

COPOLYMER ADSORPTION

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I- Introduction

The stabilization of colloidal suspensions plays an important role in many technologies such as powder processing of ceramics or water treatment. The attractive Van der Waals interaction between like particles must be compensated either by a repulsive electrostatic force (in a polar solvent such as water) or by a repulsive steric force. Steric stabilization of colloidal suspensions is usually achieved by adsorbing around each particle a surfactant or a polymer layer. The interactions between colloidal particles and a polymer solution are however rather subtle and do not always lead to a stabilization even when the polymer solution adsorbs onto the colloidal particles. Several necessary conditions¹ must be fulfilled for an efficient stabilization by neutral flexible polymers : the solvent must be a good solvent for the polymer chains, the polymer corona must be thick in order to prevent Van der Waals sticking between the particles and the adsorption must be irreversible.

Many flexible homopolymer chains in a good solvent adsorb onto solid particles. They form a fluffy layer with a thickness of the order of the radius of gyration of the free chains in solution which has now been described in details both experimentally and theoretically. Most of the experimental results can be understood in terms of the self-similar description of this layer first proposed by deGennes² and sketched in figure 1.

An alternative way to form a thick polymer layer is to graft by one end a non adsorbing polymer on the particles surface³. If the grafting density is high enough, the grafted chains may be in a stretched configuration and the polymer layer (sometimes called a polymer brush) has a thickness proportional to the molecular weight i.e. much larger than the radius of gyration which is the thickness obtained in homopolymer adsorption. In principle such brushes could be made by chemical grafting ; it seems however difficult to produce high grafting densities for large molecular weights. A simple and versatile method is then to use diblock copolymers : one block of the copolymer B is in a good solvent and is strongly repelled by the colloid surface, it forms the brush that stabilizes the suspension ; the other block A is strongly attracted by the surface, it forms an adsorbed layer on the surface and is used as a grafting agent. The important parameter is then the grafting density σ (the number of chains per unit surface) which controls the stretching of the brush and which

may be monitored by the chemical potential of the bulk copolymer solution in equilibrium with the adsorbed layers. Finally, diblock copolymers are also interesting as a model for classical surfactants which are often used for steric stabilization of colloidal suspensions.

Other copolymer architectures can also be used to form polymer coronas around colloidal particles. A particularly interesting one is that of random copolymers for which the structure of the adsorbed layer is intermediate between the brush and the self-similar layer configurations. The random copolymer is composed mainly of B monomers repelled by the wall and in a good solvent, a small fraction f of the monomers being A monomers strongly attracted by the surface. The adsorbed layer still has loops as in homopolymer adsorption but the size of the loops seems to be much larger for random copolymers.

In this short review we first discuss diblock copolymer adsorption in the two extreme limits where the anchoring block A is in a poor solvent and in a good solvent, focussing on the grafted chain density σ and on the geometry of the adsorbed layer. We then briefly study random copolymer adsorption insisting on the loop distribution. The discussion section is devoted to possible connections with experiments.

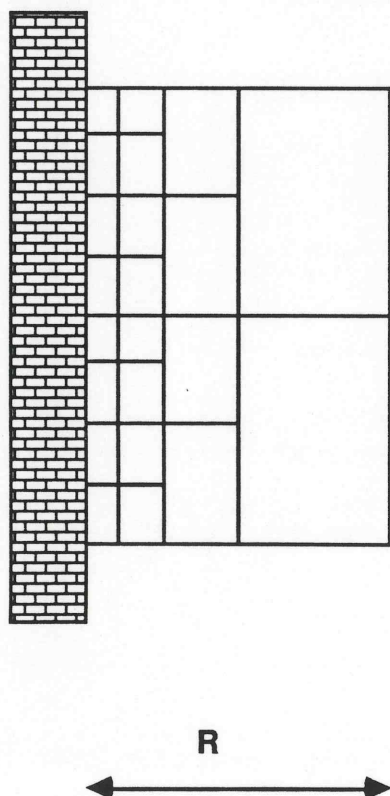


Figure 1 : Self-similar picture of an adsorbed homopolymer layer ; the local mesh size ξ is equal to the distance to the wall, the monomer concentration decays with the distance z from the wall as $\phi(z) \sim z^{-4/3}$, the layer thickness is the chain Flory radius R .

II- Adsorption of diblock copolymers

The colloidal particle is idealized as a planar solid wall. The structure of the copolymers has been outlined in the introduction : the B block forming the brush has N_B monomers, it is in a good solvent and is repelled by the surface ; the anchoring block A with N_A monomers is strongly attracted by the surface. Polymers A and B are assumed to be strongly incompatible as it is usually the case for chemically different polymers. The structure of the adsorbed layer is controlled by three parameters :

- the asymmetry of the copolymer which is measured by the ratio of the radii of the two blocks $\beta = \frac{R_B}{R_A}$ (we are interested here in thick layers and we will consider only situations where $\beta > 1$)

- the copolymer concentration in the bulk of the solution which imposes a chemical potential μ_{ex} that depends strongly on the tendency of the copolymer to self-associate and form mesophases

- the quality of the solvent for the anchoring block A which ranges from a poor solvent where the A block forms very dense regions to a good solvent where the A regions are swollen

1- Adsorption in a highly selective solvent⁴

We first consider the limit where the solvent is so poor for the A block that A monomers form molten regions from which both the solvent and the B monomers are excluded. The natural radius of the A block is then the gaussian radius $R_A = N_A^{1/2}a$ (where a is the size of both A and B monomers) and $\beta \sim \frac{N_B^{3/5}}{N_A^{1/2}}$.

In such a solvent, the copolymer has a strong tendency to self-aggregate and to form mesophases in the bulk. We will consider here as an example that the bulk is a micellar solution just above the critical micelle concentration (The core of the micelles is a molten A region, the B blocks dangling in the solution). The critical micelle concentration has been studied in details in reference 4, it has been shown to be an exponentially decaying function of the molecular weight N_A

$$\text{Log } \phi_{cmc} \sim - \frac{\gamma_{AS} a^2}{T} N_A^{2/3} \quad (1)$$

where γ_{AS} is the interfacial tension between the molten A core and the solvent. Taking the molten state as a reference state for A monomers the chain chemical potential at the c.m.c. scales as

$$\mu_{ex} \sim T N_A^{2/5} \left(\frac{\gamma_{AS} a^2}{T} \right)^{3/5} \quad (2)$$

In contact with the wall, the micellar solution forms a molten A layer of thickness d with the B blocks dangling in the solution and forming a brush. Mass conservation relates the molten layer thickness to the chain density σ

$$N_A \sigma a = d \quad (3)$$

The properties of the B brush have been studied by Alexander⁵ within the framework of a blob model and in a more precise way by Milner et al.⁶. The simpler blob model is used here : the thickness L of the brush is related to the chain density σ by

$$L \sim N_B \sigma^{1/3} a \quad (4)$$

the free energy per unit surface of the brush is

$$F_B \sim T a^{-2} N_B \sigma^{11/6} \quad (5)$$

The free energy of the molten layer includes both a molecular contribution and a configurational contribution (confinement of the chains in the layer of thickness A). The confinement energy of a melt has been shown to vanish by deGennes⁷, the energy of the molten layer has thus only a molecular contribution which for simplicity we will assume to be dominated by Van der Waals forces with a negative Hamaker constant $-A^8$

$$F_A = \frac{A}{12\pi d^2} \quad (6)$$

The grand canonical free energy of the adsorbed copolymer layer per unit surface may then be written as

$$G = -S + F_B + F_A - \mu_{ex} \sigma a^{-2} \quad (7)$$

S (the so-called spreading power) takes into account the various interfacial tension contributions between the wall, the molten A region and the solvent ; F_B is the free energy of the brush , F_A that of the molten layer and the last term is the chemical potential contribution.

The structure of the adsorbed layer in equilibrium with a micellar solution is given by minimization of the free energy (7) with a chemical potential given by (2). Two different regimes are found :

i- Symmetric polymers : if the radius ratio β is of order 1, the Van der Waals contribution to the free energy is small and the chain surface density is

$$\sigma = N_A^{-13/25} \beta^{-2} \left(\frac{\gamma A s a^2}{T} \right)^{18/25} \quad (8)$$

This is slightly smaller than the chain density in a micelle. The thickness of the brush is equal to that of a micelle

$$L = R_B N_A^{4/25} \left(\frac{\gamma A s a^2}{T} \right)^{6/25} \quad (9)$$

R_B being the Flory radius of the B blocks ($R_B \sim N_B^{3/5}$)

ii- Dissymmetric polymers : as soon as the radius ratio is larger than 1, the chemical potential contribution to the free energy is small and

$$\sigma = \left(\frac{A N_A}{T} \right)^{6/23} \frac{1}{N_A} \beta^{-10/23} \quad (10)$$

In the brush, the chains are almost fully extended

$$L = R_B \left(\frac{AN_A}{T} \right)^{2/3} \beta^{12/23} \quad (11)$$

which scales approximately linearly with the mass of the B block.

2- Adsorption in a nonselective solvent⁹

If the solvent is not extremely selective, it swells the A regions both in the bulk and on the surface, we now consider the extreme limit where it is equally good for both blocks. In this limit, the natural radius of the blocks is their Flory radius and $\beta \sim \left(\frac{N_B}{N_A} \right)^{3/5}$. In a nonselective solvent, mesophase formation occurs way above the overlap concentration and as soon as we consider only dilute solutions, they remain homogeneous : the chain chemical potential varies with the overall monomer concentration as

$$\mu_{ex} = T \text{Log } \phi_b$$

On the wall, the B monomers still form a brush with a free energy per unit surface given by eq.(5). The A monomers form a swollen fluffy layer quite similar to the self-similar grid obtained in homopolymer adsorption; the free energy of this layer still contains a configurational contribution and a Van der Waals contribution, however even close to the wall the solution is rather dilute and the Van der Waals term is in general small ; the free energy of the A layer can then be written as a functional $F_A[\phi_A(z)]$ of the local concentration of A monomers.

The structure of the adsorbed layer is obtained by minimization of the grand canonical free energy per unit surface G with respect to the two variables σ and $\phi_A(z)$. These two variables are however not independent, the two blocks being linked in a copolymer :

$$\sigma = \frac{1}{N_A} \int_0^{\infty} \phi_A(z) \frac{dz}{a} \quad (12)$$

This constraint is taken into account by introducing a Lagrange multiplier λ and by minimizing

$$\Omega = G - \lambda T a^{-2} \left\{ \sigma - \frac{1}{N_A} \int_0^{\infty} \phi_A(z) \frac{dz}{a} \right\} \quad (13)$$

Minimization with respect to ϕ_A gives the structure of the A layer. The important result is that although the presence of the B blocks reduces the number of adsorbed chains (λ is positive), the decay of the concentration is the same that would be obtained from adsorption of a homopolymer A,

$$\phi_A(z) \sim z^{-4/3} \quad (14)$$

only the thickness of the A layer is reduced from the Flory radius R_A to

$$d = \left(\frac{N_A}{\lambda} \right)^{3/5} a \quad (15)$$

Inserting the concentration profile (14) in the constraint (12), we obtain a relationship between d and the chain density

$$N_A \sigma = 1 - \left(\frac{a}{d} \right)^{1/3} \quad (16)$$

The last needed equation is obtained by minimization of the free energy with respect to the chain density σ

$$\lambda + \frac{\mu_{ex}}{T} = N_B \sigma^{5/6} \quad (17)$$

where when the bulk solution is dilute, the chemical potential makes only a small contribution.

In the limit where the radius ratio β is smaller than $N_A^{1/2}$, this continuous description retains a meaning and the structure of the adsorbed layer is given by eqs (15-17)

$$\sigma = \frac{1}{N_A}, \quad d \sim \frac{N_A^{1/2}}{\beta} a, \quad L \sim N_B N_A^{-1/3} a \quad (18)$$

A comparison with the structure of the adsorbed layer in a highly selective solvent shows as expected that a highly selective solvent is more efficient for colloid stabilization (denser and thicker layer); however these results also show that the formation of a brush is possible even in a nonselective solvent.

When the copolymer is too dissymmetric ($\beta \gg N_A^{1/2}$), the thickness d of the A layer becomes of the order of a monomer size a and the adsorbed layer tends to break. In the limit where β is extremely large, the adsorbed layer is a patchwork of individual chains. For each chain, the A block forms a very flat pancake on the wall with a thickness of the order of the monomer size and the B block is stretched towards the solution. The free energy of a single chain adsorbed on a wall being proportional to the number of monomers, the free energy of the A blocks is

$$F_A \sim T N_A \sigma a^{-2} \quad (19)$$

Inserting this in the overall free energy of the adsorbed layer, we obtain the chain density in the discontinuous regime

$$\sigma \sim \beta^{-2} \quad (20)$$

As the asymmetry is reduced, this two-dimensional dilute solution of adsorbed chains first becomes a semidilute solution ($\beta < N_A^{-3/4}$) then crosses over smoothly to a continuous adsorbed layer.

III- Adsorption of random copolymers¹⁰

We now study copolymers still formed from A monomers strongly attracted by the wall and B monomers strongly repelled by the wall but with a different architecture: A monomers are distributed randomly along the chain

with a probability $f = \frac{N_A}{N_A + N_B}$. In the limit where $f=1$ this is a homopolymer and adsorption from a dilute solution leads to a self-similar layer; in the limit where f goes to zero ($N_A = 1$) the polymers stick by one end on the solid surface and form a grafted layer if the chain surface density is imposed (experimentally, the surface may have specific sites where adsorption occurs, if the attraction between these sites and the A monomers is very strong the surface density of A monomers is equal to the density of specific sites). Varying the fraction f of A monomers, one thus crosses over from the brush to the self-similar structure. This crossover is described here in terms of a blob model.

In each chain, we group the B monomers into subunits each containing one A monomer. The average number of monomers per subunit is $P = f^{-1}$ and the Flory radius of these blobs is $r = P^{3/5}a$. We first assume that we know the density of adsorbed monomers on the surface ϕ_S or equivalently the distance between A monomers D , $\phi_S = (a/D)^2$ and that this distance D is smaller than the radius of the blobs. The blobs attached to the surface are thus in a stretched configuration and form a brush with a size given by equation (4)

$$L_0 = P \phi_S^{1/3} a \quad (21)$$

At distances from the surface larger than L_0 , one must take into account the fact that some of the blobs forming this brush are loops of P monomers (on average). The size of these loops is a finite fraction of L_0 , and these loops cannot contribute to the concentration profile at larger distances. Paralleling the construction of the self-similar grid we conjecture that a finite fraction of the blobs (say a half) in contact with the surface are such loops. At distances larger than L_0 the chains are less constrained and thus less extended, they are in the same configuration as in a brush of surface density $\phi_S/4$. We can then iterate the process to successive generations of size L_i and distance between chains D_i as soon as D_i is larger than the size of the individual blobs r . This leads to a geometrical structure of the adsorbed layer sketched in figure 2. When L_i becomes larger than r the chains are not constrained any more and the layer becomes the usual self-similar grid.

This construction contains all the information on the adsorbed layer, details will be given elsewhere we only quote here the essential results.

If the distance z from the wall is smaller than L_0 the concentration profile is that of a (polydisperse) polymer brush. In the blob model discussed above, the concentration ϕ is a constant. At larger distances the concentration decays with distance as

$$\phi(z) \sim \frac{P^2 \phi_S^{4/3}}{z^2} \quad (22)$$

The crossover with the usual self-similar behavior occurs at a distance

$$L' \sim P^{7/5} \phi_S^{2/3} a \quad (23)$$

At larger distances, the profile decays as

$$\phi(z) \sim \frac{p^{16/15} \phi_s^{8/9}}{z^{4/3}} \quad (24)$$

this last regime exists only for large enough polymers.

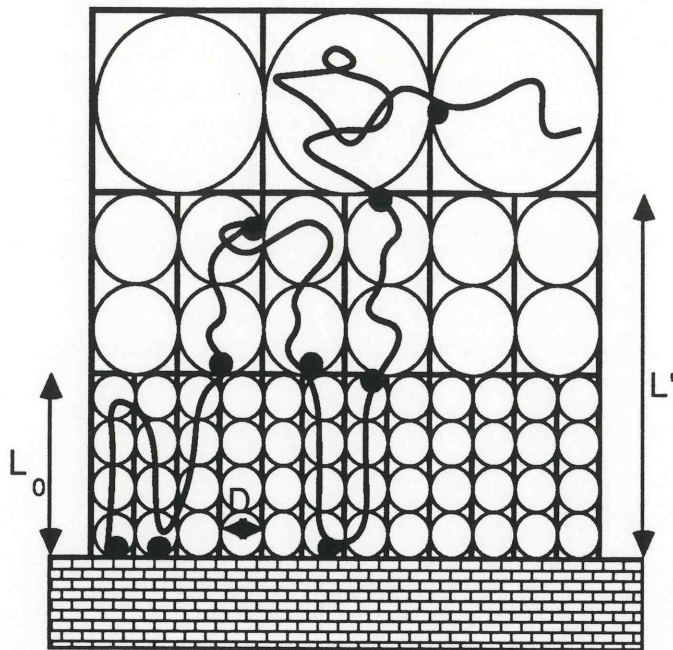


Figure 2 : Blob description of an adsorbed random copolymer layer on a surface. Two generations of blobs are shown before the crossover to the usual self similar layer. The black dots are the A monomers.

The constraint of a given surface concentration ϕ_s on the surface may then be relaxed. The equilibrium surface concentration is obtained by minimization of the free energy of the layer. This energy has two contributions, the direct adsorption energy of A monomers on the surface and the excluded volume energy of the layer. If the adsorption energy is of order T , the distance between monomers on the surface is $D = r$ and the chains are not extended.

This blob description of the adsorbed layer remains somehow qualitative but it shows in qualitative agreement with experiments that random copolymers build larger loops than homopolymers on the surface¹¹.

III- Discussion

Several experimental methods have been developed to investigate the structure of adsorbed polymer layers : hydrodynamic thickness, ellipsometry, neutron scattering, mica force measurement apparatus... However few of those have been applied to copolymers for which only few data are available. We discuss here in more details the force measurements between mica plates

coated by diblock copolymers adsorbed from solution due to the groups of Tirrell¹², Klein¹³ and Hair¹⁴.

If the distance between plates is larger than the thickness of the copolymer layers, the force between the plates due to the copolymer is extremely small ; the onset of apparition of this force is thus a measure of the brush thickness L . All experiments show that this thickness is larger than the Flory radius of the blocks and are compatible with a thickness scaling linearly with the molecular weight of the B block. A more quantitative comparison is in general difficult : few copolymer compositions are available and the solvent is neither highly selective nor nonselective but rather intermediate between these two extremes. Hair's experiments are done in a rather non selective solvent and seem to agree reasonably well with the predictions of eq. (18). In a more selective solvent, we must emphasize that the structure of the adsorbed layer depends strongly on the phase behavior of the bulk solution in equilibrium with the surfaces which is not often known in experiments.

At shorter distances, the variation of the force with the distance h between the plates characterizes the compression of the brush at constant chain density σ (the adsorption is in general irreversible); a scaling analysis leads to

$$f \sim \frac{T}{a^3} \left(\frac{N_B \sigma}{h a^2} \right)^{9/4} \quad (26)$$

where the chain density is given by eq (8), (10) or (18) in the various regimes. The power law dependence in h is in reasonably good agreement with some data of Klein or Tirrell.

We are not aware of any measurements with random copolymer solutions ; in the intermediate regime of distances, the above blob model predicts a variation of the force between plates with distance

$$f \sim \frac{T}{a^3} \left(\frac{P a}{h} \right)^{9/2} \phi_S^3 \quad (27)$$

In conclusion, we must stress that all our conclusions were reached by assuming that the adsorbed polymer layer is in thermodynamic equilibrium with a bulk solution ; in real systems this might sometimes be questionable (in particular with block copolymers), it would thus be of prime interest to study the dynamic of formation of adsorbed copolymer layers.

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