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Phase stability of colloidal spheres mixed with semiflexible supramolecular polymers

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**Graphical Abstract**

**Abstract**

**Hypothesis:** Mixtures of colloids and supramolecular polymers may exhibit stimuli-responsive phase behaviour. However, in theoretical descriptions of such systems, the polymers are commonly described either as flexible chains or as rigid rods, while in experimental systems supramolecular polymers usually fall in between these two limits. We expect the flexibility of the polymers to have a profound effect on the stimuli-responsive phase behaviour.

**Theory:** We propose a general approach to predict the phase behaviour of colloidal hard spheres mixed with covalent or supramolecular polymers of arbitrary persistence length using free volume theory and an interpolation between flexible and rigid chains.

**Findings:** The binodals are predicted to shift to lower monomer concentrations as the persistence length is increased, making the polymers more efficient depletants. The persistence length is therefore an additional degree of freedom for manipulating the phase behaviour of colloid–polymer mixtures. We show that by manipulating the persistence length of temperature responsive supramolecular polymers, a wide range of phase diagrams with various topologies can be obtained. For example, we find phase diagrams with a critical point but no triple point or displaying two triple points for temperature-sensitive supramolecular polymers mixed with hard spheres.

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**1. Introduction**

Mixtures of colloidal particles and nonadsorbing polymers can show a wealth of phase states and coexistences [1–4] and such
mixtures can be encountered both in biology and industry products. Typically this phase behaviour is insensitive to temperature as it is driven by entropy. However, supramolecular polymers are responsive to external stimuli like light or temperature [5–7] and could lead to stimuli-responsive phase behaviour of colloidal–polymer mixtures when used instead of conventional polymers. The stimuli-responsive nature of supramolecular polymers stems from the noncovalent bonds between the monomers, leading to a responsive polymer chain length distribution [8,9]. Previously we have derived theoretical predictions [10,11] for the phase behaviour of colloids mixed with nonadsorbing supramolecular polymers. In Ref. [10] the polymer was treated as a flexible Gaussian coil, while in Ref. [11] it was treated as a rigid spherocylinder. It turned out that the phase behaviour differed strongly in a quantitative sense; for rigid depletants phase transitions occur at relatively low concentrations. However, these descriptions are only valid in the two extreme limits of (non) flexibility, while in reality supramolecular polymers are often in between these limits [12–14], denoted as semiflexible. Hence this provided for us the motivation to find a way to predict the phase behaviour for colloids mixed with semiflexible supramolecular polymers.

The phase behaviour of mixtures of colloids and nonadsorbing polymers is commonly understood in terms of the depletion interaction [4,15,16]. The configurational entropy of the polymer is lower close to the colloidal surface and therefore a zone around the colloidal particles is depleted of polymers. When the depletion zones of different colloidal particles overlap, the available volume and thus the entropy of the polymers increases. This leads to a net attraction between the colloidal particles. The resulting phase behaviour can be predicted semi-quantitatively using for instance free volume theory (FVT) [17].

In previous work on the phase behaviour of semiflexible covalent polymers mixed with colloidal particles [18] FVT was extended using a Padé approximation of the excluded volume between the polymers and colloidal particles [19]. This method, however, is not applicable close to the fully rigid polymer limit. Hence we derive a new framework to calculate the phase behaviour of covalent polymers mixed with colloidal spheres based on similar methodology using FVT for the full range of polymer chain stiffness. Then we apply this to supramolecular polymers to compute the phase behaviour as a function of polymer persistence length.

2. Theory

2.1. Free volume theory

Within the framework of free volume theory a mixture of colloidal spheres and nonadsorbing semiflexible supramolecular polymers is in equilibrium with a polymer reservoir through a hypothetical semi-permeable membrane. The colloidal particles are considered hard spheres and thus cannot overlap with each other or the polymers. Excluded-volume interactions between polymer segments are ignored, which according to our previous predictions for both limits [10,11] should still lead to a semi-quantitative result. The supramolecular polymers are considered to be described by a simple equilibrium polymer model [20], where the scission energy $E$ needed to break a bond between two monomers, is the same regardless of polymer length. This is most consistent with an isodesmic growth mechanism [8,9], where the addition of each monomer has the same energy gain, though it can also be valid for a cooperative growth mechanism in the polymeric regime, by adjusting the scission energy $E$ with an activation or nucleation energy. We consider the monomers themselves to be cylinders with length $l_m$, diameter $D_m$, and volume $v_m = \pi l_m D_m^2/4$.

In the equilibrium polymer model the polymers are characterised by an average number of monomers $\langle N \rangle = \sqrt{\phi^p \exp U}$ [20], where $\phi^p$ is the monomer volume fraction in the reservoir and $U = E/(k_BT)$ is the normalised scission energy, with $k_BT$ the thermal energy. From FVT it follows that the semi-grand potential $\Omega$ is given by [4,21]:

$$\Omega = \Omega_{\text{free}} - \int_0^{V^p} \left( \frac{3}{2} D v_2 R \right) \frac{\partial \Gamma^R}{\partial \phi^p} d\phi^p,$$

(1)

where $v_2 = \pi D^2/6$ is the volume of a colloidal sphere, $D_c$ the colloid diameter, $V$ the system volume, $f^0$ the normalised Helmholtz free energy of a pure colloidal dispersion, $\alpha = (V_{\text{free}}/V)$ the ensemble-averaged free volume fraction, and \(\Pi^R = \Pi^p v_2/(k_BT)\) the normalised osmotic pressure in the reservoir. As we ignore the excluded-volume interactions between polymer segments $\Pi^R$ is Van ‘t Hoff-like and given by:

$$\Pi^R = \frac{v_2}{v_m} \phi^p \left( \langle N \rangle \right)$$

(2)

$$- \frac{2 \phi^p}{3 s^3 \lambda \langle N \rangle},$$

(3)

where $s = D_m/D_c$ the monomer diameter to colloid diameter ratio and $\lambda = l_m/D_m$ the monomer length to diameter ratio. The free energy for the phase states in a pure colloidal dispersion is approximated by the Carnahan-Starling equation of state for the fluid phase [22] and the Lenard-Jones–Devonshire cell theory for the solid phase [23]:

$$f^0_s = 2 \frac{1306}{\eta^3} + 3 \eta \ln \left( \frac{1 - \eta}{\eta^{3/2}} \right).$$

(4)

$$f^0_s = 2 \frac{1306}{\eta^3} + 3 \eta \ln \left( \frac{1 - \eta}{\eta^{3/2}} \right).$$

(5)

where $\eta$ is the colloid volume fraction, $\eta_{\text{cp}} = \pi/(3 \sqrt{2}) = 0.74$ the colloid volume fraction at close packing, and the numerical constant 2.1306 comes from computer simulation results [24].

The free volume fraction $\alpha = (V_{\text{free}}/V)$ is approximated by that of an undisturbed (polymer-free) colloidal dispersion, $(V_{\text{free}}) = (V_{\text{free}})$. For covalent semiflexible polymers a term for $\alpha$ was derived previously [18]. A Padé approximation of the excluded volume was utilised that is in agreement with Monte Carlo calculations over the complete flexibility range [19]. This in turn allowed for quantifying the depletion thickness $\delta$ [18]. The dependence used for the free volume fraction $\alpha$ as a function of $\delta$ is however only applicable for relatively flexible polymer chains and the resulting phase behaviour therefore is not valid close to the rigid chain limit, which is relevant for the supramolecular polymers of our work. However, both for flexible and rigid polymers, the free volume fraction can be approximated using $\alpha = (1 - \eta) \exp(-Q)$ [10,11], where $Q$ is based on the work of inserting the polymer in a hard sphere dispersion. Therefore we apply the Padé approximation to the expressions of $Q$ for conventional polymers to find an interpolation that leads to the correct limiting expressions and subsequently apply a similar interpolation to the supramolecular polymers. Then using the expressions for $\alpha$, we can derive expressions for the colloidal chemical potential $\mu$ and osmotic pressure $\Pi$ in the system. The phase behaviour can be computed by imposing the equilibrium conditions between phases I and II:

$$\mu_1 = \mu_{\text{I}} \left(6\right)$$

$$\Pi_1 = \Pi_{\text{I}} \left(7\right)$$
2.2. Covalent polymer

We consider a polymer chain composed of $N$ monomers with monomer length $l_m$, diameter $D_m$, and volume $v_m = \pi l_m^2 D_m^2 / 4$. The polymer contour length is given by $L_c = l_m N_c l_i N_i$, where $N_i$ is the number of Kuhn segments, each with Kuhn length $l_i$ [25]. Each Kuhn segment has a volume $v_i$ and can freely rotate with respect to the other Kuhn segments in the chain. In the flexible chain limit Gaussian chain statistics imply that the radius of gyration is then given by [26,27]:

$$ R_g = l_i \sqrt{\frac{N_i}{6}}. $$

The two relevant (normalised) length scales are illustrated in Fig. 1 for three different Kuhn lengths $l_i$. These 'effective' Kuhn segments are invoked to represent the flexibility of the polymer and are different from the actual monomers the polymer is composed of. For example, a stiff polymer is modelled with only a small number of Kuhn segments $N_i$, but can still be composed of a large amount of actual monomers $N$.

In the rigid chain limit it is assumed the polymer is a spherocylinder with diameter $D_m$ and length $L$ (total length $L + D_m$). We then assume that the total volume of the Kuhn segments $N_i v_i$ should be equal to the volume of the spherocylinder $\pi D_m^2 l_i + \pi l D_m^2 / 4$. This allows us to relate Kuhn segment properties to spherocylinder properties:

$$ \frac{L}{D_m} = \frac{4 v_i}{\pi D_m^2 N_i} - \frac{2}{3}. $$

The spherocylinder length and contour length should have the same dependency on $N_i / \partial L_c / \partial N_i = \partial l / \partial N_i$. With $L_c = l_i N_i$ this leads to $l_i = 4 v_i / (\pi D_m^2)$ and:

$$ \frac{L}{D_m} = \frac{l_i}{D_m} N_i - \frac{2}{3}. $$

The Kuhn segments can thus be considered as cylinders with $v_i = \pi D_m^2 l_i / 4$, characterised by an aspect ratio $l_i / D_m$. While the fully rigid chain limit has a different shape at the ends of the polymer chains than the Kuhn segments, this should still have minimal effect as we will only consider $(L)/D_m \gtrsim 10$. By equating the total volume of the Kuhn segments $N_i v_i$ to the total volume of the monomers $N v_m$ the following relation between the size ratios for the monomers and Kuhn segments is found:

$$ \Lambda N = l_i N_i / D_m. $$

In order to apply the Padé approximation, we first need to discuss the limiting expressions of $Q$ for rigid and flexible chains. The polymer is assumed to become a spherocylinder when it consists of a single Kuhn segment and thus $N_i = 1$. Also, it should behave as a fully flexible Gaussian polymer coil when $N_i \to \infty$. As $Q$ is also dependent on the excluded volume between the colloid and the polymer, the Kuhn segment–colloid size ratio $t = l_i / D_c$ is an important quantity that is typically ignored in theoretical descriptions of colloid–polymer mixtures. When the Kuhn length is much larger than the colloid size, the excluded volume is similar to that between a spherocylinder and a colloidal sphere [19]. Hence $Q$ should follow the rigid chain limit expression when the Kuhn segment–colloid size ratio $t = l_i / D_c \to \infty$. So while for $N_i \to \infty$ and $t \to \infty$ the polymer might behave as a flexible Gaussian coil, the polymer chain will appear rigid for the colloidal sphere and the expression for $Q$ with a rod-like depletant is more appropriate. Thus the flexible chain limit expression should only apply when both $N_i \to \infty$ and $t \to 0$.

For polymer coils as depletants $Q$ is approximated as follows [17]:

$$ Q_{\text{coil}} = \begin{cases} \frac{3}{2} \pi \left( \frac{2}{3} \right)^3 y + \frac{3}{2} \left( \frac{2}{3} \right)^3 y^2 + 3 \left( \frac{2}{3} \right)^3 y^3, \\
+ \frac{3}{2} \frac{2}{3} \pi \left( \frac{2}{3} \right)^3 y^2 + 3 \left( \frac{2}{3} \right)^3 y^3, \\
\end{cases} $$

Here $y = \eta/(1 - \eta)$ and $2 \delta / D_c$ follows from the ideal Gaussian chain result for the depletion thickness at a spherical surface [28,21]:

$$ \frac{2 \delta}{D_c} = \left[ 1 + \frac{2 \delta t_i}{2 \delta t_i + \frac{3}{4} (2 \delta t_i)^2} \right]^{1/3} - 1, $$

with the depletion thickness at a flat surface given by [29]:

$$ \frac{2 \delta t_i}{D_c} = \frac{2t}{\sqrt{\pi}}, $$

where $q = 2R_g / D_c$.

For the rigid chain limit $Q$ is approximated as for spherocylinder depletants, which is given by [4]:

$$ Q_{\text{rod}} = (3s + 3s^2 + s^3) y + \frac{3}{2} (s^2 + 3s^3) y^2 + 3s^3 y^3 + \frac{3}{2} [1 + 2s + s^2] y + (3s + 3s^2) y^2 + 3s^3 y^3. $$

Using $L/D_c = t N_i - 2s / 3$, this can be rewritten as:

$$ Q_{\text{rod}} = (2s + s^2) y + \frac{1}{2} s^2 y^2 + t N_i [1 + 2s + s^2] y + (3s + 3s^2) y^2 + 3s^3 y^3. $$

As Eq. 13 for $\delta$ is not a simple polynomial in terms of $N_i$ and $t$, Eqs. 12 and 16 for $Q$ are unsuitable for a Padé approximation in these variables. In order to circumvent this problem we carry out the interpolation in the coordinates $t$ and $q$. This means we rewrite Eq. 16 using $q = 2t \sqrt{N_i / 6}$ and find:

---

**Fig. 1.** Sketch illustrating the key polymer length scales, radius of gyration $R_g$ and Kuhn length $l_i$, in relation to the colloid diameter $D_c$ and the number of Kuhn segments for polymers with various degrees of flexibilities with $N_i = 1000$ (left), $N_i = 8$ (middle), and $N_i = 1$ (right) for fixed $R_g$. 

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\[ Q_{\text{rod}} = \frac{(2s + s^2)y + \frac{3\sqrt{3}}{2}y}{2} + \frac{3\sqrt{3}}{2}y \left(1 + 2s + s^2\right)y + (3s + 3s^2)y^2 + 3s^2y^3. \]  

We first consider the limit \( N \to \infty \), for which we should obtain \( Q_{\text{rod}} \) when \( t \to \infty \) and \( Q_{\text{coal}} \) when \( t \to 0 \). The following Padé approximation can account for this:

\[ Q_{N_i \to \infty} = \frac{A_0 + A_1t}{1 + A_2t}. \]

The constants \( A_0, A_1, \) and \( A_2 \) are chosen such that a Taylor series leads to \( Q_{\text{coal}} \) for \( t \to 0 \) and a Taylor series for \( 1/t \to 0 \) leads to \( Q_{\text{rod}} \). The constants are given by:

\[ A_0 = Q_{\text{coal}}, \]
\[ A_1 = 2A_2 \frac{Q_{\text{coal}}(2s + s^2)y + \frac{3\sqrt{3}}{2}y}{2}, \]
\[ A_2 = \frac{Q_{\text{coal}}(2s + s^2)y + \frac{3\sqrt{3}}{2}y}{2P_2[(1 + 2s + s^2)y + (3s + 3s^2)y^2 + 3s^2y^3]}. \]

Now we have an expression for \( Q \) in the limit of \( N \to \infty \) and \( N_i \to 1 \) in the coordinates \( t \) and \( q \). As we need to stay consistent with our coordinate system both expressions are considered not to depend on \( N_i \) explicitly and the Padé approximation would then revert to the following simple series:

\[ Q = B_0 + \frac{B_1}{N_i}. \]

The phase behaviour for mixtures of covalent semiflexible polymers and colloids can be predicted by applying the equilibrium conditions of Eqs. 6 and 7. Here the normalised colloid chemical potential and osmotic pressure are found with \( \mu/(k_BT) = \mu = \partial \Pi/\partial \eta \) and \( \Pi = \mu \eta - \omega \). For \( \omega \) we can use Eq. 1 with \( \alpha = (1-\eta)\exp(-Q) \) and \( \partial \Pi/\partial \eta \) do not depend on \( \phi^s \) the expression for \( \omega \) can be simplified to:

\[ \omega = \frac{\rho^s}{2\sqrt{3}\Lambda N}. \]

2.3. Supramolecular Polymer

For supramolecular polymers we use a similar interpolation and assume that the different limits apply based on the average amount of Kuhn segments \( N_i \) and the Kuhn segment to colloid size ratio \( t \) of this average. Hence polymer coils should only be found when \( (N_i) \to \infty \) and \( t \to 0 \), while a rod-like behaviour is expected for either \( (N_i) \to 1 \) or \( t \to \infty \). Similar to Eq. 11 for the relation between the size ratios of Kuhn segments and monomers for covalent polymers, we should get the following expressions for \( (N_i) \):

\[ (N_i) = \begin{cases} \frac{1}{\rho^s} \sqrt{\rho^s \exp \left(\frac{\mu}{k_BT} U \right)} & (N_i) \geq \frac{1}{\rho^s}, \\ 1 & (N_i) < \frac{1}{\rho^s}. \end{cases} \]

The second expression in Eq. 21 was added due to the implication that \( (N_i) \) is considered continuous and can range from 0 to \( \infty \), while \( t \) and \( \Lambda \) are considered constant for a specific colloid–supramolecular polymer mixture. For \( (N_i) < t/(s\Lambda) \), the first expression would lead to \( (N_i) < 1 \), which is inconsistent with the interpolation, where the lower limit of \( (N_i) \) is considered 1. For \( (N_i) < t/(s\Lambda) \) we therefore automatically assume the rigid chain limit for the expression of \( Q \) which should be valid.

In the equilibrium polymer model the supramolecular polymers have an intrinsic polydispersity. The polydispersity of polymers on average increases the extent of the depletion zones around the colloidal spheres [30] and the depletion thickness \( \delta \) increases. For the supramolecular polymer coils the same expressions for \( Q \) and \( \delta \) can be used as in Eqs. 12 and 13, but a different expression needs to be formulated for the depletion thickness at a flat surface \( \partial \delta \). As we do not account for the excluded volume interactions between polymer segments, \( \partial \delta \) can be approximated by [30]:

\[ \frac{2\partial \delta}{\partial \nu} = \frac{2}{\nu_0} \int \frac{N\rho_N\partial \delta_N d\nu}{\nu_0} \]

where \( \partial \delta_N \) represents the depletion thickness for monodisperse chains with length \( N \) and \( \rho_N = \phi^s \exp(-N\nu)/\left(N^2\nu\right)^2 \) the dimensionless concentration for equilibrium polymers of length \( N \) [10,20]. Using Eqs. 8 and 14 and using \( \ln N = \ln \nu \), we obtain:

\[ \partial \delta_N = 2l_q \sqrt{\frac{N}{6\pi}} \]

Resolving Eq. 22 then leads to:

\[ \frac{2\partial \delta}{\partial \nu} = \frac{3q}{\nu} \]

with \( q = 2\sqrt{\nu_0/N\nu} \). This definition of \( q \) is analogous to that of covalent polymers \( q = 2R_q/\nu_0 \), if we consider \( R_q \) to be the radius of gyration of a polymer of length \( (N_i) \).

For the limit of supramolecular rods, \( Q_{\text{rod}} \) is given by [11]:

\[ Q_{\text{rod}} = \frac{(2s + s^2)y + \frac{3\sqrt{3}}{2}y}{2} + 3s\Lambda(N)(1 + 2s + s^2)y + (3s + 3s^2)y^2 + 3s^2y^3. \]

This can be rewritten in terms \( t \) and \( q \) using Eq. 21:

\[ Q_{\text{rod}} = \frac{(2s + s^2)y + \frac{3\sqrt{3}}{2}y}{2} + 3s\Lambda(N)(1 + 2s + s^2)y + (3s + 3s^2)y^2 + 3s^2y^3. \]

The Padé approximation is then almost identical with the constants now being given by:

\[ A_0 = Q_{\text{coal}}, \]
\[ A_1 = 2A_2 \frac{Q_{\text{coal}}(2s + s^2)y + \frac{3\sqrt{3}}{2}y}{2P_2[(1 + 2s + s^2)y + (3s + 3s^2)y^2 + 3s^2y^3]}. \]

The second step in the interpolation is also similar:

\[ Q = B_0 + \frac{B_1}{(N_i)}, \]

with \( B_0 = Q_{\text{coal}}, \)
\[ B_1 = Q_{\text{rod}} - Q_{\text{coal}}. \]

The phase behaviour can be calculated by applying the equilibrium conditions of Eqs. 6 and 7, where \( \mu \) and \( \Pi \) are derived from \( \omega \) as in the previous section. The integral in the expression for \( \omega \) of Eq. 1 however should be split in two parts due to the different limits of Eq. 21. As \( (N_i) \) is concentration dependent the crossover value \( (N_i)_{\text{crossover}} = t/(s\Lambda) \) can be rewritten in terms of the reservoir monomer volume fraction \( \phi^s_{\text{crossover}} = t^2/(s^2\Lambda^2 \exp U) \). When \( \phi^s \leq \phi^s_{\text{crossover}} \), the free volume fraction is given by the fully rigid limit where
\[ \alpha_{\text{rod}} = (1 - \eta) \exp(-Q_{\text{rod}}) \] as determined from Eq. 26. When \( \phi^R > \phi_{\text{crossover}}^R \), the free volume fraction is given by the interpolation with \( \alpha = (1 - \eta) \exp(-Q) \) with \( Q \) given by Eq. 28. Thus we rewrite the integral as follows:

\[
\omega = \int_0^{\phi_{\text{crossover}}^R} \frac{\alpha}{\phi^R - \phi_{\text{crossover}}^R} d\phi^R - \int_{\phi_{\text{crossover}}^R}^{\phi^R} \frac{\alpha}{\phi^R} d\phi^R - \int_0^{\phi_{\text{crossover}}^R} \frac{\phi_{\text{crossover}}^R}{\phi^R} d\phi^R. \tag{29}
\]

where \( \partial \Pi^R / \partial \phi^R \) is given by Eq. 3. In practice the integral from 0 to \( \phi_{\text{crossover}}^R \) is only relevant close to the rigid chain limit as otherwise \( \phi_{\text{crossover}}^R \) is much lower than \( \phi^R \) and the value is close to 0.

3. Results and discussion

3.1. Effectiveness interpolation

In Fig. 2 we show \( Q \) as a function of a Kuhn length to colloid size ratio \( t \) for both covalent (left) and supramolecular (right) polymers for covalent volume fraction \( \eta = 0.15 \) and monomer size ratios \( s = 0.01 \) and \( \Lambda = 0.2 \). These monomer size ratios were chosen to roughly correspond to a typical monomer for supramolecular polymers such as benzen-1,3,5-tricarboxylate (BTA). The value of \( \Lambda = 0.2 \) means that the monomer can be estimated by a disk-like shape and the value of \( s = 0.01 \) corresponds to a monomer diameter of around 1 nm and colloid diameter of around 100 nm. For the covalent polymer the number of monomers is held constant with \( N = 668 \), which is also the average number of monomers \( \langle N \rangle = 668 \) for the supramolecular polymer. The (average) number of Kuhn segments \( N_K \) are also indicated. While we have specified the values of \( s \), \( \Lambda \), and \( N \) or \( \langle N \rangle \), the graphs will be similar for other values as long as the ratio of monomer contour length to colloid diameter \( s \Lambda N = s \Lambda \langle N \rangle \approx 1.34 \) remains constant, since the dominant terms in \( Q \) scale with \( s \Lambda N \) or \( s \Lambda \langle N \rangle \). In Section 3.3 changes in the polymer to colloid size ratio are discussed.

The solid curves show the interpolation function, while the dashed and dotted curves indicate the flexible coil and rod limits. Here we considered a situation where \( t \) is relatively small and goes up to \( t = s \Lambda N = s \Lambda \langle N \rangle \approx 1.34 \). The interpolation follows the appropriate limiting expressions for \( t \rightarrow 0 \) and \( N = \infty \) or \( \langle N \rangle \rightarrow \infty \) (coil) and for \( N = \langle N \rangle = 1 \) (rod). Note that the rod limit of \( N = \langle N \rangle = 1 \) is reached before the limit of \( t \rightarrow \infty \). The figure itself looks similar to the results found for the Padé approximation and Monte Carlo calculations of the excluded volume between a hard sphere and a semiflexible polymer [19], since the excluded volume increases as the polymer becomes more rigid.

When comparing the results for covalent or supramolecular polymers, both figures look similar. However, the values of \( Q \) are considerably lower for the covalent polymers than for the supramolecular polymers. This is due to the different expressions for \( Q_{\text{rod}} \) and \( Q_{\text{coi}} \), which can be attributed to polydispersity effects. In both limits the polymer dispersity of supramolecular polymers increases the depletion zone and therefore increases the average excluded volume between colloids and polymers and \( Q \) [10,11].

3.2. Comparison phase behaviour

In Fig. 3 we show phase diagrams for mixtures of colloids and covalent or supramolecular polymers of variable flexibility with \( s = 0.01 \), \( \Lambda = 0.2 \), and different Kuhn length ratios \( t \). For covalent polymers \( N = 668 \) and \( N_K \) is indicated for the different values of \( t \). For the supramolecular polymers \( \langle N \rangle \) is concentration dependent; these are instead characterised by the scission energy \( U = 19 \). At \( \phi^S = 0.0025 \) the average number of monomers \( \langle N \rangle = 668 \) is equal to that of the covalent polymers. Note that we deliberately plot the phase diagrams as a function of monomer volume fraction \( \phi \) instead of the concentration relative to overlap \( \rho / \rho^* \), which is commonly used in literature for colloid–polymer mixtures. Here the polymer number density \( \rho \) is normalised to the overlap concentration \( \rho^* \). Since the overlap concentration is correlated to the size and flexibility of the polymer, this makes the interpretation of the results more difficult. This is especially true for supramolecular polymers as the size of the polymer is concentration dependent. Again these results will be similar for other values of \( s \), \( \Lambda \), and \( N \) or \( \langle N \rangle \), as long as \( s \Lambda N \) or \( s \Lambda \langle N \rangle \) remains the same. However, as \( s \) is changed the values of \( \phi = x \phi^S \) would vary as well to obtain the same reservoir osmotic pressure \( \Pi^R \) (Eq. 3).

At low polymer concentrations and \( \eta \lesssim 0.49 \) there is a single colloidal fluid (F) phase and at \( \eta \gtrsim 0.54 \) there is a single solid (S) phase.
As indicated by the binodals there is fluid–solid coexistence at $0.49 \leq \eta \geq 0.54$. In all cases this coexistence region widens as the polymer concentration is increased. It is also possible for the fluid phase to demix into a low (gas) and high (liquid) density fluid phase when the depletion interaction becomes sufficiently long-ranged. The onset of gas–liquid coexistence is indicated in the graphs by the critical point for $t=0.03$ (supramolecular polymer only), $t=0.1$ and $t=0.2$. For $t=0.1$ (covalent polymer only) and $t=0.03$ gas–liquid coexistence is metastable. Additionally, for the supramolecular polymers $\langle N_s \rangle$ and $\langle N_i \rangle$ are indicated for the critical point or in the case of $t=0.03$ for $\eta = 0.3$.

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There are some quantitative differences between the results for both types of polymers, which can be attributed to the concentration dependence of $\langle N \rangle$ and the polydispersity effects discussed for Fig. 2. However, the trends regarding the flexibility are very similar for the covalent and supramolecular polymers. The polymer behaves Gaussian coil-like for $t=0.03$ as the (average) number of Kuhn segments $N_s$ of the polymers is large. For smaller $t$ the binodal shifts to higher monomer volume fractions (note that $\phi \to 1$ corresponds to a polymer melt). For $t=0.1$ and $t=0.2$ the polymers are semiflexible and the binodal shifts to lower monomer volume fractions than for $t=0.03$. At $t=1.34$ the rod limit is reached for the covalent polymer and the binodal is at the lowest concentration. At $t=0.85$ the rod limit is reached for the supramolecular polymer at the critical point. For larger $\phi^p$ the rod limit is not reached completely as the contour length of the polymer increases while the Kuhn length does not. The binodals for the different $t$ for both types of polymers show that as the polymer becomes more rigid and the excluded volume between the colloids and polymers becomes larger, the polymer becomes a more effective depletant. The changes in the phase behaviour can become quite large meaning the experimental persistence length is expected to strongly influence the extent of the phase stability region. Additionally, if the persistence length would be dependent on external stimuli, this could boost the stimuli-responsive phase behaviour significantly.

Fig. 3. Phase diagrams of mixtures of spherical colloids and covalent (left panels) or supramolecular (right panels) polymers as a function of $\eta$ and reservoir (upper panels) or system (lower panels) monomer volume fraction $\phi^R$ and $\phi$ with $s=0.01, \Lambda=0.2$, and different $t$. Critical points for colloidal gas–liquid coexistence are indicated with data points. For the covalent polymers $N=668$ and $N_s$ is indicated. For the supramolecular polymers $U=19$ and $\langle N_s \rangle$ and $\langle N_i \rangle$ are given for the critical point or in the case of $t=0.03$ for $\eta = 0.3$. 

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To illustrate how a tunable Kuhn length could impact the phase behaviour, we have plotted the binodals as a function of the Kuhn length to colloid diameter ratio \( t \) for constant \( \varphi^0 = 0.0025 \) in Fig. 4. Besides the colloidal fluid (F) and solid (S) phase states, the colloidal gas (G) and liquid (L) phase states are now also indicated explicitly. As the value of \( t \) increases this simultaneously enhances the polymer chain stiffness. For colloid volume fractions in the range of \( \eta \approx 0 – 0.48 \), an increase in polymer stiffness initiates phase separation into a gas–liquid or gas–solid phase. Note that the range of \( t \) values explored in Fig. 4 is modest and is neither close to the fully flexible nor to the rigid limit but is in between, indicating the importance of subtle changes in \( t \) on the phase behaviour for semiflexible polymers.

### 3.3. Temperature-responsive phase behaviour

Lastly we have explored the effect of the persistence length on the stimuli-responsiveness of mixtures of hard spheres and semiflexible supramolecular polymers in Fig. 5. Here phase diagrams are shown as a function of temperature \( T \) for a constant \( \varphi^0 = 0.0025 \), three different values of \( t \), and an absolute scission energy \( E = 19k_B T_0 \) with \( T_0 = 298 \) K. Hence we would obtain \( U = 19 \) like used in the previous Figures for \( T = T_0 \). As the temperature is increased the supramolecular polymer becomes shorter. For \( t = 0.1 \) changes in temperature barely impact the phase behaviour, but for \( t = 0.2 \) gas–liquid coexistence appears at low temperatures and low colloid volume fractions. A wide range of different phase states and coexistences become available at \( t = 0.3 \), similar to the results we obtained for the supramolecular rod limit [11]. It is also remarkable that for \( t = 0.2 \) and \( t = 0.3 \), the G–L coexistence is either not accompanied by a G–L–S triple point at all (\( t = 0.2 \); middle) or by two triple points (\( t = 0.3 \); right) as generally only a single G–L–S triple point is found. This is resulting from an intricate interplay of effects resulting from changes in temperature: when the temperature increases, the polymer size decreases and in turn the strength of the depletion interaction is...
impacted differently via the depletion thickness and reservoir osmotic pressure. Additionally the range of the interaction also decreases. Note that for higher values of $\phi^2$ all the phase behaviour changes drastically and for $t = 0.1$ the phase behaviour will similarly become sensitive to temperature as well. Overall, the phase diagrams show that for experimental mixtures of supramolecular polymers and colloids, the persistence length has to be taken into account to find the right conditions for applications of stimuliresponsive phase behaviour.

It is interesting to remark that similar graphs are obtained if we plotted the average polymer length $\langle N \rangle$ instead of the temperature. In fact, it is even possible to obtain phase diagrams for covalent polymers with the same characteristics when plotting $N$ versus $\eta$, however obviously it is not practical to tune this parameter through external stimuli with covalent polymers. Nevertheless, these phase diagrams indicate the effect of changing $\Delta N \sigma$ or $\sigma \langle N \rangle$, regardless of this is accomplished indirectly by changing the temperature, or through $N \sigma$ or $\Delta$ directly.

4. Concluding remarks

We have derived theoretical expressions that enable to predict the phase behaviour of mixtures of colloids and semiflexible covalent or supramolecular polymers with variable persistence length. The binodals shift to much lower monomer concentrations for larger persistence lengths due to the increase in the excluded volume between colloids and polymers. The theory is an improvement on a previous theory on semiflexibility byTuinier [18] in covalent colloid–polymer mixtures as this was only correct near the flexible limit. Our results lead to an increased understanding of the phase behaviour of complex colloid–polymer mixtures and allows for a more direct comparison with experimental systems for colloids mixed with polymers for a wide range of chain stiffnesses in between the two extremes of semiflexibility. Additionally, the temperature-responsive phase behaviour of mixture of colloids and supramolecular polymers is shown to be highly sensitive to the polymer semiflexibility and leads to new peculiarities in the phase behaviour like two colloidal gas–liquid–solid points. While it was shown previously that supramolecular polymers can induce phase behaviour changes in colloidal systems [31] and we have demonstrated the temperature-responsiveness before [10,11], this work opens the way to designing systems with temperature-responsive colloidal phase behaviour using supramolecular polymers due to more accurate modelling of them by including the semiflexibility.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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