Interactions between charged colloids in semi-dilute polyelectrolyte

BY LUC BELLONI\textsuperscript{1} AND PAULA G. FERREIRA\textsuperscript{1,2}

\textsuperscript{1}CEA/SACLAY, Service de Chimie Moléculaire, 91191 Gif-sur-Yvette Cedex, France
\textsuperscript{2}Rhodia Recherches, 52 rue Haie Coq, 93300 Aubervilliers, France

Mixtures of like-charged colloids and flexible polymers in solution are studied at the statistical mechanics of liquids level. The spatial correlations between monomers inside the semi-dilute polyelectrolyte are investigated using the polymer reference interaction site model. In the bare Debye–Hückel picture, charged sites (colloids and monomers) interact via ion-averaged, screened coulombic potentials. The network of the entangled charged chains exert a depletion attraction of entropic and electrostatic origins onto the colloidal particles, which leads to a phase separation of the solution between colloid-rich and polymer-rich phases. The presence of hydrophobic sites on partly charged polymer chains (sequential copolymers) alters this picture and induces steric repulsion and bridging attraction between colloids.

\textbf{Keywords:} colloid; polyelectrolyte; electrostatic interactions; depletion

1. Introduction

In recent years, mixed solutions of \textit{large} spherical colloids and \textit{small} polymer chains have been extensively studied as models of pure hard-sphere mixtures. In the dilute regime, below the overlap polymer concentration, the specific form of the linear chains is lost and each polymer coil is considered as a hard sphere that exerts an osmotic pressure on the colloidal surfaces. It results in a short-range depletion attraction of excluded volume or entropic origin between colloids (Asakura & Oosawa 1954; Vrij 1976), which may lead to a destabilization of the solution towards phase separation between colloid-rich and polymer-rich phases. A large number of nice experimental and theoretical works have shown how the shape of the full colloid phase diagram, in particular the existence of the \textit{liquid}-like phase, is monitored by the range of the depletion effective attraction, namely the size of the polymer coils (see Dijkstra \textit{et al.} 1999; Frenkel 1999; Lekkerkerker \textit{et al.} 1992, and references cited therein). When each component carries a charge of the \textit{same} sign, the ion-averaged, screened coulombic repulsion between the different particles magnifies the effective interaction (Richetti & Kékicheff 1992; Sharma & Walz 1996; Walz & Sharma 1994) and static correlations between the colloids. The competition between the direct repulsion and the indirect electrostatic depletion attraction induces a local demixion or charge ordering, as observed in latex mixtures (Lutterbach \textit{et al.} 1999; Ottewill \textit{et al.} 1995).

What happens then when the charged colloids are immersed in a \textit{semi-dilute} polyelectrolyte (again of the same sign)? The picture is now totally different (figure 1).
Figure 1. Schematic of a colloid–polymer mixture in the semi-dilute regime. Each worm-like chain of persistence length \( l_p \) is composed of \( N \) interacting, connected sites of length \( b \).

The polymers strongly overlap and form an entangled network of long flexible linear chains. The colloids are much larger than the individual monomers but still smaller than or of similar size to the full chains. The simultaneous existence of numerous characteristic lengths of different scale (colloidal size, monomer length, persistence length and radius of gyration of the polymer, correlation length of the network) and of coulombic repulsions between like-charged species induces complex couplings which control the equilibrium and structural properties of the whole solution (Joanny & Barrat 1996). Many industrial applications—such as those in the paint industry, paper making, food additives, waste-water treatment, protein purification, etc.—deal with such colloid–polyelectrolyte mixtures and must confront the problem of their stability. From the theoretical point of view, any treatment at the level of the statistical mechanics of liquids is much more difficult than for hard-spheres mixtures due to the presence of the long, flexible, overlapped chains. In this paper, we will show how the polymer reference interaction site model (PRISM) (Honnell et al. 1990; Schweizer & Curro 1987, 1988) is able to give detailed answers about the local structure of the mixture, the effective, polymer-averaged interaction between colloids, and the stability of the solution. Section 2 briefly describes the PRISM approach. The results corresponding to fully charged homopolymers are given in §3, while §4 presents a few preliminary results about charged, hydrophobic copolymers.

2. Theory

The PRISM was proposed by Schweizer & Curro (1987), as an extension of the RISM of polyatomic molecules of Chandler & Andersen (1972), in order to treat polymeric systems at the level of statistical mechanics of liquids. Since then, numerous PRISM studies have concerned neutral homopolymers (Yethiraj & Hall 1992), neutral copolymers (David & Schweizer 1994a,b), polyelectrolytes (Dymitrowska & Belloni 1998; Genz et al. 1989; Yethiraj 1998; Yethiraj & Shew 1996) and colloid–polymer mixtures (Khalatur et al. 1997; Yethiraj et al. 1992). Within PRISM, each polymer is considered to be a collection of \( N \) interacting spherical connected sites, the monomers. The connectivity of the monomers that belong to the same chain is taken into account by the site–site single chain form factor \( P(q) \) (in Fourier
Colloid–polyelectrolyte mixtures

that describes the intra-molecular correlations. By definition, \( P(0) = N \) and \( P(\infty) = 1 \). The inter-molecular correlations between monomers that belong to different chains are characterized by the site–site pair distribution function \( g(r) \). The main goal of the theory is to derive \( g(r) \) from the spherically symmetric monomer–monomer pair potential \( v(r) \) for a given intra-structure \( P(q) \). The starting point of the PRISM approach is a modified Ornstein–Zernike (OZ) equation which relates intra-correlations and inter-correlations. For a one-component homopolymer system neglecting end effects, this equation reads, in Fourier space,

\[
(P(q) + h(q))(1 - c(q)P(q)) = P(q),
\]

where \( h(q) \) and \( c(q) \) represent the Fourier transforms, normalized by the monomer density \( \rho \), of the total, \( h(r) = g(r) - 1 \), and direct, \( c(r) \), inter-correlation functions. Thus, the sum \( I(q) = P(q) + h(q) \) gives the scattered intensity due to the polymeric system. With \( N = 1 \) \((P = 1)\), one recovers the standard OZ equation valid for simple (monomeric) liquids. The usual atomic integral equations (PY, HNC) relating the functions \( g(r) \), \( c(r) \) and \( v(r) \) will be used below as closures to (2.1).

Before continuing, one recalls the intrinsic limits and weaknesses of such a bare PRISM approach. First, contrary to the case of simple liquids, the somewhat phenomenological RISM-OZ equation (2.1) has no rigorous theoretical (diagrammatic) justification. It is only in practice that (2.1) with atomic closures has been proven to be successful for various polymer systems. New ‘molecular’ integral equation closures which improve the bare version have recently been proposed (Laria et al. 1991; Schweizer & Yethiraj 1993). An alternative to the PRISM is the elegant CSL model (Chandler et al. 1982), which rigorously defines both a molecular OZ equation and integral equation closures in a proper diagrammatic expansion. Unfortunately, this \( a \) priori appealing theory leads, in practice, to unphysical results (negative \( g(r) \)) for most polymers (L. Belloni 1998, unpublished work). Lastly, all these theories are devoted to the calculation of the intersolution structure only and must assume \( a \) priori a given intra-macromolecule form. Some preliminary extensions have recently shown how intra-correlations and inter-correlations could be self-consistently derived (Schweizer et al. 1992; Yethiraj 1998). In the following, we will instead consider each polymer to be a semi-flexible, worm-like chain, characterized by the monomer length \( b \) and the persistence length \( l_p \) of fixed value (figure 1).

The extension of the PRISM to colloid (c)–polymer (m) mixtures is straightforward. The OZ equation (2.1) becomes a matricial equation which involves the cc, cm and mm correlation functions. The Fourier transform of a function \( f_{ij}(r) \) is normalized by the density factor \((\rho_i \rho_j)^{1/2}\). The matrix \( P \) is diagonal with \( P_{mm} \equiv P \) and \( P_{cc} = 1 \) (monomeric colloid). In the present study, the electrostatic interactions inside the charged mixture are treated at the Debye–Hückel level: the various charged sites (monomers and colloids) interact via ion-averaged, screened coulombic Derjaguin–Landau–Verwey–Overbeek (DLVO) potentials:

\[
\frac{v_{ij}(r)}{kT} = \begin{cases} 
+\infty, & r < a_i + a_j, \\
Z_i Z_j L_B \exp[-\kappa(r - a_i - a_j)] / \left( r(1 + \kappa a_i)(1 + \kappa a_j) \right), & r > a_i + a_j,
\end{cases}
\]

where \( a_i \) is the radius of species \( i \), \( Z_i \) is its charge, \( L_B = e^2 / (4\pi\varepsilon_0 \varepsilon kT) \) is the Bjerrum length (7.189 Å with \( T = 298 \) K and \( \varepsilon = 78 \)), and \( \kappa = (8\pi L_B I)^{1/2} \) is the screening.

Phil. Trans. R. Soc. Lond. A (2001)
constant, which depends on the ionic strength $I$. In the absence of added salt, $I$ reduces to the counterion contributions, and the electroneutrality condition implies $I = \frac{1}{2}(Z_m\rho_m + Z_c\rho_c)$ for monovalent ions.

As usual, the charges which appear in the DLVO potentials (2.2) are not the structural ones, but represent some effective, post-condensation values. Indeed, in highly charged colloidal and polyelectrolyte solutions, the strong attraction between macromolecules and counterions induces an accumulation or electrostatic condensation of these ions near contact. This nonlinear effect is not taken into account by the linear Debye–Hückel analysis from which are derived the DLVO potentials. As a consequence, the condensation must be assumed explicitly a priori through effective $Z_i$ parameters, whose values can be derived from cylindrical or spherical Poisson–Boltzmann theories (Alexander et al. 1984; Belloni 1998; Belloni et al. 1984). For the linear polymer component, it is sufficient to use Manning’s (1969) simple expression, $Z_m = b/L_B$, valid in principle for rigid rods only. A recent polyelectrolyte PRISM study with explicit description of ions and bare coulombic potentials has shown how this expression remains correct in the presence of flexible linear macromolecules (Dymitrowska & Belloni 1999). Lastly, one must keep in mind that the screened coulombic repulsions (2.2), even corrected with effective charge values, become qualitatively incorrect at strong electrostatic coupling when the colloids or polymers are highly charged or the counterions are multivalent. In these situations, a short-range effective attraction appears between like-charged objects due to the ion–ion correlations. Our present model ignores these non-classical effects.

The OZ equation (2.1) with the Koyama worm-like chain form factor (Koyama 1984, 1986) $P(q)$ and the atomic $PY_{mm}$, $PY_{mc}$, $HCN_{cc}$ integral equations with pair potentials (2.2) are numerically solved using a standard iterative procedure which involves Fourier transforms and powerful Newton–Raphson techniques (Belloni 1988). The resolution is more difficult in the colloid–polymer mixture than in
Figure 3. Colloid–colloid partial structure factor. Same legend as figure 2.

the pure systems, due to the large size and charge asymmetry between the colloids and the monomers that compose the long chains. Once the convergence is reached, the local correlations and structures are deduced from the pair distribution functions \( g_{ij}(r) \) and the partial structure factors or scattered intensities \( F_{ij}(q) + h_{ij}(q) \).

In numerous real situations, the experimental observation is sensitive to the colloidal component only. Therefore, it is tempting to formally replace the mixture with a one-component system composed of colloids that interact via effective, polymer-averaged potentials. In the following, we will use the effective pair potential \( v_{cc}(r) \), classically defined as the potential that leads, within the effective one-component model, to the same colloid–colloid pair correlations as in the original mixture, at equal colloidal density. The potential \( v_{cc} \) is derived by numerically inverting the one-component \( \text{OZ} + \text{HNC} \) problem. In principle, there is no more information in \( v_{cc}(r) \) than in \( g_{cc}(r) \) or in the structure factor \( S_{cc}(q) = 1 + h_{cc}(q) \). In practice, this notion of effective pair potential is successful in illustrating the effect of the polymer chains on the colloid interactions. \( v_{cc} \) is a solvent plus ion plus polymer averaged potential. It depends on the polymer density as well as on the colloid density due to the many-body character of the polymer-mediated interactions. At zero \( \rho_c \), \( v_{cc} = -kT \ln g_{cc} \) represents the effective interaction between two colloids immersed in a polyelectrolyte reservoir.

3. Homopolymers

The reference polymer studied in this paper is characterized by \( N = 500 \), \( b = 2.5 \, \text{Å} \), \( a_m = 1.25 \, \text{Å} \), \( l_p = 25 \, \text{Å} \), \( Z_m = 0.347 \), as for a typical fully charged polystyrene sulphonate system. The radius of gyration of the chain is thus \( R_g \approx 100 \, \text{Å} \), and the overlap monomer density is \( \rho_m^* \approx 0.2 \, \text{M} \). The reference colloid is defined by \( a_c = 50 \, \text{Å} \), \( Z_c = 50 \).

*Phil. Trans. R. Soc. Lond. A* (2001)
Figures 2–4 correspond to a colloidal density of 5% in volume fraction and four increasing monomer densities, $\rho_m = 0$ (pure colloidal system), 0.1 M (dilute regime), 0.5 M and 1 M (semi-dilute regime). In order to clarify the picture, the Debye length $\kappa^{-1}$ is fixed equal to 15 Å during the addition of polymer. The pair distribution functions $g_{ij}(r)$ are given in figure 2. The shape of $g_{mm}(r)$ is typical of mm correlations in polymer solution (Honnell et al. 1990; Schweizer & Curro 1987, 1988). In the dilute regime, the characteristic ranges of $g_{mm}(r)$ are $R_g$ and the mean distance between isolated coils, $(\rho_m/N)^{-1/3}$. In the semi-dilute regime, the important characteristic distance is the correlation length or mesh size of the polymer network (correlation hole), $\xi \approx \rho_m^{-1/2}$. As $\rho_m$ increases in figure 2, $g_{mm}(r)$ becomes shorter range, as expected. The cross-function $g_{mc}(r)$ reveals a depletion region for the monomers in the vicinity of each colloid due to the connected nature of the chains (as in neutral systems, cost in configuration entropy prevents the approach of central monomers from a hard surface) and to the direct electrostatic repulsion. At high monomer density, a peak appears in $g_{mc}(r)$ at intermediate distances, which reflects some kind of structuring of the polymer fluid around the colloidal particles. In the absence of added polymer, the function $g_{cc}(r)$ presents a classical three-dimensional order peak, located at the mean distance $D \approx \rho_c^{-1/3}$, due to the strong electrostatic repulsion between particles. As polymer is added, this peak disappears and is replaced by a high peak near contact, which reveals a partial aggregation of the colloids inside the mixture. As expected, the colloid–colloid partial structure factor $S_{cc}(q)$ given in figure 3 presents the corresponding behaviour: the structure order peak located at $2\pi/D$ is replaced by a weak and broad peak located at $\pi/a_c$, while the osmotic compressibility given by $S_{cc}(0)$ increases and seems to diverge. Both functions unambiguously reveal the existence of effective attraction between colloids, due to the polymer fluid. The effective pair potential $v_{\text{eff}}(r)$ that quantifies this effect is presented in figure 4. In the absence of polymer, $v_{\text{eff}}$ coincides with the direct DLVO repulsion $v_{cc}$. As $\rho_m$ increases (again, at fixed $\kappa$ for clarity), an extra attraction appears which gradually
Colloid–polyelectrolyte mixtures

Figure 5. \((\phi_c, \rho_m)\) phase diagram of colloid–polymer mixtures. \(\phi_c\) is the colloid volume fraction. Each line separates one-phase (1\(\Phi\)) and two-phase (2\(\Phi\)) regions. Neutral or like-charged mixtures.

dominates the full effective interaction. This attraction is of depletion origin, as in hard-sphere mixtures, although its detailed description is not so simple. In neutral colloid–polymer mixtures, it has been shown how the shapes of the colloid–colloid correlations and effective interactions are essentially controlled by the correlation length \(\xi\) of the supporting fluid (Chatterjee & Schweizer 1998a,b). In the presence of electrostatic interactions, the picture becomes more complex due to the coupling between the different direct repulsions and characteristic lengths. The main effect is governed by the entropic plus coulombic repulsion between colloids and polymers. In order to release this constraint, colloids are inclined to approach near contact, which gives rise to a depletion effective attraction (first-order effect in \(\rho_m\)), which adds to the direct repulsion (zero-order effect). On the other hand, the electrostatic repulsion between chains favours the accumulation of chains near surfaces, seen in the peak of \(g_{mc}(r)\). As a consequence, this formation of ‘adsorbed’ layers induces a steric repulsion between particles (second- and higher-order effects). All these effects mix up, and the shape of the total interaction \(v_{cc}^{\text{eff}}\) is not universal and depends on the different parameters. For a precise description, see the more recent study by Ferreira et al. (2000).

At high polymer density, the attraction observed in the effective colloidal interactions may be strong enough to destabilize the solution and induce a demixion between two phases, one dilute in colloid and rich in polymer, the other rich in colloid and dilute in polymer. Figure 5 presents such a phase diagram \((\rho_c, \rho_m)\) for our reference mixture, with \(\kappa\) calculated consistently from the counterion density. The line dividing the phase diagram in one-phase and two-phase regions is, in practice, the locus of points where the PRISM with the chosen integral equations ceases to have a solution. This line may be identified with the spinodal line, although, as usual, no true divergence is observed in the osmotic compressibility (Belloni 1993). The corresponding line for neutral mixtures, given in figure 5 for comparison, is located at lower polymer concentration. Thus, the presence of charges of the same sign on both macromolecules leads to a stabilization of the mixture with respect to the purely neutral case. This indicates that the direct coulombic repulsion between colloids

*Phil. Trans. R. Soc. Lond. A* (2001)
overcomes the strong electrostatic depletion attraction due to the colloid–polymer repulsion (Ferreira et al. 2000).

4. Copolymers

What happens when the polyelectrolyte chain is not fully charged? What is the role of the partial hydrophobicity of the monomers on the stability of the mixture? These questions arise for instance in partly sulphonated polystyrene aqueous solution, where the uncharged styrene monomers are in bad solvent and are exposed to monomer–monomer and monomer–colloid hydrophobic attractions of van der Waals origin. In order to consider these specific effects, the previous PRISM approach is extended by investigating copolymers. Each chain is now composed of \( N_A \) charged monomers A and \( N_B \) neutral monomers B (figure 6). The intra-structure of the chain, in particular the position of the different types of monomers along the full skeleton, is characterized by the partial form factors \( P_{AA}(q) \), \( P_{AB}(q) \) and \( P_{BB}(q) \). In practice, the parameters defining the previous worm-like shape are conserved for the full chain of \( N = N_A + N_B \) monomers, and each site is labelled according to the copolymer nature. In the present case, we will investigate sequential copolymers with \( x_A = N_A/N = \frac{1}{3} \). Each charged site is followed by two neutral sites. For copolymer–colloid mixtures, the OZ equation (2.1) is now a 3 × 3 matricial relation. The matrix \( P \) is diagonal by block (\( P_{c\neq i}(q) = 0 \)). The average colloid–monomer pair distribution function is given by \( g_{cm} = x_A g_{cA} + x_B g_{cB} \). The potentials of interaction are given by the DLVO expressions (2.2) with \( a_A = a_B = a_m \), \( Z_A = 1 \) and \( Z_B = 0 \). Note that, with this choice, the linear charge density of the copolymer is almost identical to that of the previously studied homopolymer. The hydrophobic nature of the B monomers is introduced by adding a short range attraction in the cB potential:

\[
\frac{v_{cB}(r)}{kT} = -K \frac{a_c + a_m}{r} \exp \left[ -\frac{r - a_c - a_m}{d} \right], \quad r > a_c + a_m, \tag{4.1}
\]

where \( K > 0 \) and \( d \) represent the depth (in \( kT \) units) and the range of the attraction, respectively. In order to emphasize the specific effect of the hydrophobicity on the

\[\text{Figure 6. Schematic of a colloid–copolymer mixture. Each chain is a sequential series of one charged site A and two hydrophobic sites B.}\]
colloid–polymer mixture (rather than on the polymer fluid itself), no attraction has been added to the BB interaction.

Figure 7 presents the $g_{mc}(r)$, $g_{cc}(r)$ and $v_{cc}^{\text{eff}}(r)$ functions for the colloid–copolymer mixture in the semi-dilute regime ($\rho_m = 0.5$ M) at increasing values of the cB affinity $K$, with $d = 7.5$ Å (less than $\kappa^{-1} = 15$ Å). For all cases, the difference between $g_{cA}$ and $g_{cB}$ is almost negligible, despite the strong difference in the pair interaction, $v_{cA} > 0$, $v_{cB} < 0$. The origin of this behaviour is related to the connectivity of the chains: A and B neighbouring sites in a sequence ABB are forced to stay together along the skeleton and, thus, must interact as a whole with the colloids, without local demixing (differences between $g_{cA}$ and $g_{cB}$ are more important for much less charged chains, $x_A \ll 1$, or for block copolymers (Ferreira & Belloni 2001)). The case $K = 0$ can be compared with the corresponding homopolymer case of figures 2–4. The depletion attraction in the effective colloid interaction $v_{cc}^{\text{eff}}(r)$ is slightly stronger in the copolymer geometry, although the polymer charge density is identical in both cases. The reason is that the statistically averaged colloid–monomer potential deviates from and becomes more repulsive than the mean potential at short distances (Ferreira & Belloni 2001). As the cB affinity $K$ is turned on, an accumulation of monomers or pieces of chain around the colloids is observed in $g_{cm}$, as expected. Consequently, the depletion attraction in $v_{cc}^{\text{eff}}$ gradually disappears and is replaced by a steric, stabilizing repulsion between the adsorbed charged layers (see inset in figure 7). In parallel, the colloidal clusters seen in $g_{cc}$ are destroyed. If the affinity still
increases, an extra attraction appears at intermediate distances (in the case where \( K = 3.7 \)), which is due to the bridging between colloids through doubly adsorbed chains. Although this scenario is formally equivalent to that obtained in hard-sphere mixtures or in colloid-adsorbing coil mixtures, the details of the successive correlations and local structures observed in our colloid–polyelectrolyte mixtures strongly depend in practice on the charged, connected and entangled nature of the polymer network.

References

Ferreira, P. G. & Belloni, L. 2001 (In preparation.)