Phase stability of a reversible supramolecular polymer solution mixed with nanospheres

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Abstract

Theory is presented for the phase stability of mixtures containing nanospheres and non-adsorbing reversible supramolecular polymers. This was made possible by incorporating the depletion thickness and osmotic pressure of reversible supramolecular polymer chains into generalized free-volume theory, recently developed for investigating the phase behaviour of colloidal spheres mixed with interacting polymers (Fleer and Tuinier 2008 Adv. Colloid Interface Sci. 143 1–47). It follows that the fluid–fluid phase stability region where reversible supramolecular polymer chains can be mixed with nanospheres is sensitive to the energy of scission between the monomers and to the nanoparticle radius. One can then expect the fluid–fluid coexistence curves to have a strong dependence on temperature and that shifting of phase boundaries within a single experimental system should be possible by varying the temperature. The calculations reveal the width of the stability region to be rather small. This implies that phase homogeneity of product formulations containing reversible supramolecular polymers is only possible at low nanoparticle concentrations.

1. Introduction

Reversible supramolecular polymers are polymer chains that form due to spontaneous self-assembly of monomers [1]. Recent progress in supramolecular chemistry led to the development of several types of reversible supramolecular polymers including hydrogen-bonded equilibrium polymers [2–6] or coordination polymers that self-assemble via, for instance, metal ion–ligand group interactions [7]. Another class of such reversible polymers that behave similarly are worm-like surfactant micelles [8]. Such supramolecular polymers can be used to form a large diversity of self-organized multifunctional materials [9].

The chain length (distribution) of these polymers is determined by the end-cap or scission energy and the polymer concentration [8]. The scission energy, $U$, is the energy required to create two new chain ends. A schematic picture of the formation of these reversible polymers is drawn in figure 1. A larger monomer concentration and stronger attraction between the monomers enhance self-assembly into longer chains. Often the bonds form and break on timescales that are accessible experimentally. The fact that the bonds between the monomers are noncovalent provides solutions of reversible supramolecular polymers with a chain length distribution that depends on monomer concentration and temperature. Here a simple mean-field model [8] is adopted to describe the equilibrium chain length distribution. For sake of simplicity only athermal chains are considered. For a given segment volume fraction $\psi$, the segment volume fraction that has a chain length $M$, $\psi_M$, is then given by the exponential distribution:

$$\psi_M = \frac{\psi}{\langle M \rangle} \exp(-M/\langle M \rangle).$$

(1)

The brackets $\langle \cdot \rangle$ denote the ensemble average; $\langle M \rangle$ is the number-averaged chain length given by:

$$\langle M \rangle = \sqrt{\psi} e^{U/2},$$

(2)

where $U$ is the scission energy between the monomers (normalized by $kT$). Following van der Gucht et al [10], the relative concentration of reversible supramolecular polymers (further denoted as equilibrium polymers) $\phi_p$ is defined as

$$\phi_p = \psi \langle M \rangle,$$

(3)
with \( \phi_p = 1 \) defining the overlap concentration of equilibrium polymers at which the equilibrium polymer coils exactly fill the total volume.

In this paper the effect of adding nanospheres to solutions of non-adsorbing equilibrium polymers is considered. Such nanoparticles can add a certain functionality to the supramolecular polymer solution. With the increasing interest in supramolecular polymers and widening possibilities to synthesize them, the phase stability of such mixtures will become increasingly relevant. As far as I am aware, only a single (preliminary) experimental study on the phase stability of nanoparticles mixed with (non-adsorbing) equilibrium polymers has been reported [11]. Knoben et al examined 2,4-bis(2-ethylhexylureido)toluene solutions mixed with stearylated silica nanospheres in cyclohexane and detected a liquid–liquid phase separation at equilibrium polymer concentrations at and above \( 10 \text{ g} \text{l}^{-1} (\phi \gtrsim 0.01) \).

The system of interest is sketched in figure 2. The equilibrium polymers are depleted from zones around the spheres, termed depletion layers (dashed). In this paper, the mixture of nanospheres and equilibrium polymers in a solvent is studied using free-volume theory.

In the early 1990s Lekkerkerker and others put forward free-volume theory (FVT) for mixtures of spherical particles and (ideal) polymers [12, 13]. For solutions containing non-adsorbing polymers, the nanoparticles are surrounded by depletion layers [14–16]. Overlap of depletion layers results in attraction between the particles [14, 15] and these attractive forces, in turn, induce phase transitions in nanoparticle plus polymer mixtures [17–20]. The phase diagram topology depends on the polymer-to-sphere size ratio.

The power of FVT is that it is simple, insightful, and accurate (see for instance [21–24]). Over the years, FVT has been shown to be flexible in that it can be used to describe the phase behaviour of mixtures of colloidal rods and polymers [25], dispersions of colloidal spheres and (small) colloidal rods [26], charged spheres mixed with polymer chains [27, 28], and mixtures of interacting polymers and colloidal spheres [29–31].

Here I present generalized free-volume theory for a mixture of spherical nanoparticles in a supramolecular polymer solution. The theory is outlined in section 2, and the results for the phase stability are presented in section 3.

2. Theory

2.1. Semi-grand-canonical potential

Within generalized free-volume theory (GFVT), a nanoparticle–polymer mixture is described by the semi-grand-canonical ensemble. The system of interest is held in osmotic equilibrium with a reservoir (\( r \)). This reservoir is separated from the system via a hypothetical membrane that allows permeation of equilibrium polymers and solvent molecules, but which does not allow the nanospheres to enter the reservoir. The equilibrium polymer concentration in the system is set by the chemical potential of the polymer chains in the reservoir, \( \mu_p \). The system, with volume \( V \) and temperature \( T \), consists of \( N_n \) nanospheres with radius \( a \) in a solvent with equilibrium polymers. The solvent can safely be considered as ‘background’ [12, 32, 20]. An expression is needed for the semi-grand potential \( \Omega \) for the mixture of nanoparticles and equilibrium polymers in solution, in order to be able to compute the thermodynamic properties of the mixture. At a given system volume and temperature, the normalized semi-grand-canonical potential, \( \omega = \beta \Omega v_n / V \), can be written in normalized form as [29, 20]

\[
\omega = f^0 + \omega_p,
\]

with

\[
\omega_p = -\beta v_n \int_{\phi_p}^{\phi_p^0} \alpha \left( \frac{\partial \Pi}{\partial \phi_p} \right) \, d\phi_p.
\]

where the reduced canonical free energy \( f^0 = \beta F^0 v_n / V \). Here \( 1/\beta = k_B T \) is the thermal energy, \( v_n = 4\pi a^3/3 \) is the volume of a nanosphere, and \( F^0 \) is the Helmholtz energy of the
pure nanoparticle dispersion. The nanoparticle concentration is expressed in the volume fraction \( \eta = N_v/v_a/V \).

In order to calculate the polymer concentration in the system one needs the free-volume fraction \( \alpha \) for the polymer chains in the system, defined as \( \alpha(\eta, \mu_p) = (V_{\text{free}})/V \), where \( V_{\text{free}} \) is the free volume in the system not occupied by the nanospheres and their depletion zones.

For the free-volume fraction \( \alpha \) the standard scaled-particle result is used [33–35, 13, 29]:

\[
\alpha = (1 - \eta) \exp(-Ay - By^2 - Cy^3),
\]

where \( y = \eta/(1-\eta), A = (1+\delta/a)^3 - 1, B = 3(\delta/a)^2(\delta/a + 3/2), \) and \( C = 3(\delta/a)^3 \). Here \( \delta \) is the thickness of the depletion zone around a nanosphere with radius \( a \). From (5) and (6) it follows that the quantities \( \delta \) and \( \partial \Pi/\partial \phi_p \) are needed to calculate \( \omega_p \). These will be given below.

2.2. Reversible supramolecular polymer contribution

The ensemble-averaged chain length \( \langle M \rangle \) as a function of the normalized polymer concentration \( \phi_p \) follows from inserting (3) into (2):

\[
\langle M \rangle = \phi_p^{1/3}\left(e^{U/3}\right)^{2/3}.
\]

The size of the equilibrium polymers \( R_e \) is defined as:

\[
R_e = \sqrt{\langle M \rangle / 6}.
\]

It is noted that all length scales are normalized with the size of a polymer segment in this paper.

The depletion thickness for dilute and semi-dilute equilibrium polymer solutions next to a flat wall, \( \delta_p \), was obtained previously [10],

\[
\delta_p = \frac{R_e}{\phi_p} \left[ 2\sqrt{1 + 2\phi_p} - \sqrt{2(\phi_p + 2)} \right].
\]

In the dilute limit (\( \phi_p \to 0 \)), \( \delta_p \) vanishes and in the semi-dilute limit (\( \phi_p \gg 1 \)), the depletion thickness follows the mean-field scaling relation \( \delta_p \sim \phi_p^{-1/2} \) [10].

It is important to also account for curvature effects to accurately describe the depletion thickness, \( \delta \), around a spherical particle. In the mean-field case \( \delta \) can be approximated accurately by the simple power law [20]:

\[
\frac{\delta}{a} = 0.842 \left( \frac{\delta_p}{a} \right)^{0.9}.
\]

In figure 3 the characteristic polymer size \( R_e \) and depletion thickness \( \delta \) of equilibrium polymers are plotted as a function of the relative polymer concentration \( \phi_p \) for a few values of the scission energy. It illustrates how the size of the equilibrium polymer chains \( R_e \) increases with \( \phi_p \). The depletion thickness also increases (as it follows \( R_e \)) up to concentrations close to overlap (of order unity) above which \( \delta \) decreases; in the semi-dilute polymer concentration regime \( \delta \) follows the correlation length in a polymer solution [16]. As the scission energy is larger, the chains will be larger at given relative polymer concentration \( \phi_p \). The same holds for the depletion thickness.

For the osmotic pressure \( \Pi \) of equilibrium polymers the following mean-field result is used [10]:

\[
\tilde{\Pi} = \beta v_n \Pi = \phi_p + \frac{1}{4} \phi_p^2.
\]

Here \( \tilde{\Pi} \) is the normalized osmotic pressure. The polymer concentration dependence of osmotic pressure is plotted in figure 4 for various values of the scission energy \( U \). The derivative of osmotic pressure with respect to polymer concentration is

\[
\frac{\partial \tilde{\Pi}}{\partial \phi_p} = \beta v_n \frac{\partial \Pi}{\partial \phi_p} = \left( \frac{a}{R_e} \right)^3 \left[ 1 + \phi_p \right].
\]
2.3. Free energy of a nanoparticle dispersion of hard spheres

The canonical free energy of a fluid dispersion containing only hard spheres can be accurately described using:

\[ f^0 = \eta \ln(\eta \Lambda^3 / v_n) - \eta + 4\eta^2 - \frac{3\eta^3}{(1 - \eta)^2}. \]  

(13)

where \( \Lambda = h / \sqrt{2\pi m_n k_B T} \) is the thermal wavelength, \( m_n \) is the nanoparticle mass and \( h \) is Planck’s constant. The first two terms on the right-hand side of this equation comprise the ideal contribution, whereas the last term describes the hard-sphere interaction, which follows the equation of state given by Carnahan and Starling [36]. Standard thermodynamics enables computation of the osmotic pressure of the nanoparticle dispersion and the chemical potential of the nanoparticles. The chemical potential \( \tilde{\mu}^0 = \mu^0 / kT = \partial f^0 / \partial \eta \) follows as:

\[ \tilde{\mu}^0 = \ln \eta + \frac{(8 - 9\eta + 3\eta^2)\eta}{(1 - \eta)^3} - \ln \frac{v_n}{\Lambda^3}. \]

(14)

The dimensionless pressure \( \tilde{P}^0 = P_\text{tot} v_n / kT \) can subsequently be computed from \( \tilde{P}^0 = \tilde{\eta} \tilde{\mu}^0 - f^0 \), giving

\[ \tilde{P}^0 = \frac{\eta + \eta^2 + \eta^3 - \eta^4}{(1 - \eta)^3}. \]

(15)

the well-known Carnahan–Starling pressure.

2.4. Fluid–fluid binodals

All ingredients are now available to calculate the fluid–fluid phase behaviour of the nanoparticle–equilibrium polymer mixture by solving the coexistence equations

\[ \tilde{\mu}_n^\text{I} = \tilde{\mu}_n^\text{II}, \]

(16)

and

\[ \tilde{P}^\text{I}_{\text{tot}} = \tilde{P}^\text{II}_{\text{tot}} \]

(17)

for the chemical potential of the nanospheres and the total osmotic pressure of a phase I in equilibrium with a phase II.

The phase diagrams for hard spheres plus interacting polymers using the general expression (4) and its ingredients now follow from computing the chemical potential \( \tilde{\mu}_n = (\partial \omega / \partial \eta) \) and total pressure \( \tilde{P}_{\text{tot}} = \eta \tilde{\mu}_n - \omega \),

\[ \tilde{\mu}_n = \tilde{\mu}_n^0 + \int_0^{\phi_p^c} g \left( \frac{\partial \tilde{P}^0}{\partial \phi_p^c} \right) d\phi_p^c, \]

(18)

\[ \tilde{P}_{\text{tot}} = \tilde{P}_{\text{tot}}^0 + \int_0^{\phi_p^c} h \left( \frac{\partial \tilde{P}^0}{\partial \phi_p^c} \right) d\phi_p^c, \]

(19)

with \( g \) and \( h \) given by:

\[ g = e^{-Q} (1 + [1 + y](A + 2By + 3Cy^2)) \]

(20)

and

\[ h = e^{-Q} (1 + Ay + 2By^2 + 3Cy^3) \]

(21)

with \( A, B \) and \( C \) defined in (and below) equation (6) and where \( Q \) is given by

\[ Q = Ay + B y^2 + Cy^3. \]

(22)

The normalized osmotic pressure of the equilibrium polymers in the reservoir is given by equation (11) and the osmotic compressibility by equation (12). Coexistence curves then follow from equations (16) and (17) by using the common tangent construction.

In figure 5 it is demonstrated how the (normalized) semi-grand potential depends on nanosphere particle volume fraction under conditions where the fluid phase exhibits an instability, as follows from the local maximum in \( \omega \). Such a curve depends on the reservoir equilibrium polymer concentration, the nanoparticle size and on the scission energy.

The common tangent construction in figure 5 allows the determination of the compositions of the two coexisting phases. From these binodals the full phase diagram can be constructed.

3. Results

In figure 6 fluid–fluid binodal curves are presented for nanospheres of \( a = 5, 10 \) and 20 with sizes given in units of the equilibrium polymer monomer size. The scission energy here was fixed at 20 \( (kT) \). The left panel represents the relative polymer concentration in the reservoir \( \phi_p^c \) on the ordinate versus the nanoparticle volume fraction \( \eta \) on the abscissa. In this representation, it follows that relatively larger polymer chains (smaller \( a \)) shift the fluid–fluid binodal curves to higher relative polymer concentrations. It is clear that the binodal sensitively depends on \( a \). The relative polymer concentration in the system, \( \phi_p \), follows from \( \phi_p = a \phi_p^c \). The resulting binodal curves are quite close to each other (right panel in figure 6). This is due to the fact that the free-volume fraction depends on the relative polymer concentration and passes through a maximum around \( \phi_p = 0.6 \). This result shows that the stability region is rather limited for mixtures of nanospheres and equilibrium polymers.

In figure 7 fluid–fluid binodal curves are shown for mixtures of nanospheres with fixed size \( a = 10 \) mixed...
Figure 6. Fluid–fluid coexistence curves of equilibrium polymers mixed with nanospheres at fixed scission energies \( U = 20 \) for various values of the nanoparticle radius \( a = 5 \) (solid curve), \( a = 10 \) (dashed curve) and \( a = 20 \) (dotted curve). Dots are the critical points.

Figure 7. Fluid–fluid coexistence curves of equilibrium polymers mixed with nanospheres of radius \( a = 10 \) for scission energies \( U = 15 \) (dotted curve), \( U = 20 \) (dashed curve) and \( U = 25 \) (solid curve). Dots: critical points.

with equilibrium polymers for various values of the scission energy \( U \), the change of which is experimentally accessible via manipulation of temperature. It follows that increasing \( U \) leads to a significant shift upwards of the fluid–fluid binodals when the relative equilibrium polymer concentration is plotted in the reservoir representation (left panel of figure 7). A larger value for \( U \) leads to a larger average equilibrium polymer size. Therefore these results are in agreement with (G)FVT results for (normal) polymer–sphere mixtures \([13, 17, 29]\). Conversion towards system polymer concentrations as in practice (right panel of figure 7) shows the stability region is small and the binodal curves are close.

What is observed in practice? The relative polymer concentration is insightful since it identifies the concentration regime; dilute regime for \( \phi_p < 1 \), semi-dilute regime if \( \phi_p > 1 \). The quantity \( \phi_p \) is very sensitive to the scission energy \( U \), while the segment concentration \( \phi \) is of course unaffected. The phase diagram of figure 7 (right panel) is now plotted in terms of the segment concentration on the ordinate, as represented in figure 8. It follows that variations of \( U \) can have a dramatic effect on the binodal fluid–fluid coexistence curves observed in experiment. Changing the relative size of polymer and spherical particles for mixtures of (normal) polymers mixed with nanoparticles requires significant experimental effort; one needs a different system with either particles or polymers of another size. This differs from changing \( U \) in mixtures of reversible supramolecular polymers and nanospheres in the sense that one only needs to modify the temperature. With a single mixture one can then scan through the phase diagram by diluting, concentrating and changing the temperature. No quantitative comparison can yet be performed with experimental work. The single experimental study that is available \([11]\) used chain stoppers, which means we cannot directly compare with their system. Further, their observations of (in)stability were quite limited. It will be interesting to compare the theory presented in this work to future phase diagrams on mixtures of nanoparticles and equilibrium polymer chains.

No remark was made yet on the critical point. For short-range attractions it is known that mean-field theories incorrectly predict the critical region, whereas long-ranged attractions are well described. In figures 6 and 7 it can be observed that increasing \( U \) and decreasing \( a \) imposes similar effects on the critical points and the binodals. These critical \( \phi_p \) and \( \eta \) values are plotted as a function of \( a \) and \( U^{-1} \) in a single plot in figure 9. It follows that, when scaled properly, the influence of \( a \) and \( U^{-1} \) are very similar and that one can modify the binodals in a similar fashion via adjusting \( a \) or \( U \).

4. Concluding remarks

Theory was presented for the fluid–fluid phase transition of mixtures of dispersed nanospheres in solution containing...
and concentration of the dispersion, scan through the scission energy-dependent phase diagram. Finally, it was found that the critical point scales in a similar way with scission energy as with the inverse of the nanosphere radius.

In a later contribution, the effect of polymer solvency, as well as an account of the fluid–solid equilibrium, is planned.

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