

Adsorption of water soluble ionic/hydrophobic diblock copolymer on a hydrophobic surface

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Summary. We consider the adsorption of a *A-B* diblock copolymer on a planar hydrophobic surface in aqueous solution. The hydrophobic anchor (*A*) block is envisioned to avoid water and adsorbs on the solid-liquid interface in a collapsed state. The buoy block (*B*) is a polyelectrolyte which expands in solution and forms a brush whose structure depends strongly on the ionic strength of the solution. The minimization of the grand canonical free energy of the system gives access to the surface density (σ), the thickness of the collapsed layer (L_A) and the thickness of the external polyelectrolyte layer (L_B). These three parameters L_B , L_A and σ are functions of the molecular weight of the anchored block (N_A), the molecular weight of the buoy block (N_B), the charge of the polymer (Z) and the ionic strength of the aqueous solution (ϕ_s).

Key words: Adsorption – Block copolymers – Ionic solutions – Polyelectrolytes

1. Introduction

Different macromolecular architectures can be employed to protect against flocculation of colloidal suspensions. Stabilization by adsorption of homopolymers has received much attention [1–8]. Recent studies, both experimental [9–12] and theoretical [13–17], consider end-grafted polymers, or block copolymers. The interesting case is that of selective adsorption, where attachment occurs only through the anchoring group or block. The two main advantages of these polymeric amphiphiles are, first that, in good solvent, there is no possibility of bridging (bridging occurs when one macromolecule is adsorbed on two or more particles at the same time, which is favored when the size of the macromolecule is large compared to the radius of the particle and/or when the concentration in particles is very high), and second that the range of stabilization, i.e., the average distance between two stabilized colloidal particles, can be much larger, for the same chain length, than with homopolymers. This is due to the fact that when the adsorbed amount is high enough, the chains are overlapped and adopt stretched conformations. For neutral polymer for example, the thickness of the brush then formed is directly proportional to the

polymerization degree N , whereas for homopolymers the thickness of the adsorbed layer is of the order of magnitude of the radius of gyration of the chain.

Most theoretical calculations consider the case of a grafted polymer brush where the surface density σ is a specified parameter. Note that σ has to be high enough so that the chains are effectively overlapped ($\sigma > \sigma^*$ where σ^* is the minimum overlap surface density defined by $R_g = d$, where R_g is the radius of gyration of the macromolecule and d is the distance between two adjacent grafting points). In practical experiments where the adsorption occurs from a polymer solution, σ is not a parameter but is a variable that adjusts itself to minimize the total free energy of the system. A theory based on this idea has been developed by Marques, Joanny and Leibler (MJL) [18] in the case of neutral polymer.

The aim of this work is to extend their calculations to the case of an ionic brush in order, using very simple calculations, to describe (by its surface density and thickness) the structure of a layer assembled by adsorption of a hydrophobic-electrolytic diblock copolymer on a hydrophobic surface in aqueous solution. This is achieved by introducing in MJL theory the free energy of a grafted polyelectrolyte brush calculated by Pincus [19]. Note that MJL theory has been validated by recent experiments studying the adsorption of polyvinylpyridine/polystyrene diblock copolymers on silica from toluene solution [20], and so appears to be a reliable starting point for this calculation.

According to MJL theory, the equilibrium structure of the block copolymer layer is obtained when the grand canonical free energy is minimum. Let us call this free energy per unit area G . G contains three principal contributions:

$$G \simeq F_A + F_B + F_{\text{ex}}. \quad (1)$$

F_A is the free energy of the film, $F_A = -S + A/12\pi L_A^2$. S is the spreading coefficient, representing the ability of the adsorbing group to spread and cover the surface, defined as $S = \gamma_{sl} - \gamma_{sf} - \gamma_{fl}$, where γ_{sl} , γ_{sf} and γ_{fl} are respectively the surface tensions between the surface and the liquid, the surface and the spreading film, and, the film and the liquid. A is the effective Hamaker constant characterizing van der Waals interactions. L_A is the thickness of the adsorbing film. F_B is the configurational free energy of the brush. F_{ex} is the contribution of exchange with the bulk solution: $F_{\text{ex}} = -\mu_{\text{ex}}\sigma a^{-2}$ where μ_{ex} is the chemical potential of the solution.

The minimization of G gives different regimes according to the chemical potential of the solution in contact with the surface. In the following, we will consider the regime where the structure of the layer is defined by the balance between the van der Waals interaction and the free energy of the brush. Assuming a free energy for the brush $F_B = kTa^{-2}N_B\sigma^{5/3}$ (cf. Sect. 2), the layer is characterized by a surface density σ :

$$\sigma = (A/kT)^{3/11} N_A^{-6/11} N_B^{-3/11}. \quad (2)$$

We can then calculate the thicknesses of the inner collapsed layer L_A and the outer brush L_B :

$$\begin{aligned} L_A &= aN_A\sigma \propto N_A^{5/11} N_B^{-3/11} \\ L_B &= aN_B\sigma^{1/3} \propto N_A^{-2/11} N_B^{10/11}. \end{aligned} \quad (3)$$

The paper is organized as follows: The next section is a comparison of a grafted brush constituted of neutral polymer (using a Flory approach) and a grafted

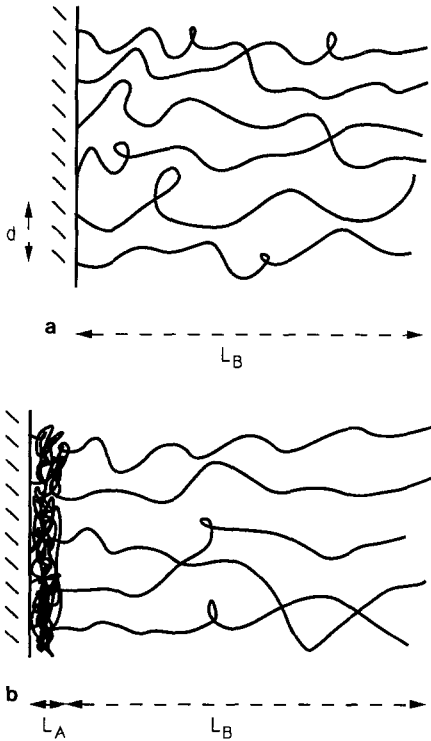


Fig. 1a,b. Schematic diagram of polymer brushes in aqueous solutions: **a** grafted polyelectrolyte, **b** adsorbed ionic/hydrophobic diblock copolymer

brush constituted of polyelectrolyte (following Pincus description [19]). In Sect. 3, we extend the MJL theory [18] to the case of the adsorption of an ionic/hydrophobic diblock copolymer.

2. Grafted layers of neutral and charged polymers

We first review the situation of end-grafted flexible neutral polymer in good solvent using the Flory mean field approach. Let us consider macromolecules of N_B monomers of length a each, grafted to a flat surface at a density σ so that the distance d between adjacent grafted points is smaller than the radius of gyration of the free coil (Fig. 1a). Two terms contribute to the free energy of a grafted chain:

$$F_{\text{ch}} = F_{\text{el}} + F_{\text{os}} \quad (4)$$

F_{el} is the elastic part of the free energy that comes from the stretching of the chain. Assuming the chain obeys Gaussian statistics, F_{el} is given by $F_{\text{el}} = L^2 / N_B a^2$. F_{os} is the osmotic part of the free energy that comes from the repulsive interactions between monomers. With an excluded volume parameter v , in the mean field approximation F_{os} is given by $F_{\text{os}} = kT v N_B c$, where c is the local monomer concentration. Assuming that the monomer concentration in the layer is constant and equals: $c = N_B / d^2 L$, the minimization of the free energy determines the equilibrium thickness of the brush L :

$$L = a N_B (v \sigma)^{1/3}. \quad (5)$$

The free energy per unit area of the brush $F = \sigma a^{-2} F_{\text{ch}}$ is then given by:

$$F = kTa^{-2}v^{2/3}N_B\sigma^{5/3}. \quad (6)$$

Note that in this approach the two contributions in the free energy F_{el} and F_{os} are overestimated. Using scaling arguments, Alexander [13] and de Gennes [14] found the same expression for the thickness L (5) but a lower free energy per unit area $F = kTa^2N_B\sigma^{11/6}$, due to excluded volume correlations not included in the mean field picture. In spite of the very crude assumption of the step-like concentration profile, the scaling variations of L with N_B and σ has been confirmed by more sophisticated self consistent field calculations [15] and experiments [9].

We consider now the case of a polyelectrolyte brush constituted of highly charged polyions grafted to a surface. We will keep the same notations as for neutral polymer and call Z the ionicity of the polymer (percentage of charged monomer). Let us consider first the case where no additional salt is added to the solution. Pincus' approach [19] for describing the brush consists in writing a force balance between the chain elasticity and the osmotic swelling due solely to the counterions. One imagines the ions to be confined to the brush as though by a membrane made impermeable by the maintenance of electroneutrality in the brush. The effects of excluded volume between monomers are here neglected. In the case of a highly charged polyelectrolyte ($Z = 1$), the balance of pressure can be written as $L/a^2N_Bd^2 = Zc$, where c is the monomer concentration. Assuming the concentration is constant in the profile ($c = N_B/d^2L$), the thickness of the brush is given by:

$$L = aN_BZ^{1/2}. \quad (7)$$

Note that L is independent of σ and can be very large comparatively to a neutral brush. In practical experiments σ is usually very small ($\sigma \ll 1$). For example for $\sigma = 10^{-3}$, the thickness of the brush is around 10 times larger for an ionic polymer than for a neutral polymer. The free energy of a grafted polyelectrolyte chain is:

$$F_{\text{ch}} = kTN_BZ. \quad (8)$$

This expression shows that the free energy of a grafted polyelectrolyte brush is much larger than for a neutral brush. For $\sigma = 10^{-3}$, the difference is around two orders of magnitude.

Equation (7) shows that the thickness of the brush is very close to the fully extended chain length, thereby invalidating the usual form of the stretching energy (L^2/Na^2) that has been used earlier. A better expression of this elastic energy, that diverges when the chain is completely stretched is:

$$F_{\text{el}} = kT/N_Ba^2(L^2/l - (L/L_{\text{max}})^2) \quad (9)$$

where $L_{\text{max}} = aN_B$. Assuming this expression, the balance of pressure determines the thickness of the brush L :

$$L = aN_B(Z/1 + Z)^{1/2} \quad (10)$$

which is very similar to Eq. (7), indicating that finite extensibility of the chain does not change the qualitative behavior even though they are highly stretched.

We consider now the case where a concentration c_s of monovalent salt is added to the solution. We suppose $Z = 1$. The free energy of a grafted stretched

chain has two contributions: An elastic contribution $F_{el} = L^2/N_B a^2$ and an osmotic contribution F_{os} . From Witten and Pincus [21] expression for the osmotic pressure of a semi-dilute polyelectrolyte solution, one can determine the osmotic contribution in the free energy per unit volume $F \simeq c^2/(c_s + c) \simeq c^2/c_s$. (We suppose that the concentration of additional salt is much larger than the concentration of counterions brought with the polymer.) This result can be understood by describing the chain as a succession of segments of size L_e , where L_e is the persistence length of the chain. (The contribution of the backbone is supposed negligible vis-à-vis the electrostatic contribution in the total persistence length.) The concentration of segments is $c_e = ca/L_e$, each characterized by an excluded volume $v_e = L_e^3$. By analogy with the neutral case, the main contribution in the osmotic free energy per unit volume is $F = v_e c_e^2$. As L_e scales as $(c_s + c)^{-1} \simeq c_s^{-1}$, F is given by $F \simeq c^2/c_s$. The osmotic part of the free energy per chain is then $F_{os} = FN_B/c \simeq N_B c/c_s$. Thus, as $c = N_B/Ld^2$ and $\sigma = (a/d)^2$, the free energy of a chain is $F_{ch}/kT \simeq c_s L^2/N_B a^2 + N_B^2 \sigma/c_s L a^2$. The thickness of the polyelectrolyte brush is thus determined by the minimization of the free energy:

$$L_B \simeq N_B \sigma^{1/3} c_s^{-2/3}. \quad (11)$$

Introducing $\phi_s = c_s a^3$, the free energy of a grafted chain is given by:

$$F_{ch} \simeq kTN_B \sigma^{2/3} \phi_s^{-1/3}. \quad (12)$$

The thickness of the brush decreases with the salt concentration as an effect of the screening of the electrostatic repulsions between charged groups. If we compare the thickness of the brush constituted of completely charged polyelectrolyte L_{pol} and of neutral polymer L_{neu} of same molecular weight, we find $L_{pol}/L_{neu} = (v/\phi_s)^{1/3}$. As usual, v is of the order of magnitude of 1 and ϕ_s much smaller than 1, therefore L_{pol} can here again be much larger than L_{neu} .

3. Adsorption of an ionic/hydrophobic diblock copolymer

In this part we consider the adsorption of an ionic/hydrophobic diblock copolymer dissolved in aqueous solution on a neutral hydrophobic surface. The hydrophobic block is in a bad solvent and adsorbs on the surface in a collapsed state ($R_g = aN^{1/3}$), whereas the polyelectrolyte block dangles in solution (Fig. 1b). The structure of the layer will depend on the ionic strength of the solution. We examine the two cases when additional salt is or is not added to the solution.

Case 1: No additional salt

The only electrolytes present in solution (except H^+ and OH^-) are the counterions that neutralized the polymer. We will assume that the polymer is highly charged ($Z \simeq 1$) and that the surface density is high enough so that the outer layer is overlapped ($d < R_{gB}$). In that case the free energy of the polyelectrolyte brush is from Eq. (8).

$$F_B = kT\sigma N_B Z. \quad (13)$$

According to the MJL theory, the grand canonical energy of the system per unit area G is given by $G = F_A + F_B + F_{\text{ex}}$, that is:

$$G = -S + A/12\pi L_A^2 + kTa^{-2}\sigma N_B Z - \mu_{\text{ex}}\sigma a^{-2}. \quad (14)$$

The hydrophobic block adsorbs in a compact state so that:

$$L_A = aN_A\sigma. \quad (15)$$

The equilibrium surface density is obtained by minimization of the free energy of Eq. (14) at constant chemical potential. We will restrict ourselves to the case where the concentration of polymer is small so that μ_{ex} is slightly positive and where $N_B > N_A$. The minimization of G then leads to (omitting all numerical coefficient):

$$-A/12\pi N_A^2\sigma^3 + kTN_B Z = 0. \quad (16)$$

We can thus determine the surface density, which is directly linked to the adsorbed amount of polymer:

$$\sigma = (A/12\pi kT)^{1/3} N_A^{-2/3} N_B^{-1/3} Z^{-1/3} \quad (17)$$

σ is a decreasing function of N_A , N_B and of the degree of ionicity of the polymer. The former is due to the fact that, the smaller the anchor block is, the larger the number of chains that can adsorb for the same compaction is. Indeed the area occupied by one anchored block on the surface is proportional to $R_{gA}^2 \propto N_A^{2/3}$. The latter can be understood by, the thicker and the more charged the brush is, the more energy it will cost for another charged chain to penetrate the brush and adsorb on the surface. Let us note that the same qualitative sense of variation of σ with N_A and N_B has already been observed with neutral polymer. Knowing σ we can then calculate the equilibrium thicknesses of the two layers, L_A and L_B :

$$\begin{aligned} L_A &= aN_A\sigma \propto N_A^{1/3} N_B^{-1/3} Z^{-1/3} \\ L_B &= aN_B Z^{1/2} \end{aligned} \quad (18)$$

L_B is independent of σ .

Case 2: Some additional salt

We consider a diblock copolymer with a completely charged polyelectrolyte block ($Z = 1$) dissolved in an aqueous solution of a monovalent salt at a concentration c_s . (We will characterize the ionic strength of the solution by the volume fraction in salt ϕ_s with $\phi_s = c_s/a^3$.) Assuming that the adsorbed amount of polymer is sufficient so that the outer layer is a brush, the free energy of the polyelectrolyte brush is given by Eq. (12):

$$F_B = N_B\sigma^{5/3}\phi_s^{-1/3}. \quad (19)$$

By taking F_B into account the grand canonical free energy per unit area is written as:

$$G = -S + A/12\pi a^2\sigma^2 N_A^2 + kTa^{-2}N_B\sigma^{5/3}\phi_s^{-1/3} - \mu_{\text{ex}}\sigma a^{-2}. \quad (20)$$

The minimization of G in the case where the contribution of the bulk solution is small gives:

$$-A/12\pi N_A^2\sigma^3 + kTN_B\sigma^{2/3}\phi_s^{-1/3} = 0. \quad (21)$$

The surface density is then given by:

$$\sigma = (A/12\pi kT)^{3/11} N_A^{-6/11} N_B^{-3/11} \phi_s^{1/11}. \quad (22)$$

We check that σ is here again a decreasing function of N_A and N_B , this for the same reason as in the case of no additional salt (Case 1). More interesting is the variation of σ with the ionic strength of the solution. The increase of σ with the salt concentration is a direct effect of the screening of the electrostatic repulsion between charged groups. The bigger the ionic strength is, the less energy it costs for a free macromolecule to penetrate the brush in order to adsorb on the surface. From the knowledge of σ , one can describe the structure of the adsorbed layer by:

$$\begin{aligned} L_A &= aN_A\sigma \propto N_A^{5/11} N_B^{-3/11} \phi_s^{1/11} \\ L_B &= aN_B\sigma^{1/3} \phi_s^{-2/3} \propto N_A^{-2/11} N_B^{10/11} \phi_s^{-7/11}. \end{aligned} \quad (23)$$

The variations of L_A and L_B with the molecular weights of the two blocks N_A and N_B are the same as for a neutral polymer (cf. Introduction). L_A increases with ϕ_s as an effect of σ . As far as the thickness of the outer layer is concerned, the increase of the ionic strength has two antagonist effects. On the one hand it increases the adsorbed amount, but on the other hand the conformation of the polyelectrolyte block is more contracted because of the screening of coulombic repulsions. The second effect is more important and the thickness of the brush decreases when the salt concentration increases, but with a smaller exponent than for a grafted layer where σ is supposed constant.

4. Conclusion

We examined the adsorption of a hydrophobic/ionic diblock copolymer in aqueous solution on a neutral hydrophobic surface. A description of the adsorbed layer is obtained through the dependence of the surface density (σ), the thickness of the collapsed inner layer (L_A) and the thickness of the outer polyelectrolyte layer (L_B) as a function of the molecular weight of the anchored block (N_A), the molecular weight of the buoy block (N_B), the charge of the polymer (Z) and the ionic strength of the aqueous solution (ϕ_s).

It would be very interesting to check out the validation of these calculations using surface force apparatus experiments. An amenable experimental system appears to be a diblock poly-*t*-butylstyrene-polystyrene sulfonate in aqueous NaCl solutions adsorbed on mica that has been hydrophobically modified by adsorption of a monolayer or deposition of a Langmuir–Blodgett film. Experiments are in progress.

An interesting extension of this study concerns curved interfaces, which are involved in many practical and commercially important applications such as the stabilization of colloidal aqueous systems.

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