Effects of polymer nonideality on depletion-induced phase behaviour of colloidal disks and rods

Vincent F D Peters, Remco Tuinier and Mark Vis

Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry & Institute for Complex Molecular Systems, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

E-mail: r.tuinier@tue.nl

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Abstract
Colloidal dispersions composed of either platelets or rods exhibit liquid crystalline phase behaviour that is strongly influenced by the addition of nonadsorbing polymers. In this work we examined how polymer segment–segment interactions affect this phase behaviour as compared to using either penetrable hard spheres (PHS) or ideal (‘ghost’) chains as depletants. We find that the simplified polymer description predicts the same phase diagram topologies as the more involved polymer descriptions. Therefore the PHS description is still adequate for qualitative predictions. For sufficiently large polymer sizes we find however that the precise polymer description significantly alters the locations of the phase coexistence regions. Especially the stability region of isotropic–isotropic coexistence is affected by the polymer interactions. To illustrate the quantitative effects some examples are presented.

Keywords: phase behaviour, colloids, polymers, depletion interaction, thermodynamics, rods, disks
(Some figures may appear in colour only in the online journal)

1. Introduction
Anisotropic colloidal particles can be found in a number of biologically and technologically relevant systems like blood or soil. One may think of red blood cells, clays, viruses, or cellulose nanocrystals [1–7]. Rod-like and plate-like colloids may, depending on their exact shape and concentration, exhibit liquid crystal phases. The addition of nonadsorbing polymers to these anisotropic dispersions has been shown to induce (new) phase transitions in otherwise stable systems and thereby enrich the phase behaviour [8–13]. This offers a wide range of possibilities to self-organise colloidal particles.

The presence of nonadsorbing polymer chains close to the surfaces of the colloidal particles leads to a loss of configurational entropy for the chains. As a result, a zone depleted of polymer is present near the colloidal surface. Whenever two colloidal particles get closer and these depletion zones overlap, there is an effective (depletion) attraction mediated by the osmotic pressure of the polymers. The effect of this depletion attraction has also been modelled by theory and simulations for mixtures of hard disks or rods and polymers [14–24].

To quantify relevant physical properties of these systems the polymers are often described as (penetrable) hard spheres [8, 14–24]. Within a penetrable hard spheres (PHS) description the polymers are considered spherical particles that cannot overlap with the colloidal particles but can freely overlap with each other. The accuracy of this approximation has
been studied for mixtures of colloidal spheres and polymers using free volume theory [25–27] and other approaches [28–34]. These studies revealed that when the polymers are much smaller than the colloidal spheres, and thus the depletion attraction is short-ranged, the PHS description leads to quantitative agreement with experiments [26, 35, 36]. The experimental phase behaviour with polymers comparable in size to the colloidal particles [36, 37] show however significant deviations compared to the theoretical binodals. It was demonstrated that these deviations occur because the polymers no longer behave ideally at the relevant concentrations. The theoretical method could be improved by incorporating the effects of polymer–polymer interactions based on scaling relations for the polymer properties in the semi-dilute polymer concentration limit [25–27, 37].

In this study it is examined how effective the penetrable hard sphere approximation of polymer properties is in describing mixtures of colloidal disks or rods and nonadsorbing polymers. The phase behaviour of these mixtures is much richer than for colloidal spheres. While it might still be expected that, based upon the results for spherical colloids, deviations occur for large polymer sizes, it is difficult beforehand to predict the magnitude of the deviations due to the different colloid shape. Additionally, it is unknown whether the topology of the phase diagrams changes or the same multi-phase coexistences occur upon accounting for (self-)interacting polymers instead of using the penetrable hard sphere description of depletants [21–24]. In order to examine this we will apply free volume theory similarly as in previous work for mixtures of PHS and hard disks [22] or spherocylinders [23], but incorporate excluded volume interactions between the polymer segments.

2. Theory

The colloidal particles are approximated as hard particles meaning that they only interact through their excluded volumes: they cannot overlap and there are no additional interactions. The discotic colloids are approximated as disks and the rod-like colloids as spherocylinders where \( D \) is the diameter and \( L \) is the length (in case of rods the total spherocylinder length is \( L + D \)). It is useful to define the aspect ratios \( \Lambda = L/D \) and \( \Gamma = L/D + 1 \) for the disks and rods respectively. The colloidal particle volume \( v_c \) is given by either \( \pi L D^2 / 4 \) (disks) or \( \pi L D^2 / 4 + \pi D^3 / 6 \) (spherocylinders).

Hard disks and rods can exhibit isotropic, nematic, smectic-A, columnar, AAA crystal and ABC crystal phase states, illustrated in figure 1 [38–44]. In the isotropic phase the particles have no preferred orientations or positions. For the nematic phase the particles have a preferred orientation with respect to a nematic director, but still no preferred positions. Disks can assume a columnar phase, in which the particles are confined in columns that are packed hexatically and the particle orientation is aligned alongside the columns. Within these columns the particles are free to move similarly as in a one-dimensional fluid. Similarly, in the smectic-A phase rod-like particles are confined in layers and the particle orientation is aligned alongside the normal of the layers. The particles can move freely inside the layers similarly as in a two-dimensional fluid. Smectic phases can also be observed in discotic experimental systems due to polydispersity [45, 46] or charge effects [47], but are metastable for monodisperse hard disks. For similar reasons the columnar phase can be observed in systems of rods [48–50], but it is metastable for hard spherocylinders. Lastly crystal phases can be found for rod-like particles, where the particles are confined in layers like the smectic-A phase, but ordered hexatically within the layers. For the AAA phase the particles of adjacent layers are stacked on top of each other, while in the ABC phase they are stacked in between.

To predict the phase behaviour of colloid–polymer mixtures, we use free volume theory which yields a semi-grand potential for the mixture [51]. This allows for the determination of the chemical potential and osmotic pressure in a mixture and in turn the prediction of binodals at chemical and mechanical equilibrium. The colloidal particles are mixed with polymers characterised by the radius of gyration \( R_g \) and the ratio \( q = 2R_g / D \). The mixture is in contact with a hypothetical polymer reservoir separated by a semi-permeable membrane that is impermeable to the colloidal particles. From thermodynamic considerations, it follows that the semi-grand potential \( \Omega \) in such a system can be written as [26]:

\[
\omega = \frac{\Omega}{k_b T V} = f^0 - \int_0^{\phi_R} \alpha \frac{\partial \Pi^R}{\partial \phi^R} \, d\phi^R, \tag{1}
\]

where \( k_b T \) is the thermal energy, \( V \) is the system volume, \( f^0 = F v_c / (k_b T) \) is the normalised free energy of the unperturbed colloidal system, \( \alpha = (V_{\text{free}}) / V \) the ensemble-averaged free volume fraction for the polymers in the mixture, \( \Pi^R = \Pi^R(v_c / k_b T) \) the normalised osmotic pressure, and \( \phi_R = \rho_R^* / \rho_c^* \) is the relative polymer concentration in the reservoir, where \( \rho_R^* \) and \( \rho_c^* \) are the number densities in the reservoir and at the overlap concentration, respectively. Note that \( 1 / \rho_R^* = v_p = 4\pi R_d^3 / 3 \) and thus \( \phi_R \) can also be interpreted as the reservoir polymer coil volume fraction with \( \phi_R = \rho_R^* 4\pi R_d^3 / 3 \).

The expressions for \( f^0 \) depend on the phase state and the particle shape. For disk-like [17, 18] and rod-like [19] colloidal particles it has been verified by computer simulations that the same phase states as those shown in figure 1 are expected when a depletant is added. For disks we follow equations of state as formulated by Wensink and Lekkerkerker [44] with a slight adjustment as indicated in the appendix A, while for the rods we refer to our earlier work [52].

The free volume \( \alpha \) quantifies the relative volume in the system that is available for the polymers. Typically this is estimated from the unperturbed colloidal system using scaled particle theory. This leads to the following expressions for disk–polymer [22] or rod–polymer mixtures [53]:
\[ \alpha = (1 - \eta) \exp(-Q), \]

with

\[ Q_{\text{disk}} = \left[ \left( \frac{1}{\Lambda} + 2 \right) \left( \frac{2\delta}{D} \right) + \left( \frac{\pi}{2\Lambda} + 1 \right) \left( \frac{2\delta}{D} \right)^2 \right] \frac{\eta}{1 - \eta} + \left( \frac{1}{2\Lambda^2} + \frac{2}{\Lambda} + 2 \right) \left( \frac{2\delta}{D} \right)^2 \frac{\eta^2}{(1 - \eta)^2} + \frac{2\Pi^0}{3\Lambda} \left( \frac{2\delta}{D} \right)^3, \]

\[ Q_{\text{rod}} = \left[ \frac{6\Gamma}{3\Gamma - 1} \left( \frac{2\delta}{D} \right) + \frac{3(\Gamma + 1)}{3\Gamma - 1} \left( \frac{2\delta}{D} \right)^2 \right] \frac{\eta}{1 - \eta} + \frac{1}{2} \left( \frac{6\Gamma}{3\Gamma - 1} \right)^2 \left( \frac{2\delta}{D} \right)^2 \frac{\eta^2}{(1 - \eta)^2} + \frac{2\Pi^0}{3\Gamma - 1} \left( \frac{2\delta}{D} \right)^3. \]

Here the depletion thickness \( \delta \) quantifies the size of the zone around the colloidal particle that is effectively depleted of polymer, \( \eta = \rho_c/v_c \) is the colloid volume fraction, and \( \Pi^0 \) is the osmotic pressure of the unperturbed colloidal phase. This osmotic pressure follows from the same equations of state used for \( f^0 \).

The two quantities \( \delta \) and \( \Pi^R \) depend on how we describe the polymer properties. In the following we will focus on three cases: the PHS model, the dilute polymer model, which includes self-interaction between the polymer segments of the same chain, and the interacting polymer model, where the interactions between different polymer chains are also considered. In the simplest case of PHS, the PHS radius could be interpreted as the polymer radius of gyration \( R_g \). As the PHS can freely overlap each other the reservoir osmotic pressure follows van’t Hoff’s law. With the correct normalisation this leads to \( \delta = R_g \) and \( \Pi^R = \rho^0 v_c/v_p \), where \( v_c/v_p = 3\Lambda/2\eta^3 \) for disks or \( v_c/v_p = (3\Gamma - 1)/2\eta^3 \) for rods.

An initial improvement on the description of colloid–polymer mixtures is to replace the PHS with ideal polymer chains. In this case we define ideal polymers as ‘ghost’ chains that have no interactions with other polymers, but which are depleted by a nonadsorbing surface. This still leads to the same (ideal) osmotic pressure as for PHS, but the depletion thickness \( \delta \) should be adjusted. Next to a flat hard surface, Eisenriegler’s analytical results [54] for the density profile leads to \( \delta = 1.13R_g \) for ideal chains. When the surface curvature is increased, more polymer configurations become possible at shorter distances next to the colloidal particles and the configurations entropy loss is decreased. Hence the depletion thickness becomes smaller and for cylindrical [53] or spherical [25, 55] surfaces expressions have been derived.

A next step is to account for hard core excluded volume interactions between the polymer chain segments themselves to mimic a polymer chain in a good solvent. Such polymers will be denoted as interacting polymers. For a dilute polymer solution Hanke et al [29] found \( \delta = 1.07R_g \). In the following we refer to this case as a dilute polymer, since the polymer chain still does not interact with other polymer chains. Additionally, we restrict ourselves to the good solvent case and will not discuss the theta solvent situation separately.

For dilute polymer solutions the depletion thickness next to a cylindrical [53] or spherical [25, 55] hard particle can be approximated as follows:

\[ \frac{2\delta_{\text{cyl}}}{D} = \left[ 1 + 2\frac{2\delta_k}{D} - k_1 \left( \frac{2\delta_k}{D} \right)^{1.6} + k_2 \left( \frac{2\delta_k}{D} \right)^{1.77} \right]^{1/2} - 1, \]

\[ \frac{2\delta_{\text{sph}}}{D} = \left[ 1 + 3\frac{2\delta_k}{D} + k_3 \left( \frac{2\delta_k}{D} \right)^2 - k_4 \left( \frac{2\delta_k}{D} \right)^3 \right]^{1/3} - 1, \]

where \( \delta_k \) is the depletion thickness next to a flat surface, \( k_1 = 0.51215 \), \( k_2 = 1.214 \), \( k_3 = 2.273 \), \( k_4 = 0.0975 \), and \( \delta_k = 1.07R_g \).

This results in a smaller \( \delta \) for curved surfaces as indicated in the left graph of figure 2 [27], which uses \( 2\delta/D = q\delta/R_g \). The surface curvature for a disk or spherocylinder is not uniform and as a result the actual value of \( \delta \) varies across the surface. While the majority of the disk surface is flat, at the edges the surface is cylindrical. Additionally, there is a sharp corner at the intersection of these surfaces influencing the curvature at

Figure 1. Schematic two-dimensional representation of (top) the isotropic (I), nematic (N), and columnar (C) phase for dispersions of (sideview) discotic colloids and (bottom) of the I, N, smectic-A (Sm), AAA crystal and ABC crystal phase for dispersions of rod-like colloids.
the edges as well. For the spherocylinder surface the majority of the surface is cylindrical, but at the endcaps it is spherical. Here, we have only used the equation for the curvature that is valid for the majority of the cylindrical deformation zones. This means that we assume δ_disk = δ_l and δ_rod = δ_cyl. For the polymer sizes we have considered, the polymer is at least a factor 2 smaller than the disk diameter D or rod length L meaning that a large portion of the polymer configurations near the surface is unaffected by the disk edges or rod endcaps and therefore consider this approximation is accurate.

The last step is to consider the interactions between different polymers. For these ‘interacting’ polymers expressions can be obtained by interpolation functions between the dilute limit and the semi-dilute limit, where the polymer physics is governed by a correlation length $\xi \propto (\phi R^3)^{-0.77}$. This makes both $\delta_l$ and $\partial \tilde{\Pi}^R / \partial \phi^R$ concentration-dependent and they can be approximated as [26]:

$$\frac{2 \delta_l}{D} = \frac{pq}{1 + \beta \phi R^3},$$

$$\tilde{\Pi}^R = \frac{\nu_c}{\nu_p} \left( \phi R + \zeta \phi R^{3+1} \right),$$

$$\frac{\partial \tilde{\Pi}^R}{\partial \phi^R} = \frac{\nu_c}{\nu_p} \left( 1 + 3 \gamma \zeta \phi R^{3+1} \right),$$

with $p = 1.07$, $\beta = 3.95$, $\gamma = 0.77$, and $\zeta = 1.62$. We can recognise the semi-dilute good solvent limits $\delta_l \propto \phi R^{0.77}$ and $\tilde{\Pi}^R \propto \phi R^{3+1}$, where $\delta_l$ scales as the correlation length $\xi$ and $\tilde{\Pi}^R$ as $\xi^{-3}$. This means that the depletion thickness $\delta_l$ can increase significantly when the polymer concentration is increased due to polymer–polymer interactions as indicated in the right plot of figure 2. This graph only displays the depletion thickness at a flat surface. As the polymer reservoir relative concentration $\phi^R$ becomes of the order of 0.15 the depletion thickness has reduced to about the same value as for the PHS description ($\delta = R_0$), see the right panel of figure 2. Thus for increasing polymer concentrations the depletion attraction becomes shorter ranged. In this case we also still consider the surface curvature by using $\delta_{\text{disk}} = \delta_l$ and $\delta_{\text{rod}} = \delta_{\text{cyl}}$, but now $\delta_l$ is given by equation (7).

Phase coexistence between two phases requires chemical and mechanical equilibrium:

$$\tilde{\mu}_1 = \tilde{\mu}_2,$$

$$\tilde{\Pi}_1 = \tilde{\Pi}_2,$$

where the normalised colloid chemical potential $\tilde{\mu} = \partial \omega / \partial \eta$ and the normalised system osmotic pressure $\tilde{\Pi} = \tilde{\mu} \eta = -\omega$. For the PHS and dilute polymer models the expressions for $\omega$ can be reduced to $\omega = f^0 - \alpha \tilde{\Pi}^R$ as $\alpha$ and $\partial \tilde{\Pi}^R / \partial \phi^R$ are independent of polymer concentration. Additionally, phase coexistences between more than two phases may be found when all these phases are in thermodynamical and mechanical equilibrium. It is also possible to have an isostructural coexistence of a low and high concentration phase of the same type (e.g. isotropic–isotropic coexistence) for polymer reservoir concentration above the critical point, which is given by:

$$\frac{\partial^2 \omega}{\partial \eta^2} = \frac{\partial^3 \omega}{\partial \eta^3} = 0.$$  \hspace{1cm} (12)

This isostructural coexistence is however only observed in a phase diagram if it is preferred (lowest $\omega$) over coexistence with other phases (e.g. isotropic–nematic (I–N)). The boundary for this is denoted as the critical endpoint, where all the mentioned conditions apply (e.g. $\tilde{\mu}_1 = \tilde{\mu}_N$, $\tilde{\Pi}_1 = \tilde{\Pi}_N$, $\partial^2 \omega_1 / \partial \eta^2 = \partial^3 \omega_1 / \partial \eta^3 = 0$).

3. Results and discussion

3.1. Phase diagrams of disk–polymer mixtures

In figure 3 phase diagrams are shown for disk–polymer mixtures with a disk aspect ratio $L/D = 0.08$ for various polymer–disk size ratios $q = 2R_0 / D$. Phase diagrams are plotted in terms of the colloidal platelet volume fraction $\eta$ versus the polymer reservoir concentration $\phi^R$ (a) or the polymer system concentration $\phi$ (b)–(d). Here the solid curves indicate the binodals predicted using the PHS approximation, the dotted curves refer to the binodals using the dilute polymer description, and the dashed curves represent the binodals for the interacting polymer description.

In figure 3 the following phases and coexistences can be identified at small polymer concentrations: a single colloidal isotropic (I) phase at $\eta \lesssim 0.28$, an I–N coexistence at $0.28 \lesssim \eta \lesssim 0.34$, a single nematic (N) phase at $0.34 \lesssim \eta \lesssim 0.44$, a nematic–columnar coexistence at $0.44 \lesssim \eta \lesssim 0.53$, and a single columnar (C) phase at $\eta \gtrsim 0.53$. As the polymer concentration increases the I–N and N–C coexistence regions widen. The I–N and N–C coexistence regions coincide at a particular value of $\phi^R$ depending on $q$ (around 0.017 in figure 3(a)) and a triple I–N–C coexistence is predicted. These are indicated by the dashed lines only for the PHS and interacting polymer descriptions of depletants. For higher polymer concentrations only I–C coexistence is found. The triple lines (figure 3(a)) become three-phase coexistence regions (figures 3(b)–(d)) when plotting the polymer system concentration on the ordinate.

For $q = 0.05$ (figures 3(a) and (b)) the curves for the dilute and interacting polymer are almost indistinguishable as the effects of polymer–polymer interactions are negligible at these low polymer concentrations (below $\phi^R = 0.3$). While not indicated, the triple coexistence for the dilute polymer case also negligibly differs from the interacting polymer description. The deviation of PHS from the other approximations is quite small. From figure 2 it follows that in these cases the depletion thickness for PHS is smaller than for flat surfaces, which causes the phase coexistences to happen at slightly higher polymer concentrations.

In figures 3(c) and (d) phase diagrams are shown at the same $L/D$ but for higher $q$ values. In figure 3(c) the deviation between the different descriptions has increased with respect to the upper graphs ($q = 0.05$). Again the onset of the coexistences is at higher polymer concentrations for the
PHS model than for the other models. This difference is most pronounced when looking at the shift of the triple I–N–C coexistence regions at low colloid concentrations. This region also denotes the borders of the I–N and I–C coexistences, which therefore have also shifted. While the binodal curves for the dilute and interacting polymer depletants look again similar, the triple coexistence region for the dilute polymers (not shown) is similar to PHS instead. This can be explained by focusing at the free volume fractions. When the polymer concentration increases, the I–N binodals widen and the differences in colloid volume fractions $\eta$ in the coexisting phases increase. As a result the differences in free volume fractions $\alpha$ between the two phases become quite large. The variation in $\delta$ for the PHS and dilute polymer description becomes negligible compared to the difference in $\alpha$. As the difference in free volume is a determining factor in the concentrations of the binodals, the deviations between the PHS and dilute polymer descriptions themselves therefore become negligible at high polymer concentrations. When polymer–polymer interactions are accounted for, however, $\delta$ decreases upon increasing polymer concentration leading to a much smaller increase in the free-volume difference between the phases and thus leading to different phase behaviour as for the other models.

In figure 3(d) at $q = 0.4$ there are several changes as compared to figures 3(a)–(c). Due to the longer-ranged attractions $I_1$–$I_2$ coexistence is now possible. This modifies the topology of the phase diagram, because it also leads to an $I_1$–$I_2$–N triple region. As a result the deviation between the I–N–C regions has increased significantly. The regions for I–N, N–C, and I–N–C coexistence have only a small amount of overlap. The triple coexistence regions for dilute polymers (not shown) are indistinguishable from those for PHS. However, inclusion of the polymer–polymer interactions now significantly modifies the locations of several phase equilibria regions. This is caused by the fact that the binodals are now located at concentrations close to polymer coil overlap where nonideal behaviour (decreasing $\delta$ with increasing $\phi^R$ and increasing $\partial \Pi^R / \partial \phi^R$ with $\phi^R$) gets increasingly important. Hence it follows that polymeric interactions should be properly accounted for in case of larger $q$ values at which the phase equilibria get near or above the polymer coil overlap concentrations.

Unfortunately, it is difficult to directly assess how much better the interacting polymer description would compare to experimental systems. In reported investigations of the disk–polymer phase behaviour [8, 11] the discotic colloids have a high degree of dispersity that significantly impacts the phase behavior. Therefore, it would be needed to account for this degree of dispersity in our model system, a difficult endeavour which is beyond the scope of this paper. However, there is a continuing development in synthesizing more well-defined colloidal model systems. Additionally, the shifts of the binodals presented upon varying $q$ are in line with expectations from the case of spherical colloids [26, 27, 37]. There the gas–liquid coexistence region is also predicted to be much larger using a PHS description instead of a more accurate polymer description or than in experimental results. It is clear that the effect of polymeric excluded volume interactions will shift the binodals and multi-phase coexistence regions to other polymer concentrations and that the deviations from PHS and dilute polymer descriptions will increase with $q$. The direction of the shifts of the phase state regions differ per system. While for mixtures of colloidal spheres and polymers for instance the single phase fluid region expands due to accounting for polymeric interactions, this is different for disks or platelets.

### 3.2. Phase coexistence overview disk–polymer mixtures

Previous studies on disk–PHS mixtures revealed various interesting features regarding the topology of the phase diagrams as mediated by the shape parameters [21, 22]. Here we focus on what kinds of phase coexistence regions are found as a function of $L/D$ and $q$, to verify whether the inclusion of excluded volume interactions between the polymer segments affects the nature of the observed phases and to which degree.

Therefore we have computed when a critical endpoint or four-phase coexistence appears in a phase diagram [22] at a particular $L/D$ and $q$ (figure 4). The critical endpoints indicate the onset of certain isostructural coexistences ($I_1$–$I_2$, $N_1$–$N_2$, $C_1$–$C_2$). For the PHS description the occurrence of a critical
Figure 3. Effect of using different polymer descriptions on the phase behaviour of disk–polymer mixtures. Phase diagrams for mixtures of hard disks and polymers for disk aspect ratio \(L/D = 0.08\) and different relative polymer sizes \(q = 2R_g/D\) as a function of colloid volume fraction \(\eta\) and (a) polymer reservoir concentration \(\phi^R\) or (b)–(d) polymer system concentration \(\phi\). The different colloidal phase states and phase coexistences are comprised of the isotropic (I), nematic (N), and columnar (C) phase. The different curves correspond to binodals using different polymer descriptions: PHS (solid curves), dilute polymer (dotted), and interacting polymer (dashed). The dashed lines and shaded areas indicate the I–N–C coexistence for the PHS and interacting polymer descriptions. In (d) additional coexistences are found involving a low and high concentration isotropic phase (I₁–I₂).

The inset shows a critical endpoint in the phase diagram is indicated by the solid curves. The isostuctural two-phase coexistence in a phase diagram is also accompanied by a certain additional three-phase coexistence (see I₁–I₂–N in figure 3(d)). The type of three-phase coexistence is indicated by the colours of the enclosed regions. At the intersections of the coloured regions, where three-phase coexistence regions meet, are curves along which four-phase equilibria are predicted. Although possible theoretically [23] no five phase coexistence was found. In the graphs four-phase equilibria are indicated for PHS by the long-dashed curves. For instance in figure 4, at relatively high \(q\), I₁–I₂ coexistence is predicted with I₁–I₂–N coexistence in the left region and I₁–I₂–C coexistence in the right region. The long-dashed curve intersecting these regions indicates the parameter where an I₁–I₂–N–C coexistence is observed in a phase diagram. The dotted and short-dashed curves show the occurrence of critical endpoints and four-phase coexistences for the dilute and interacting polymer descriptions respectively.

When comparing the results for the different descriptions it is important to note that at higher \(q\), we also observed higher polymer concentrations for the critical endpoints and four-phase coexistences than at lower \(q\). This is in line with the observations in figure 3, where the relevant polymer concentration range increases for higher \(q\). Additionally, it was found that the \(L/D\) value is of much smaller impact on the polymer concentration at the different curves. Hence when looking in a certain \(q\) range the differences between the various models are quite similar regardless of the \(L/D\) value.

For example, similar results are found for the N₁–N₂ and C₁–C₂ coexistence at small \(q\) and all \(L/D\) values. The dilute and interacting polymer descriptions are indistinguishable due to the low polymer concentrations in those regions. The smaller depletion thickness for PHS causes a slight shift.
While this means that I1–I2 coexistence will be present in the curves of the interacting polymers and PHS coincide. In figure 5 phase diagrams are shown for rod–polymer mixtures shift to higher coexistence the polymer–polymer interactions start to affect critical endpoints and four-phase coexistences for the dilute and interacting polymer respectively. Interestingly however, at the critical endpoints for I1–I2 coexistence the polymer–polymer interactions start to affect the phase behaviour making the curves of the interacting polymers shift to higher q than for dilute polymers. This makes the curves of the interacting polymers and PHS coincide. While this means that I1–I2 coexistence will be present in the phase diagrams for the same parameters, the particle concentrations can still differ significantly as indicated by figure 3(d). Overall however this means that the previous results regarding the topology of the phase diagrams [21, 22] still hold well when accounting for polymer–polymer interactions.

### 3.3. Phase diagrams of rod–polymer mixtures

In figure 5 phase diagrams are shown for rod–polymer mixtures with aspect ratio (a) and (b) $L/D = 5$ or (c) and (d) $L/D = 100$ for various q values as indicated. The phase diagrams are presented in a similar way as for disk–polymer mixtures. Besides the fact that phase transitions occur at quite different concentrations, the specific phase states are different. Not all coexistences are indicated explicitly in the graphs. Additionally, for (c) and (d) $L/D = 100$ only a low colloidal concentration range is shown as differences in the models are mainly found in this region. At lower q values (figures 5(a) and (c)) the results are very similar to disk–polymers mixtures (figures 3(a) and (b)). The curves for the dilute and interacting polymer are rather similar and the deviation with the PHS model is small. Additionally for figure 5(c) $L/D = 100$ the I–N coexistence region does not widen upon increase of the polymer concentration regardless of the polymer description.

Hence, the results remain in agreement with calculations based on a simpler second virial coefficient model, which predicted the widening of this binodal would only occur at much higher polymer concentrations for these long rods [56].

In figures 5(b) and (d) the phase behaviour of rod–polymer mixtures is plotted for higher q values. For (b) $q = 1$ it is somewhat difficult to identify the different phase coexistences in the graph, but the main trends are quite similar as for disks at $q = 0.4$ (figure 3(d)). There is a significant change in all coexistence regions between the PHS and interacting polymer model and the I1–I2 region is smaller for the interacting polymer description as well. The dilute polymer case is almost identical to the PHS model in both binodals and three-phase coexistences. From figure 2 we can see that in these cases the depletion thickness for PHS is smaller than for flat or cylindrical surfaces, which causes the phase coexistences to happen at slightly higher polymer concentrations.

For the longer rods at $L/D = 100$, a much higher q value is needed to find significant deviations between the different polymer descriptions than for the shorter rods at $L/D = 5$, since the polymer concentrations at the binodals are much smaller at similar q values. Therefore in figure 5(d) the phase diagram is plotted for $q = 8$. Here, I1–I2 coexistence is found for the PHS and dilute polymer model, but it is metastable for the interacting polymer model as the range of the depletion attraction for the interacting polymer model (indicated by the depletion thickness $\delta$) becomes too small. Interestingly, in this case the dilute polymer model is now different from the other models as well. It appears that for this high q value the depletion thickness is lowered compared to the PHS model due to the cylindrical surface curvature, but not as small as for the interacting polymer model, leading to a phase behaviour that is somewhat in between the other cases.

Again, a direct verification of our results with reported experimental results is difficult. Unlike for disk–polymer mixtures there are quite monodisperse model systems in the form of rod-like viruses [9, 12]. However, there are other issues in describing these systems, namely the semiflexibility and surface charge of the rods. Nevertheless, similar to the disk–polymer mixtures, the results for the rod–polymer mixtures are in line with the expectations for sphere–polymer mixtures [26, 27, 37].

### 3.4. Phase coexistence overview rod–polymer mixtures

For rod–PHS mixtures a similar phase behaviour overview was predicted by calculating the different critical endpoints and four-phase coexistences [24]. In this case additional four-phase coexistences and a five phase coexistence are obtained which do not include isostructural coexistence. In figure 6 we have indicated the occurrence of non-isostructural four-phase coexistences (left) and critical endpoints and related four-phase coexistences (right) for the different polymer descriptions. Just like with the disks, it was found that the polymer concentration at the curves is larger at high q values than low q values. However, now the $D/L$ value impacts the polymer concentration at the curves as well: within a certain q range a smaller polymer concentration is found for lower $D/L$ values.
Figure 5. Phase diagrams for mixtures of hard spherocylinders ((a) and (b) \( L/D = 5 \); (c) and (d) \( L/D = 100 \)) and polymers for size ratios (a) and (c) \( q = 0.3 \), (b) \( q = 1 \), and (d) \( q = 8 \) using various descriptions of the polymeric depletants. The different colloidal phase states and phase coexistences are comprised of the isotropic (I), nematic (N), smectic-A (Sm), AAA crystal, and ABC crystal phase. In (b) and (d) additional coexistences are found involving a low and high concentration isotropic phase (I1–I2).

Figure 6. Overview of the different non-isostuctural (left) and isostructural (right) phase coexistences found for mixtures of hard spherocylinders and polymers as a function of \( L/D \) and \( q \). In the left plot the solid curves indicate the four-phase coexistence curves for the PHS model, while in the right graph they indicate the occurrence of a critical endpoint. The long-dashed curves in the right plot indicate the four-phase coexistences related to the isostructural coexistence. The dotted and short-dashed curves indicate the dilute and interacting polymer model, respectively.

At low \( q \) roughly similar results (although with different dense phase states) are obtained as for disk–polymer mixtures, which is not surprising as this was also observed in the phase diagrams. For the I–N–AAA–ABC and N–Sm–AAA–ABC (left) and the Sm1–Sm2, AAA1–AAA2, and ABC1–ABC2 coexistence (right) the curves are nearly indistinguishable between the dilute and interacting polymer models and these are located only slightly below the PHS model. In these cases the polymer concentrations at the curves are well below the overlap concentration at all \( D/L \) values.

The other curves at higher \( q \) (I–N–Sm–AAA, I–N–Sm–ABC, I–Sm–AAA–ABC, I1–I2, N1–N2) are more affected by inclusion of polymer–polymer interactions. The curves for the interacting polymers shift to higher \( q \) as compared to those for the dilute polymers. While for most conditions the result is still very similar as for the PHS model, for the I1–I2 coexistence there is a more significant change when accounting for polymeric interactions. We also do not see as big of a difference between the dilute polymer and PHS model as for the I1–I2 coexistence for disk–polymer mixtures.
in figure 4, since $\delta$ will decrease at high $q$ for cylindrical surfaces (see figure 2) and at the high $q$ values in figure 6 it will become closer to the $\delta$ for PHS. At much higher $q$ than plotted in figure 6, there might be more significant changes between the PHS model and both other models as the surface curvature continues to decrease the depletion thickness further. We found that at much higher $q$ the value of $\phi^0$ does not change significantly when moving along the I$_1$–I$_2$–N and I–N$_1$–N$_2$ curves, so the difference between the dilute and interacting polymer model should stay fairly constant as well. Overall though the results remain very similar to what has been reported previously for rod–PHS mixtures [24]. This means that the same type of multi-phase coexistences are still found at similar shape parameters.

4. Concluding remarks

In this paper the influence of the description of polymeric depletants on the phase behaviour of colloidal disk–polymer and rod–polymer mixtures was investigated. We have found that in the region where the isostructural isotropic fluid–fluid coexistence becomes favourable, the polymer nonideality starts to influence the phase behaviour. Especially in case of relatively large polymer chains, there are significant shifts of the phase coexistence regions. This influence is of a quantitative nature as the particle concentrations of the coexistence regions differ. The phase diagram topology is, however, not affected. The same kinds of phase equilibria are observed at similar particle aspect ratios and polymer size including the four- and five-phase coexistences. Therefore we have developed a model which should be particularly more accurate for relatively large depletant sizes compared to simpler models, while also having shown that the simpler models should still be accurate for smaller depletant sizes and qualitatively predictive for larger depletant sizes. However, there is an urgent need for systematic model experiments and computer simulations of well-defined mixtures of containing either colloidal rods plus nonadsorbing polymers or colloidal discs plus nonadsorbing polymers.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix A. Pure disk dispersions

To describe the equations of state of a pure hard disk dispersion in isotropic or nematic states, we use the following expression for the normalised free energy $f = F_{Vc}/(k_B TV)$ following a Parsons–Lee approach [44, 57–59]:

$$f_{\text{UN}} = \ln \eta - 1 + \frac{f_{\text{os.LN}}}{\eta} + \frac{4\eta - 3\eta^2}{2\pi \Lambda (1 - \eta)^2} \Theta_{\text{LN}},$$  \((A.1)\)

where $k_B T$ is the thermal energy, $V$ the system volume, $\eta = \rho_v \nu_c$ the colloid volume fraction with colloid number density $\rho_v$ and colloidal particle volume $\nu_c = \pi LD^2/4$. Here $f_{\text{os}}$ is the orientational entropy contribution to the free energy, while $\Theta$ reflects the normalised averaged excluded volume between disks. Both $f_{\text{os}}$ and $\Theta$ differ for the isotropic and nematic phase as they depend on the orientational distribution function $\psi(\theta)$, which gives the probability for a particle to assume a certain orientation. For the isotropic phase $\psi(\theta) = 1/(4\pi)$ this leads to [44]:

$$f_{\text{os.I}} = 0,$$ \((A.2)\)

$$\Theta_I = \frac{2}{8} + \frac{3\pi \Lambda}{4} + \frac{\pi^2 \Lambda}{4} + \frac{\pi \Lambda^2}{2}.$$ \((A.3)\)

For the nematic phase we apply the Gaussian approximation for the distribution function [60]:

$$\psi(\theta) \approx \begin{cases} \frac{(\kappa/4\pi) \exp[-(1/2) \kappa \theta^2]}{\kappa} & \text{for } 0 \leq \theta \leq \pi/2, \\ \frac{(\kappa/4\pi)(\pi/2 - \theta^2)}{\kappa} & \text{for } \pi/2 \leq \theta \leq \pi, \end{cases}$$ \((A.4)\)

with $\theta$ as the angle between the disk and the nematic director. This leads to [44]:

$$f_{\text{os.N}} = \ln \kappa - 1,$$ \((A.5)\)

$$\Theta_N = \frac{\pi^{3/2}}{2\sqrt{\kappa}} + 2\pi \Lambda,$$ \((A.6)\)

$$\kappa = \frac{\pi (4\eta - 3\eta^2)^2}{64\Lambda^2 (1 - \eta)^2},$$ \((A.7)\)

where $\kappa$ quantifies how sharply peaked the orientation distribution function is and can be found by minimising the free energy with respect to $\kappa$. This leads to the following expressions for the osmotic pressure and chemical potential:

$$\tilde{\mu}_{\text{UN}} = \ln \eta + \frac{f_{\text{os.LN}}}{\eta} + \frac{8\eta - 9\eta^2 + 3\eta^3}{2\pi \Lambda (1 - \eta)^2} \Theta_{\text{LN}},$$ \((A.8)\)

$$\tilde{\Pi}_{\text{LN}} = \eta + \frac{2\eta^2 - \eta^3}{\pi \Lambda (1 - \eta)^3} \Theta_{\text{LN}}.$$ \((A.9)\)

For the columnar phase the free energy expression is derived from an extended cell theory [43, 44]. However we use an additional factor $-\ln 4$ as it has led to improved agreement with computer simulation results for both pure disk dispersions and mixtures of disks and PHS [61]:

$$f_{c} = \ln \eta - 1 + 2 \ln \left( \frac{3\pi \Delta^2}{2\Lambda (1 - \Delta^2)} \right) - 2 \ln \left( \frac{1 - \Delta^2}{3} \right) - 2 \ln \left( \frac{1}{\Delta} \right) - \ln 4,$$ \((A.10)\)
with
\[ \Delta = \frac{\sqrt{27K^{2/3}} - 4\sqrt[3]{3}x}{6^{2/3}x^{2/3}}, \]
(A.11)
\[ K = 27x^2 + \sqrt{3}x^3(243x + 32), \]
(A.12)
\[ x = \frac{\eta}{\eta_p}, \]
(A.13)
where \( \kappa \) can be similarly interpreted as for the nematic phase, \( \Delta \) is related to the distance between disks in different columns, and the volume fraction at close packing is given by \( \eta_0 = \pi/(2\sqrt{3}) \). This leads to the following expressions for the osmotic pressure and chemical potential:
\[ \mu c = f c \frac{3}{\eta} + \frac{3}{1 - \chi \Delta^2}, \]
(A.14)
\[ \tilde{\Pi}_c = \frac{3\eta}{1 - \chi \Delta^2}. \]
(A.15)

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