Effect of polymer chain-length polydispersity on the phase behavior of model athermal mixtures of colloids and flexible self-excluding polymers

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Abstract

The effect of polymer polydispersity on the fluid–fluid demixing of an athermal mixture of colloids and self-excluding polymers is analysed with the first-order thermodynamic perturbation theory (TPT1) of Wertheim. The colloidal particles and the segments making up the polymer chains are modeled as hard spheres of different diameters. The polydispersity of the polymer is represented by a distribution of chain lengths. The polydispersity increases the extent of demixing; the critical composition remains relatively unaffected, while the critical packing fraction decreases substantially. The polymers with the longest chains are responsible for the increase in the extent of immiscibility.

1. Introduction

A great deal of attention has been paid to understanding the nature of the phase behaviour of binary mixture of hard colloids and non-adsorbing polymers since the discovery of a fluid–fluid demixing transition in athermal colloidal dispersions (see review of Tuinier et al. [1]). Colloidal systems have many important industrial applications in the production and formulation of food, paint, and detergents. Similar systems are also of relevance to the area of nanotechnology, e.g., the creation of designer materials/devices by directed assembly using mixtures of polymers attached to polyhedral oligomeric silsesquioxane (POSS) cubes [2].

Depending on the size asymmetry and the concentration, the depletion of polymers around the hard colloids induces an effective attractive interaction between the colloids, which results in a phase separation between colloid poor and colloid rich phases. Experimental work in this area has been accompanied by extensive simulation [3–6] and theoretical [7–16] studies. The main focus of these studies has been the determination of the depletion potential between the colloid particles and the calculation of phase diagrams from simple pair interactions between the colloid–colloid, polymer–polymer, and colloid–polymer species. In the simplest Asakura–Oosawa (AO) model [7], the colloid–polymer system is treated as a binary mixture of hard spheres, where the polymer is represented as a hard sphere with a diameter which is equal to the average dimension of an ideal chain. The interaction between the ideal polymer chains is neglected, which restricts the applicability of the AO model to short polymers and to the so-called theta condition (where the polymers are in a fully expanded state). The effect of the solvent is not explicitly included in

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the model, the solvent may play an important role in the stabilization or otherwise of the demixing [17]. There have been several attempts to include the polymer–polymer interaction into the AO model [11–16]. In most of these studies, the polymer is modeled as a penetrable hard sphere with a soft polymer–polymer Gaussian-like potential [18] or a step function pair potential [14,15]. The use of more realistic models, in which for example the polymers are treated at the level of the segment making up the chain, are still very rare. We are only aware of a PRISM integral-equation study [13], and of our work [19] with the first-order thermodynamic perturbation theory (TPT1) of Wertheim [20,21].

A very important feature of real colloid–polymer mixtures [1,22,23] is that the polymers and the colloidal particles are naturally polydisperse in terms of molecular weight (chain length or size). In most theoretical approaches the colloids are represented as spherical particles of the same diameter (corresponding to the average size) and the polymers as chains of equal length (corresponding to the number average chain length). The phase behaviour is, however, very sensitive to the degree of polydispersity. There are only a few studies of the effect of polydispersity on the demixing transitions in colloid–polymer systems [24,25], or of the nature of the depletion pair potential between two colloidal particles in the presence of polydisperse polymer [26–28] (also see the excellent reviews by Sollich and co-workers [29,30]).

The aim of our current Letter is to investigate the effect of polydispersity in the chain length (molecular weight) of the polymer on the fluid phase behaviour of colloid–polymer mixtures. To treat the polymers at the level of its constituent monomer segments, the Wertheim TPT1 approach is generalized to deal with continuous chain length distributions of the polymer. By describing the polydispersity of the parent phase (cloud curve) in terms of a continuous distribution function, we are able to make quantitative comparisons of the phase diagrams of the monodisperse and polydisperse polymer–colloid systems.

2. Theory

Following our previous work [19], we consider athermal mixtures of colloids and flexible chain molecules, where the colloids are modeled as hard spheres of diameter \( \sigma_C \), while the polymer chains consist of \( m \) tangentially bonded hard spherical segments of diameter \( \sigma_P \). We use hard-sphere pair potentials to describe the like colloid–colloid and polymer–polymer segment–segment interactions, as well as the unlike interactions through an additive cross diameter \( \sigma_C P = (\sigma_C + \sigma_P)/2 \). The colloids are taken to be monodisperse, while the polymer chains are polydisperse in terms of number of segments \( m \) making up the chains. The expressions are derived using a continuous approach to polydispersity [29,30] instead of a discrete multicomponent treatment [31].

The Helmholtz free energy density \( \mathcal{A}(V) \) of the system of volume \( V \) can be separated into ideal and a residual contributions. The reduced free energy density \( a = \mathcal{A}(V)kT \), where \( T \) is the temperature and \( k \) is the Boltzmann constant, is expressed in terms of the ideal \( a^{\text{ideal}} \) and a residual \( a^{\text{res}} \) terms as

\[
a = a^{\text{ideal}} + a^{\text{res}}.
\]

The ideal free energy density of the binary mixture of colloids and polydisperse polymers can be written as

\[
a^{\text{ideal}} = \rho_C (\ln \nu_C \rho_C - 1) + \int dm \rho_P(m) (\ln \nu_P(m) \rho_P(m) - 1),
\]

where \( \rho_C \) and \( \rho_P(m) \) are the number densities of the colloid and polymer molecules of length \( m \), respectively. Note that the kinetic contributions due to translation and rotation contained in the de Broglie volumes \( \nu_C \) and \( \nu_P \) are constant at a given temperature and thus do not affect the phase behaviour of the system. The residual free energy density represents a sum of contributions due to the hard-sphere repulsions \( a^{\text{HS}} \) and chain formation \( a^{\text{chain}} \) which are derived from a generalization of the BMCSL theory of hard-sphere mixtures [32], and from the TPT1 theory [20,21]. In the case of chain length polydispersity, it is easy to show that the hard-sphere contribution to the free energy density is given by [32]

\[
a^{\text{HS}} = \frac{6}{\pi} \ln \left( \frac{\zeta_3^3 - \zeta^3_0}{\zeta_3^3 - \zeta_0^3} \right) \ln (1 - \zeta_3) + \frac{3 \zeta_1 \zeta_2}{(1 - \zeta_3) \zeta_3} + \frac{\zeta_2^3}{\zeta_3 (1 - \zeta_3)^2},
\]

where the reduced densities \( \zeta(m) \) are functions of the colloid number density \( \rho_C \), and functionals of the polymer number density distribution \( \rho_P(m) \):

\[
\zeta(m) = \frac{6}{\pi} \left[ \sigma_C \rho_C + \sigma_P \int dm \rho_P(m) m \right].
\]

The packing fraction \( \eta = \zeta_3 \) corresponds to the proportion of the total volume occupied by the molecules. A generalization of the Wertheim TPT1 approach from discrete [21] to continuous systems is also straightforward, and the contribution to the free energy density due to chain formation term is written as

\[
a^{\text{chain}} = \int dm \rho_P(m)(1 - m) \ln g^{\text{HS}}_{\rho_P}(\sigma_P),
\]

where the Boublík expression [32] for the contact value of the radial distribution function \( g_{\rho_P}^{\text{HS}}(\sigma_P) \) between spheres of radius \( \sigma_P \) in a mixture of hard spheres of diameters \( \sigma_C \) and \( \sigma_P \) is taken to be consistent with the treatment of the hard-sphere contribution (cf. Eq. (2)):
On introducing the $k$th moment $\langle \rho_p \rangle_k = \int dm \rho_p(m)m^k$ of the polymer number density distribution, it can be seen from Eq. (3) that the reduced densities $\zeta_i$ and thus the hard-sphere free energy density $a_{\text{HS}}$ (Eq. (2)) depend only on the colloidal number density and the first moment of the polymer number density:

$$\zeta_i = \frac{\pi}{6} (\sigma_c^2 \rho_C + \sigma_p^2 \langle \rho_p \rangle_1).$$

(6)

The contact value of the distribution function $g_{\text{HS}}$ only depends on the first moment of the polymer number density and thus does not have an explicit dependence on the chain length $m$; as a consequence it can be factorized out of the integral in Eq. (4). The chain contribution $a_{\text{chain}}$ is only a function of the zeroth and first moments of $\rho_p(m)$, i.e.,

$$a_{\text{chain}} = \ln g_{\text{HS}}(\sigma_p) (\langle \rho_p \rangle_0 - \langle \rho_p \rangle_1).$$

(7)

The free energy of our system thus belongs to the category of the so-called ‘truncatable’ free energies [29]. For the sake of simplicity, we introduce the following shorthand notation for the residual free energy density $a_{\text{res}} = \Phi(\rho_C; \langle \rho_p \rangle_0, \langle \rho_p \rangle_1)$.

The chemical potential $\mu_C$ of the colloids can now be derived in a compact form through the density derivative of the free energy density $a$ as

$$\mu_C = \frac{\partial a}{\partial \rho_C} = \ln [\rho_C \rho_C] + \frac{\partial \Phi}{\partial \rho_C}.$$  

(8a)

Similarly, the chemical potential $\mu_p(m)$ of the polymer chains of length $m$ is obtained as the functional derivative of the free energy density $a$ with respect to the function $\rho_p(m)$ [29]:

$$\frac{\mu_p(m)}{kT} = \frac{\partial a}{\partial \rho_p(m)} = \ln [v_p(m) \rho_p(m)] + \sum_k \frac{\partial \Phi}{\partial \rho_p(k)} m^k,$$

$$k = 0, \ldots, K.$$  

(8b)

The standard thermodynamic relation between the pressure $p$, free energy $A$, and chemical potentials $\mu_i$ ($A = -pV + \sum_i N_i \mu_i$) allows us to write the pressure as

$$p = \rho_C + \langle \rho_p \rangle_0 - \Phi + \rho_C \frac{\partial \Phi}{\partial \rho_C} + \sum_k \langle \rho_p(k) \rangle \frac{\partial \Phi}{\partial \rho_p(k)}.$$  

(9)

We note that Eqs. (8–9) are general expressions for any truncatable systems of $K+1$ independent moments of the polymer density and the colloid density $\rho_C$. In our case we only require the zeroth and first moments of the polymer density.

The conditions of the phase equilibria between phases $\alpha$ and $\beta$ are the equality of pressure, the equality of the chemical potential of the colloid $\mu_C$, and the equality of the chemical potential $\mu_p(m)$ of each chain molecule of length $m$ in each phase. By using the latter condition $\mu_p^\alpha(m) = \mu_p^\beta(m)$ and Eq. (8b), it can easily be shown that the number density distributions $\rho_p^\alpha(m)$ and $\rho_p^\beta(m)$ of the polymer molecules of phases $\alpha$ and $\beta$ are related through

$$\rho_p^\alpha(m) = \rho_p^\beta(m) \exp \left[ \sum_k \left( \frac{\partial \Phi^\alpha}{\partial \rho_p(k)} - \frac{\partial \Phi^\beta}{\partial \rho_p(k)} \right) m^k \right].$$

(10)

Moreover, from the definition of the density moments, the following system of equations can be established from Eq. (10) for the determination of the moment of the polymer densities:

$$\langle \rho_p \rangle_l = \int dm m^l \rho_p(m) \exp \left[ \sum_k \left( \frac{\partial \Phi^\alpha}{\partial \rho_p(k)} - \frac{\partial \Phi^\beta}{\partial \rho_p(k)} \right) m^k \right],$$

$$l, k = 0, \ldots, K.$$  

(11)

In our special case one simply requires $\langle \rho_p^\alpha \rangle_0$ and $\langle \rho_p^\beta \rangle_1$. If we fix the shape of the polymer number density distribution $\rho_p^\alpha(m)$ of phase $\alpha$, the integrals on the right hand side of Eq. (11) can be performed either numerically or analytically depending on the explicit form of the distribution. The resulting system of equations provides additional relations between the colloid density and the moments of the polymer density. For a given chain length distribution of phase $\beta$, which is often called the ‘parent’ distribution, the phase coexistence can thus be determined by solving a system of four non-linear equations. In representing the phase diagram of the system, the curve which corresponds to phase $\beta$ is referred to as the ‘cloud curve’, and the curve corresponding to the composition of the second coexisting phase is called the ‘shadow curve’.

In this Letter, we use the commonly employed Schulz–Flory distribution as the ‘parent’ distribution, which is defined in terms of total number density ($\rho = N/V$) and mole fraction of polymer molecules ($x_p$) [33]

$$\rho_p(m) = \rho_x b^m \Gamma(\lambda) m^{\lambda-1} e^{-bm},$$

(12)

where $\Gamma$ is the gamma function. The characteristic parameters of the distribution $\lambda$ and $b$ are related to the number average chain length $\langle m \rangle$ and to the index of polydispersity $I_p$ through $\lambda = 1/I_p-1$ and $b = \lambda\langle m \rangle$. We use $I_p$ and $\langle m \rangle$ to characterize the chain length distribution of the polymer density because these parameters have a clear physical meaning. The index of polydispersity depend on the zeroth, first, and second moments through $I_p = \langle \rho_p \rangle_0 \langle \rho_p \rangle_2 / \langle \rho_p \rangle_1^2$.

3. Results and conclusions

When the polymer is monodisperse, the index of polydispersity is $I_p = 1$. When $I_p > 1$ the polymer composition is represented by an asymmetric long tailed distribution of the number of segments $m$ in a chain. Here we consider only cases where the index of polydispersity
lies in the interval of $1 \leq I_p \leq 2$, which is the typical range found in practice. The effect of increasing the chain-length polydispersity in systems of big colloids and short chains ($d = \sigma_p \sigma_C = 0.06$, $m = 50$) is shown in in Fig. 1. In the case of the monodisperse system $I_p = 1$ (which was studied in [19]), fluid phase separation is seen in the polymer rich region between a colloid poor phase and a colloid rich phase. This kind of phase transition is often referred to as a colloidal ‘vapour–liquid’ transition. In the case of the system with moderate polymer polydispersity corresponding to $I_p = 1.25$, the phase equilibria is seen to be represented by the coexisting cloud and shadow phases. The average chain length and the polydispersity of the cloud phase are always fixed (in this case $\langle m \rangle_{cl} = 50$ and $I_p = 1.25$), while those of shadow phase result from the conditions of phase equilibrium. The critical point for the fluid phase demixing transition is no longer at a minimum in pressure, but is at the intersection of the cloud and shadow curves. It can be seen from Fig. 1a that an increase in the degree of polydispersity extends the region of immiscibility. The critical packing fraction $\eta_{cri} = \xi_{3,cri}$ also decreases with increasing polydispersity. It is interesting and unexpected to find that the effect of polydispersity on the critical composition is very weak. Within our approach the index of polydispersity $I_p$ turns out to be equal in both phases. It is, however, clear that the distributions of cloud and shadow phases do not correspond to the same number-average chain length $\langle m \rangle$. In our calculations the average chain length of the cloud phase is fixed at $\langle m \rangle_{cl} = 50$. The average chain length of the shadow phase is shown as a function of the composition of the shadow curve in Fig. 1b. The average chain length of the shadow phase is always higher than that of the parent phase, if the mole fraction of polymer in the shadow phase is above the critical composition; the opposite is true for mole fractions below the critical composition. The longest molecules are thus found in the polymer rich phase, and the shortest molecules in the colloid rich phase. This is not surprising as the longer chain molecules have a larger excluded volume (repulsive) interaction with the colloid particles than the shorter chains [19]. In support of this interpretation one can see that the slopes of the curves in Fig. 1b increase with increasing polydispersity; the proportion of polymer chains with a length larger than the average chain length $\langle m \rangle$ in the parent phase progressively increases as $I_p$ is increased. Moreover it is reasonable to expect that an increase in polydispersity will result in a broadening of the region of fluid phase coexistence, since the longer the polymer chain, the more immiscible it is with the colloid [18]. These findings confirm the general belief that differences in both size and shape between the various components are responsible for the phase separation exhibited by athermal mixtures, and that the demixing transition can be attributed to a very unfavorable contribution to the unlike packing entropy.

We now examine the effect of varying the polymer segment-colloid diameter ratio $d = \sigma_p \sigma_C$ on the demixing transition of our model polymer-colloid mixtures, both for the monodisperse ($I_p = 1$) and moderately polydisperse ($I_p = 1.25$) cases. Three distinct types of phase diagrams are exhibited for the mixture with $\langle m \rangle = 100$. When the polymer chains are much smaller than the colloids ($d = 0.01$), a colloidal ‘vapour–liquid’ transition is seen (see Fig. 2a). The intermediate case ($d = 0.05$) is shown in Fig. 2b where the demixing transition corresponds to an almost symmetrical phase diagram with a very strong fractionation. In this case neither the poly-

**Fig. 1.** (a) Effect of increasing the index of polydispersity ($I_p$) on the fluid-fluid demixing transition of athermal mixtures of colloids and flexible polydisperse polymers determined with the TPT1 approach [19,20]. Pressure-composition representations of the coexisting cloud (continuous curves) and shadow (dashed curves) phases are shown for an average chain length of the cloud curve of $\langle m \rangle_{cl} = 50$ and a polymer segment-colloid diameter ratio of $d = \sigma_p \sigma_C = 0.06$. The critical points are indicated by the diamonds. The reduced pressure is defined as $P^* = P \sigma_C^3 / kT$, and $x = x_p$ represents the mole fraction of the polymer. (b) Average polymer chain length of the shadow phase ($\langle m \rangle_{sh}$) as a function of the polymer composition. The short dashed line indicates the average chain length of the cloud phase ($\langle m \rangle_{cl} = 50$).
mer chains nor the colloids can be considered as a ‘depleting agent.’ In Fig. 2c we show the phase diagram for the system where the dimension of the polymer is larger than that of colloid ($d = 0.16$). The phase diagram of this system is essentially a mirror image of that given in Fig. 2a, and now corresponds to a polymeric ‘vapour–liquid’ transition. In all of these cases, the effect of a polydispersity in the polymer chain length is very similar to that discussed in the previous paragraph (cf. Fig. 1):

the polydispersity extends the range of demixing coexistence region and lowers the critical properties.

We have presented an extension of the Wertheim TPT1 treatment of athermal colloid–polymer mixtures for continuous chain length distributions. In comparison with the monodisperse case, only one additional relation (Eq. (11)) is necessary to locate the onset of phase separation (cloud and shadow phases). The use of the TPT1 approach to describe other types of polydispersity such as a polydispersity in the diameter of the colloid is straightforward and will be the subject of future work. The effect of the shape of the parent distribution function on the phase behaviour is also important. For example, the polydisperse hard-sphere fluid does not exhibit demixing with a Schultz–Flory distribution, but demixes with a log-normal distribution [34]. The treatment of inhomogeneous polymer–colloid systems is also particularly important in the area of nano fluids; the approach such as the one presented here can be extended to deal with non-uniform fluids by constructing an appropriate free energy functional (see the review in [35]).

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