

Irreversible Adsorption of a Polymer Melt on a Colloidal Particle.

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Abstract. - We study the irreversible adsorption of linear polymer chains from a melt onto a spherical particle of radius R . This study generalizes the recent model of Guiselin for the irreversible adsorption of linear chains onto a planar surface. Our main motivation is the major role played by adsorbed polymer layers in the stabilization of colloidal particles. We consider the following sequence of events: *a*) the particle is put in contact with the polymer melt, all the monomers touching the surface adsorb instantaneously and irreversibly, *b*) the particle is then washed out with pure solvent. Using scaling argument, we derive the volume fraction profile $\phi(r)$ (where r is the distance from the centre), the external radius R_c and the free energy F of the adsorbed layer. We then estimate the force $F(h)$ between two particles separated by a distance $2h$. We find that irreversible adsorption might represent a more efficient way of protecting the particles against coalescence than grafting.

Introduction. - Adsorption of linear polymer chains at interfaces is of both practical and theoretical importance and has been the subject of many recent studies [1-11]. The reversible adsorption of flexible neutral chains in a good solvent onto a solid surface leads to a fluffy layer with a self-similar structure [12-14]. This layer is of major importance for the stabilization of colloidal particles [15-18]. Much less is known about *irreversible* adsorption [19-23]. A very elegant scaling approach has been proposed recently by Guiselin [19] who considered irreversible adsorption from a polymer melt (or from a semi-dilute solution) onto a planar surface assuming that the time necessary to saturate all the surface sites was small compared to that of chain diffusion in the bulk. The conformation of the chains is thus not modified during the adsorption process. Guiselin considered the following sequence of events:

a) The planar solid surface is put in contact with a polymer melt (or a semi-dilute solution). All the monomers touching the surface adsorb instantaneously and irreversibly on it. Let $D_1'(n)$ and $D_2'(n)$ denote the number per unit area of loops and tails made of n monomers, respectively. If each loop of size $2n$ is considered as two pseudotails of size n , the number per unit area of pseudotails made of n monomers is then given by $D'(n) =$

$= 2D'_1(2n) + D'_2(n) \cdot D(n) = \int_n^N D'(m) dm$ is the number per unit area of pseudotails made of more than n monomers. For the melt case Guiselin showed that

$$D'(n) \approx a^{-2} n^{-3/2}; \quad D(n) \approx a^{-2} n^{-1/2}, \quad (1)$$

where a is a monomer size.

b) The surface is then washed with pure solvent. Only the initially adsorbed chains are retained onto the surface. Since the adsorption is irreversible, the pseudotail distribution (1) remains unchanged. By analogy with the Alexander-de Gennes model for monodisperse polymer brushes [24, 25], one finds [19] that the polymer volume fraction at a distance z of the surface scales as $\phi(z) \approx (a/z)^{2/5}$. The extension h of the layer is given by $h \approx aN^{5/6}$, where N is the degree of polymerization of the chains.

In the present letter, we extend Guiselin's results to the case of a spherical solid surface of radius R . Our main motivation is the major role played by adsorbed polymer layers in the stabilization of colloids [15]. Our analysis is based on the Daoud-Cotton model for polymer chains grafted on a spherical surface [26]. The paper is organised as follows. We first analyse the case of a large particle ($R > aN^{1/2}$) exposed to a polymer melt (second section). In addition to the polymer volume fraction, the layer external radius and the layer free energy we also estimate the force between two particles protected by irreversibly adsorbed layers. In the third section, the case of a small particle ($R < aN^{1/2}$) is considered. All our study is restricted to scaling laws; the exact prefactors in all our formulae remain undetermined.

Adsorption on a large particle ($R > aN^{1/2}$). - We first consider the irreversible adsorption of a polymer melt on a particle whose radius R is larger than the natural size $aN^{1/2}$ of the chains in the melt. The number of pseudotails per unit area $D'(n)$ is then identical to the planar-surface distribution (1). The total number of pseudotails made of more than n monomers on the particle is given by

$$K(n) \approx R^2 D(n) \approx (R^2/a^2) n^{-1/2}. \quad (2)$$

Let us wash the particle with pure solvent. We assume that the n -th monomers of all pseudotails larger than n are at the same distance r from the centre. We can then consider that n is a function of r . By analogy with the Daoud-Cotton model [26], we expect that locally, at a distance r from the centre, there are $K(n)$ spherical blobs, one for each pseudotails made of more than n monomers. Each blob contains $g \approx (\xi/a)^{5/3}$ monomers. Since $K(n)$ blobs cover a sphere of radius r , the blob radius is given by $\xi(r) \approx r/\sqrt{K(n)}$. The function $n(r)$ satisfies the differential equation $dn/g \approx dr/\xi$ which leads to

$$n(r) = \{1 + (1/2)(R/a)^{-2/3} [(r/a)^{5/3} - (R/a)^{5/3}]\}^{6/5}. \quad (3)$$

The polymer volume fraction $\phi(r) \approx g/\xi^3$ is then given by

$$\phi(r) = (R/r)^{4/3} \{1 + (1/2)(R/a)^{-2/3} [(r/a)^{5/3} - (R/a)^{5/3}]\}^{-2/5}. \quad (4)$$

The external radius R_c of the coated particle can be deduced from the constraint

$$\int_R^{R_c} \phi(r) 4\pi r^2 dr = Q, \quad (5)$$

where Q is the total number of monomers in the adsorbed layer: $Q = \int_1^N nR^2 D'(n) dn \approx (R/a)^2 N^{1/2}$ (see eq. (1)). Note that the total number of polymer chains adsorbed on the particle is given by $S = (R/a)^2 N^{-1/2}$. From eqs. (4) and (5) we get

$$R_c = R \left(1 + \frac{aN^{5/6}}{R} \right)^{3/5} \tag{6}$$

Two limits may be considered. If $R \gg aN^{5/6}$, then $R_c - R \approx aN^{-5/6}$: one recovers the result of Guiselin for the layer extension in the case of a planar surface. On the other hand, if $R \ll aN^{5/6}$, then $R_c \approx (R/a)^{2/5} aN^{1/2}$. This last result is identical to the external radius of a «Daoud-Cotton brush» (*i.e.* chains tethered by one end to a spherical surface) made of S chains, each of length N . Indeed, the Daoud-Cotton prediction for the external radius of a grafted layer consisting of f chains, each of length N , is $R_{DC} = f^{1/5} aN^{3/5}$ [26]. Replacing f by $S = (R/a)^2 N^{-1/2}$, one gets $R_{DC} = ((R/a)^2 N^{-1/2})^{1/5} aN^{3/5} \approx (R/a)^{2/5} aN^{1/2} \approx R_c$. The free

energy of the layer, F , is given by the kT per blob *ansatz* $F/kT \approx \int_R^{R_c} d^3r \xi^{-3}(r)$:

$$F/kT \approx (R/a)^2 N^{1/2}, \quad R \gg aN^{5/6}, \tag{7}$$

$$F/kT \approx (R/a)^{21/10}, \quad aN^{1/2} \ll R \ll aN^{5/6}. \tag{8}$$

Note that in the regime (8) the layer free energy is independent of N .

We now consider the force $F(h)$ between two particles separated by a distance $2h$ (fig. 1a). The interparticle force may be estimated by integrating the normal component of the osmotic pressure over the symmetry plane [27]. Since the osmotic pressure is given by $\Pi \approx kTa^{-3} \phi^{9/4}$ [28] we obtain, using eq. (4),

$$F = kTa^{3/2} (R/a)^{18/5} h(h^{-7/2} - R_c^{-7/2}). \tag{9}$$

It is of some interest to compare this result with the force between two spherical particles

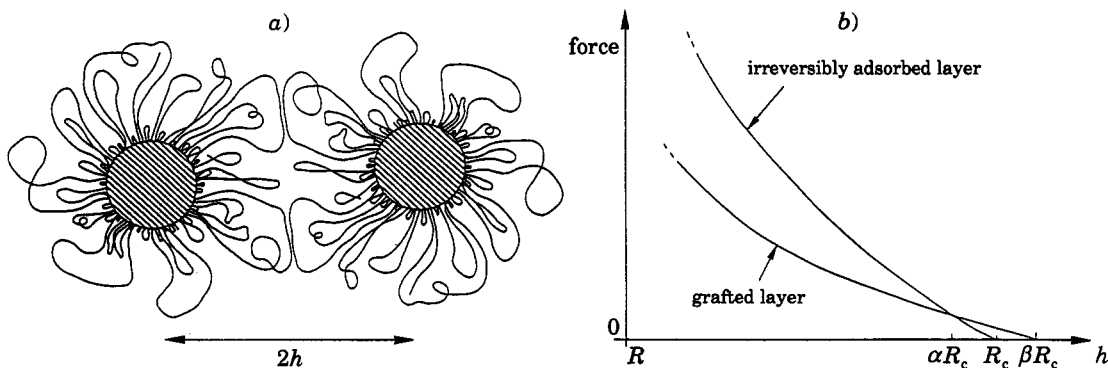


Fig. 1. - a) Sketch of two coated particles separated by a distance $2h$. The particles interact via compression of their respective layers; b) schematic representation of the force between the two particles for both irreversible adsorption and grafting. The curves crossover for $h = \alpha R_c$, where α is a numerical factor ($\alpha < 1$).

grafted with long, monodisperse polymer chains («Daoud-Cotton brushes»)⁽¹⁾. Witten and Pincus have shown that if each particle is grafted with f chains and if each chain consists of N monomers, the force between the two particles separated by a distance $2h$ is given by [27,30]

$$F_{\text{DC}} \approx kTf^{3/2}h(h^{-2} - R_{\text{DC}}^{-2}) \quad (R \ll h \ll R_{\text{DC}}), \quad (10)$$

where $R_{\text{DC}} \approx f^{1/5}aN^{3/5}$. In order to compare eqs. (9) and (10), we choose $f \approx S$ (where $S \approx (R/a)^2N^{-1/2}$ is the total number of polymer chains adsorbed on the particle). The number of chains in the layer is then the same in both situations. Assume $R \ll aN^{5/6}$. As we have already noticed, R_{DC} and R_c are then identical up to a numerical factor of order unity: $R_{\text{DC}} = \beta R_c$. Equation (10) can then be rewritten as

$$F_{\text{DC}} \approx kTN^{-3/4}(R/a)^3h(h^{-2} - (\beta R_c)^{-2}) \quad (R \ll h \ll \beta R_c). \quad (11)$$

The variations of F and F_{DC} with h are represented in fig. 1b). The two curves crossover for $h = \alpha R_c$, where α is a numerical factor of order unity ($\alpha < 1$). For $h \ll R_c$, the force F scales with h like $h^{-5/2}$, while F_{DC} scales like h^{-1} . This significant difference may be traced back to the inner structure of the layer. At a given distance r from the centre of the particle ($r \ll R_c$), the monomer volume fraction equation (4) is larger than the Daoud-Cotton expression $\phi_{\text{DC}}(r) \approx N^{-1/3}(R/r)^{4/3}$ [26]. The osmotic pressure (and hence the force) is thus larger in the case of irreversible adsorption.

Adsorption on a small particle ($R < aN^{1/2}$). – We now consider the adsorption of a polymer melt on a particle whose radius R is smaller than the natural size $aN^{1/2}$ of the chains in the melt. The pseudotail distribution of an adsorbed chain is now sensitive to the curvature of the surface and is therefore no longer given by (1). For example, in the limit of a very small particle ($R \approx a$), we expect almost no loops and two dangling tails each containing monomers of the order of $N/2$. What happens for $a < R < aN^{1/2}$? The adsorbed chain can be pictured as a random walk of subunits of size R , each subunit containing $g \approx (R/a)^2$ monomers. We assume only one of these N/g subunits to interact with the particle, the remaining subunits forming two dangling tails. The washed layer consists of two regions: a) an inner region made of the monomers of the interacting subunits, b) an outer region made of the tails. Since the number g of monomers per interacting subunits satisfies $ag^{1/2} \approx R$, the properties of the inner region can be determined from the results of the previous section by using the substitution $N \rightarrow g$: the polymer volume fraction satisfies eq. (4) and the external radius of the inner region is given by

$$R_i \approx (R/a)^{2/5}ag^{1/2} \approx a(R/a)^{7/5}. \quad (12)$$

The outer region is treated as a brush made of monodisperse chains, each of length $N - g$, tethered by one end to a spherical surface of radius R_i . The number q of chains constituting the outer region is of the order of the number of subunits interacting with the surface: $q \approx a^{-3}R^3g^{-1} \approx R/a$. Using the results of Daoud and Cotton [26], we get for the polymer volume fraction

$$\phi(r) \approx q^{2/3}(r/a)^{-4/3} \approx (R/a)^{2/3}(r/a)^{-4/3} \quad (13)$$

⁽¹⁾ In the case of two *planar* surfaces coated with irreversibly adsorbed layer Guiselin has shown that the force between the surfaces was similar to the force between two Alexander-de Gennes brushes; see [29].

and for the external radius of the coated particle

$$R_c = (R/a)^{1/5} aN^{3/5}. \quad (14)$$

One can check that eqs. (6) and (14) do crossover for $R = aN^{1/2}$.

Using eqs. (8) and (12) and the free energy of a «Daoud-Cotton brush» [26,30] we obtain for the layer free energy (omitting all numerical prefactors)

$$F/kT \approx (R/a)^{21/10} + (R/a)^{3/2} \ln(aN^{1/2}/R), \quad a \ll R \ll aN^{1/2}. \quad (15)$$

For $R_i \ll h \ll R_c$, the force $F(h)$ between two particles separated by a distance $2h$ is given by: $F(h) \approx kT(R/a)^{3/2} h(h^{-2} - R_c^{-2})$.

Concluding remarks. – In this work we have examined the irreversible adsorption of linear polymer chains from a melt onto a spherical particle of radius R . The most interesting results are obtained for $aN^{1/2} \ll R \ll aN^{5/6}$. In this regime, the free energy of the layer, F , is independent of the chain length, N , and the force, $F(h)$, between two particles separated by a distance $2h$ scales with h like $h^{-5/2}$. This result has to be compared with the force between two spherical particles grafted with the same number of chains which scales like h^{-1} [27,30]. Irreversible adsorption may therefore represent a more efficient way of protecting colloidal particles against coalescence than grafting.

Up to now we have considered the case of irreversible adsorption from a polymer melt onto a spherical particle. It is possible to generalize our result to the case of a particle exposed to a semi-dilute solution with a volume fraction Φ [19]. A given chain can be visualized as a succession of blobs of size $\xi \approx a\Phi^{-3/4}$ and the solution is essentially a closely packed system of blobs [28]. The results of the second section for the melt case can thus be generalized by taking the blobs as the basic units. For example, in the case of a large particle $R > R_f \approx aN^{1/2}\Phi^{-1/8}$, the external radius of the layer is given by $R_c \approx R \cdot (1 - aN^{5/6}\Phi^{7/24}/R)^{3/5}$. Note that the above-mentioned generalization is valid, provided that there is less than one adsorption site per blob: $m < \Phi^{-3/2}$, where $m^{-1}a^{-2}$ represents the number of adsorption sites per unit area.

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