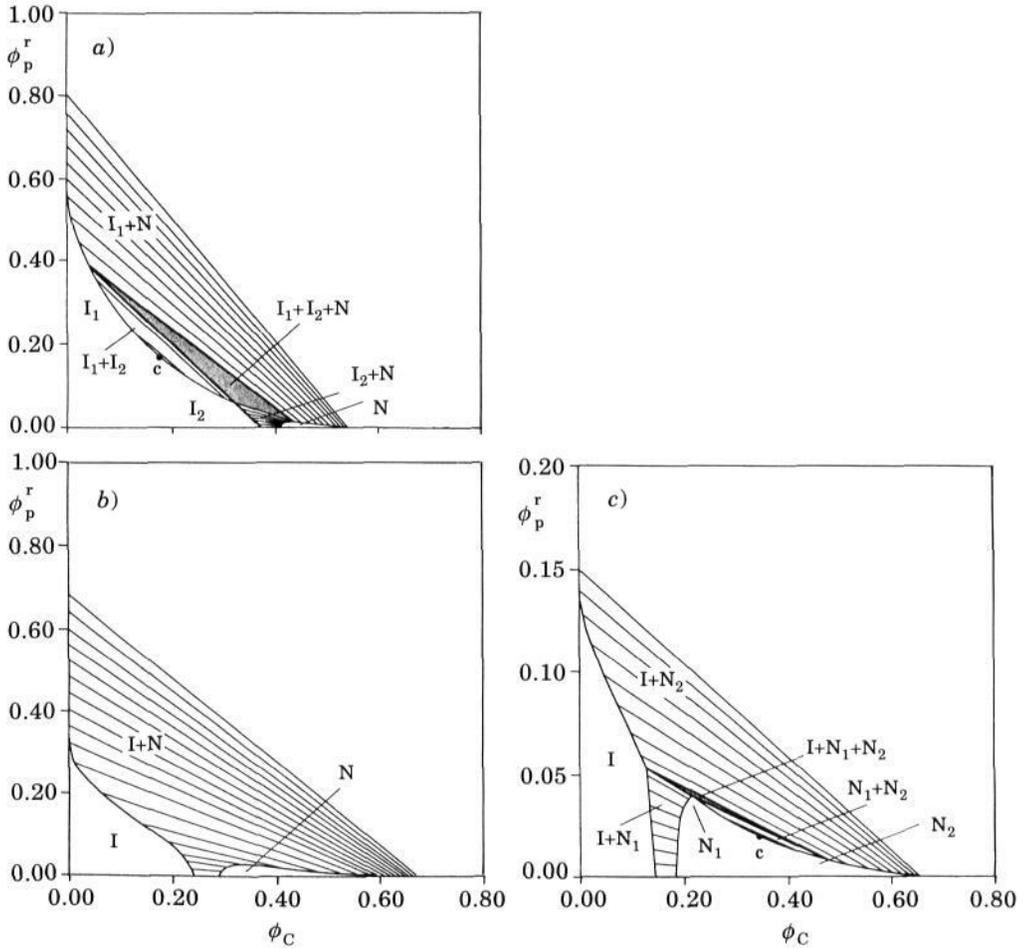


Fig. 4. - Phase diagrams for rod-like colloid + flexible polymer mixtures showing colloid volume fraction ϕ_C against polymer coil volume fraction in the system ϕ_P^r . The notation is the same as in fig. 3.

glass-like state[58]. Another issue that complicates matters here is that at sufficiently high concentrations of rod-like colloidal particles more highly ordered (liquid) crystal phases, such as the colloidal smectic A phase and the colloidal crystal phase are predicted to occur[75,76]. These more highly ordered phases were not considered in the theory presented here but on the basis of the known simulation results for pure systems of hard rod-like particles[75,76] we expect them to preempt the second (more concentrated) nematic phase in systems with added non-adsorbing polymer. More work is required to confirm this speculation.

From the work on the isolation and purification of virus particles as mentioned in the Introduction, it appears that significantly less polymer is needed to precipitate rod-like virus particles in comparison with spherical virus particles. This trend is also predicted by the theory presented here. As can be seen from fig. 4, increasing the aspect ratio of the colloidal particles leads to a situation where less polymer is required to cause phase separation. In fact the present theory, in some cases, even

leads to semi-quantitative agreement with the experimental data. For example, Leberman [47] observed that in a colloidal dispersion of Tobacco Mosaic Virus (TMV; $L \approx 300$ nm; $D \approx 18$ nm) with a concentration of 1 mg/ml, precipitation of the virus particles already occurred at a concentration as low as 5 mg/ml polyethyleneglycol (PEG) of molecular weight 6000. Using as an estimate for the diameter of the PEG molecules $\sigma \approx 7.5$ nm, the above-mentioned polymer concentration of 5 mg/ml corresponds to a polymer coil volume fraction of 11%. Our calculations yield for this system a polymer coil volume fraction of about 14% to induce phase separation.

Clearly in the system discussed above the charge interactions between the TMV particles will play a role and thus they are not simply hard rods as assumed in the theory. Similarly the PEG molecules are not freely interpenetrable coils. Given these facts the simple theory presented here gives quite reasonable results for the polymer concentration required for phase separation.

APPENDIX

Calculation of the reversible work W' required to insert a polymer coil in a dispersion of hard rod-like colloidal particles.

The basic idea of SPT to calculate the work W' required to insert at some fixed position an additional particle into the system is to expand (scale) the particle to be inserted from zero to its final size. In the case of a spherical particle this expansion can be described in terms of a single scaling parameter λ for the diameter. So the scaled particle has a diameter $\lambda\sigma$. In the limit $\lambda \rightarrow 0$ the work needed to insert a sphere can be easily calculated by inverting the relation given by eq. (16)

$$(A.1) \quad W' = -kT \ln v$$

and realizing that in the limit considered there is no overlap of excluded-volume shells and thus

$$(A.2) \quad W'(\lambda) = -kT \ln \left[1 - n_C \left\{ \frac{\pi}{6} (D + \lambda\sigma)^3 + \frac{\pi}{4} (D + \lambda\sigma)^2 L \right\} \right] \quad (\lambda \rightarrow 0).$$

For a large value of the scaling parameter λ the work required to insert an additional particle is just the work required to create the volume of the scaled particle against the osmotic pressure Π^0 of the fluid of hard rod-like colloidal particles

$$(A.3) \quad W'(\lambda) = \frac{\pi}{6} (\lambda\sigma)^3 \Pi^0 \quad (\lambda \gg 1).$$

Now, in the scaled-particle treatment it is *assumed* that the work to add a particle with arbitrary values of the scaling parameters can be obtained by expanding (A.2) in a Taylor series around $\lambda = 0$ up to quadratic terms and adding (A.3) as the third-order term

$$(A.4) \quad W'(\lambda) = W'(0) + \left. \frac{\partial W'}{\partial \lambda} \right|_{\lambda=0} \lambda + \frac{1}{2} \left. \frac{\partial^2 W'}{\partial \lambda^2} \right|_{\lambda=0} \lambda^2 + \frac{\pi}{6} (\lambda\sigma)^3 \Pi^0.$$

The reversible work to insert a polymer coil with a diameter σ in a dispersion

of hard rod-like colloidal particles is obtained from the above expression, by setting $\lambda = 1$ and using for the osmotic pressure Π^0 the result given by eq. (29). This leads to

$$(A.5) \quad W' = -\ln[1 - \phi_C] + B \left(\frac{\phi_C}{1 - \phi_C} \right)^2 + C \left(\frac{\phi_C}{1 - \phi_C} \right)^3,$$

where A , B and C have the same meaning as in eq. (17). Inserting W' obtained here in eq. (16) leads to the result given by eq. (17).

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