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Thermodynamics and kinetics of grafting end-functionalized polymers to an interface

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Résumé. — Nous étudions l'équilibre thermodynamique et la cinétique de formation de chaînes de polymères se greffant sur une interface par un groupe terminal fonctionnalisé. Nous prédisons le taux de couverture et la hauteur de la couche adsorbée, en fonction de paramètres moléculaires comme la masse moléculaire des chaînes, la concentration des chaînes en solution, l'énergie gagnée par l'adsorption d'un groupe terminal. Nous montrons l'existence de deux régimes successifs dans la cinétique d'adsorption. Le premier régime (temps courts) est gouverné par la diffusion brownienne des chaînes dans la solution, le second (temps longs), par la barrière d'activation qui apparaît dès que les chaînes adsorbées commencent à se recouvrir fortement et à s'étirer. Le temps caractéristique de construction varie exponentiellement avec l'affinité chimique du groupe terminal et de la surface d'adsorption. Nous calculons aussi le temps de désorption d'une brosse mise en contact avec le solvant pur : ce temps est toujours plus long que le temps de construction.

Abstract. — We present a theoretical study of the thermodynamics and of the kinetics of grafting end-functionalized polymers to an interface. The equilibrium surface coverage and thickness of the grafted layer are predicted as a function of molecular parameters such as the molecular weight of the chains, the solution concentration and the energy gained by adsorbing the terminal group. We show that there are two successive regimes in the kinetics of adsorption. The first one (short time) is governed by the Brownian diffusion of the chains in the solution, the second regime (long time) by the activation barrier, which appears as soon as the adsorbed chains begin to overlap strongly and to stretch. The characteristic construction time depends exponentially on the chemical affinity of the end group and on the surface. The desorption time of a brush put in contact with the pure solvent is also calculated. The desorption time is always longer than the construction time.

1. Introduction.

Colloidal particles can be protected from flocculation in a suspension by polymer chains attached by one end to their surface. Whenever two grafted layers are forced to overlap, they repel one another and, in some cases, this so called steric repulsion may overcome London-

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van der Waals attraction [1]. The relevant parameter is the surface density of grafted chains σ . A simple and versatile method for anchoring polymers to a surface consists in adsorption of end-functionalized chains [2] or block copolymers [3, 4]. The present work has two goals. First, we predict the surface coverage which can be attained by adsorption of end-functionalized chains in a good solvent as a function of molecular parameters such as molecular weight of chains, the solution concentration and the energy gained by adsorbing the terminal group. Secondly, we study the kinetics of the adsorption and of the desorption and we estimate, in particular, the time necessary to build and to destroy a dense layer of terminally anchored chains. Kinetic considerations may be also of some relevance for the interpretation of recent direct measurements of the force between two grafted layers [2-4]. Indeed, when the surfaces are in contact with the solution of adsorbing chains, the interaction force depends on whether during the characteristic experimental time the grafted and free chains exchange themselves.

Theoretical studies of « polymer brushes » focused on describing the chains conformation in a grafted layer in contact with a pure solvent. Simple Flory-type arguments and a scaling approach [5, 6] indicate that, in a moderately dense layer, grafted chains are stretched. More precise self-consistent-field methods [7, 8] show that the stretching of chains is not uniform and that, in the presence of the solvent, the polymer concentration decays parabolically from the surface [8]. Molecular dynamics [9] and Monte Carlo simulations [10] essentially confirm this picture.

The self-consistent mean-field theory of Milner *et al.* [8] enables one to calculate easily the chemical potential of grafted chains and thus provides a convenient framework for a study of adsorption of end-functionalized chains. Still, as in the case of adsorption of block copolymers [11, 12], the structure of a grafted layer is determined not only by the free energy of chains in the layer, but also by the chemical potential of the solvent and the chains in the reservoir. Hence, in section 2, we generalize slightly the Milner's *et al.* [8] theory in order to calculate the grafted chains conformation and chemical potential for a layer in contact with a solution rather than with the pure solvent. This calculation provides essential ingredients necessary to treat the equilibrium adsorption as well as its kinetics (Sect. 3). At equilibrium, the main result is that the surface coverage depends strongly on the adsorption energy of the end-group and on the molecular weight of the chains. The adsorption processes are complicated by the tendency of end-functionalized chains to self-associate in the solution. In our study of kinetics, we focus on relatively dilute case, below the critical micelle concentration. Then, one expects essentially two simple regimes. First, a classical diffusion limited regime in which the construction of the brush is controlled essentially by the diffusion of chains to the surface. This regime stops rather quickly when chains in a grafted layer start to overlap strongly and to form a barrier towards further adsorption of other chains. The penetration through and the progressive increase of the barrier are characteristic of the second regime.

When the system is close to equilibrium, there is a substantial exchange of already adsorbed and of free chains. The characteristic time, the exchange time is, in fact, of the same order of magnitude as the time of the formation of the brush. When a brush formed by terminally adsorbed chains is put in a contact with the pure solvent, the time of destruction of the brush — « washing time » — is even longer than the exchange time.

2. Equilibrium adsorption of end-functionalized chains.

We consider a wall in contact with a solution of end-functionalized polymers in a good solvent. The polymerization index of chains is denoted by N . We assume that the monomers are repelled by the wall and do not adsorb except for the one end of the chain which is attracted to the wall. At equilibrium the adsorbed chains form a brush with surface coverage

$\sigma = a^2/\Sigma$, where Σ denotes the average surface area per adsorbed chain and a is the Kuhn statistical length. By definition, the end-to-end distance for unperturbed chains is $R^2 = 3Na^2$.

The surface coverage σ depends on the chemical potential of chains μ_{ext} and the osmotic pressure π_{ext} in the reservoir. To calculate σ , one needs to know the conformation and the free energy of chains in a brush. A simple Flory-type approach enables one, for fixed σ , to estimate when the free chains penetrate the brush and to calculate the deformation of terminally attached chains. Truly self-consistent models are more difficult to solve. Here, we use Milner *et al.* [8] model for a brush in contact with a pure solvent slightly modified to take into account the osmotic pressure of external solution. We thus consider the case of relatively high σ when the attached chains are strongly stretched and their conformation can be represented by a trajectory of a classical particle subject to a potential arising from excluded volume effects and from constraints imposed on the chain ends. Milner *et al.* have shown that, in such a classical limit, the self-consistent potential acting on attached chains must be parabolic

$$\mu(z)/kT = A(\sigma) - Bz^2 \quad (1)$$

since all chains must reach the surface after the same number of steps N whatever is the position of the other end. This imposes

$$B = \pi^2/8 N^2 a^2. \quad (2)$$

In our case $\mu(z)$ arises from the excluded volume interactions of free and attached chains, i.e.

$$\mu(z) = kT(v/a^3)[\phi_a(z) + \phi_f(z)] \quad (3)$$

where v denotes the excluded volume parameter, ϕ_a and ϕ_f are the volume fractions of attached and free chains monomers, respectively.

In figure 1 we show schematically the concentration profile of a grafted polymer layer in contact with a solution. In general, we expect some penetration of free chains [6, 14] into the brush and a depletion layer [6, 13] near the brush surface. We focus on the case when both effects are weak which occurs when (cf. Appendix):

$$(v/a^3) \phi_0 \ll (h^2/N^2 a^2)$$

where ϕ_0 denotes the monomer volume fraction in the reservoir and h is the thickness of the brush defined by $\phi_a(h) = 0$. In this limit, the constant $A(\sigma)$ in equation (1) is simply given by the condition $\phi_f(h) \approx \phi_0$. Hence, for a given σ , the brush height can be calculated from the normalization condition

$$N\sigma = \frac{1}{a} \int_0^h \phi_a(z) dz = (h/a) \phi_0 \left(1 + \frac{2}{3} \alpha\right) \quad (4)$$

with

$$\alpha = \frac{Bh^2 a^3}{\phi_0 v} = \frac{\phi(0) - \phi_0}{\phi_0} \quad (5)$$

representing the relative excess of monomer concentration at the interface with respect to ϕ_0 . The average chain deformation energy is equal to

$$f_{\text{el}} = \frac{F_{\text{el}}}{kT} = \frac{1}{\sigma} \int_0^\sigma NA(\sigma') d\sigma' = N \frac{v\phi_0}{a^3} \left\{ 1 + \frac{\alpha(5+6\alpha)}{5(2\alpha+3)} \right\}. \quad (6)$$

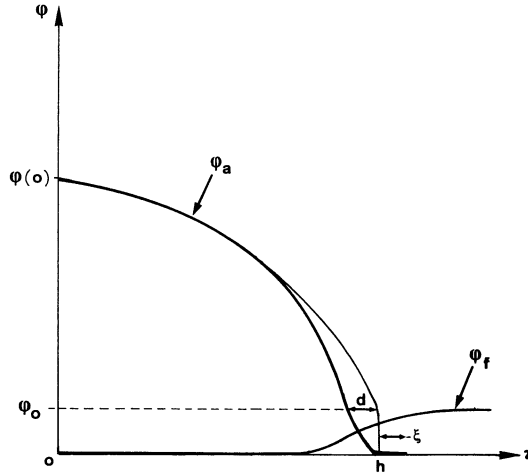


Fig. 1. — Schematic profile of monomer volume fraction profile of attached chains (ϕ_a) and free chains (ϕ_f) in a grafted polymer layer of thickness h in contact with a solution. Monomer volume fraction in the solution is ϕ_0 . $\phi_a(z)$ is parabolic, except near the extremity of the brush, where it vanishes and near the wall where there is a depletion layer. d and ξ denote respectively the characteristic penetration length of free chains in the brush, and the characteristic length of the depletion layer outside the brush. The local concentration profile ($\phi_a + \phi_f$) is expected to be essentially parabolic.

The free energy of the grafted layer is thus given by

$$F_{\text{film}}/kT = (f_{\text{el}} - \Delta) Q + Q \ln \sigma \quad (7)$$

with Q denoting the number of terminally anchored chains and Δ is the free energy gain (in kT units) when a terminal end group is fixed. The last term in (7) represents the translational entropy of chains in the brush.

At equilibrium the surface coverage can be determined from the equality of chemical potentials of attached and free chains

$$\mu_{\text{ext}} = \mu_{\text{film}} = \left. \frac{\partial F_{\text{film}}}{\partial Q} \right|_{(Q/\sigma) = \text{const}} = NA(\sigma) - \Delta + \ln \sigma + 1. \quad (8)$$

We focus on the situation when the chains in the reservoir do not form micelles so that

$$\mu_{\text{ext}}/kT \approx N(v/a^3) \phi_0 + \ln \phi_0 + 1. \quad (9)$$

Here the first term represents the excluded volume contribution and the last two the translational entropy. The grafting density can be thus obtained from equation (4) with α determined from (8) and (9):

$$N(v/a^3) \phi_0 \alpha = \Delta + \ln(\phi_0/\sigma). \quad (10)$$

This is actually an equation for the adsorption isotherm. It has a simple interpretation: the left-hand-side term represents a correction to the Gibbs isotherm arising from the excluded volume effects different in the brush and the reservoir.

It should be remarked that equation (10) enables one to determine easily the free energy gain Δ if the surface coverage σ or the brush height h are known. Ignoring the entropic terms

in equation (10), Milner [15] has estimated Δ for the system used in the experiments by Tauton *et al.* [2, 4]. However, for small ϕ_0 , the entropic terms are of the same order of magnitude as the enthalpic terms and cannot be neglected. For instance, assuming the equilibrium adsorption in surface force measurements for polystyrene chains of Tauton *et al.* [2], we can estimate Δ to be about $9 kT$ (by taking $a = 7.6 \text{ \AA}$; $v = 8 \text{ \AA}^3$; $N = 1350$; $\phi_0 = 2.52 \times 10^{-4}$; $\sigma = 8.5 \times 10^{-3}$). For block copolymers with a short end group [4], Δ can be higher.

There are two interesting limiting cases: the solution dominated regime when $\alpha \approx 1$ and the brush dominated regime when $\alpha \gg 1$. In the first case, due to osmotic pressure of reservoir, the brush is compressed so that the concentration at the interface and in the brush is essentially equal to that of the external solution. Actually, this regime cannot be described by this model because of the important penetration of free chains in the brush (cf. Appendix). Much more important is the second regime when $\alpha \gg 1$ and the brush is much denser than the surrounding solution. Then one gets

$$h \approx \left(\frac{12}{\pi^2} \right)^{1/3} \sigma^{1/3} v^{1/3} N \quad (11)$$

(as for the brush in contact with a pure solvent) and the surface coverage determined by

$$\phi_0 = \sigma \exp \left\{ -\Delta + \frac{3}{2} \left(\frac{\pi^2}{12} \right)^{1/3} \left(\frac{v}{a^3} \right)^{2/3} \sigma^{2/3} N \right\}. \quad (12)$$

It is important to stress that even in this limiting case, the surface coverage depends on the reservoir concentration ϕ_0 , especially at low ϕ_0 , and the brush thickness is not proportional to the molecular weight of chains but varies more slowly. These are general features of the adsorption process.

In practice, in order to predict σ , one needs to solve numerically equations (10) and (4). Figure 2 illustrates the dependence of surface coverage σ on the solution concentration ϕ_0 for a typical set of molecular parameters (which actually may correspond to polymers used

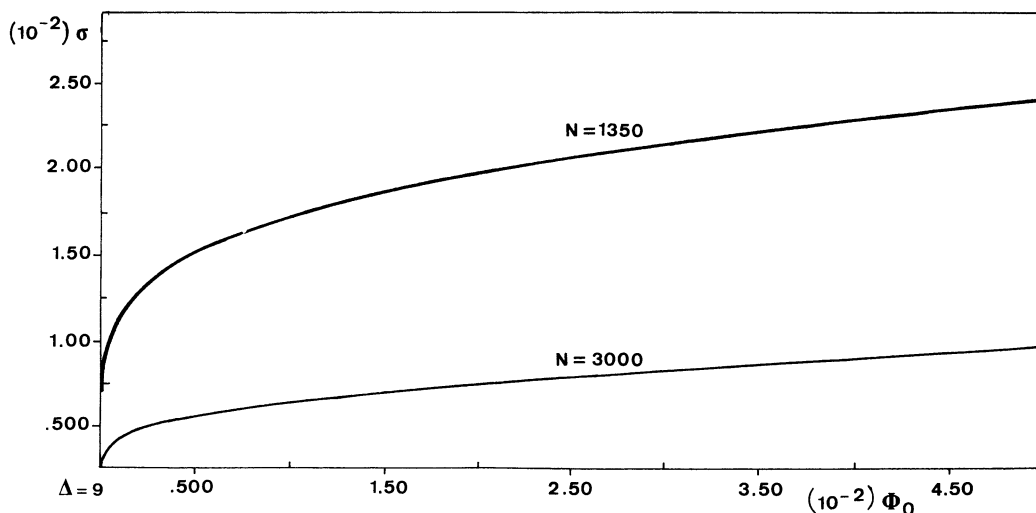


Fig. 2. — Dependence of surface coverage σ on the solution monomers volume fraction ϕ_0 for a typical set of molecular parameters (Kuhn statistical length $a = 7.6 \text{ \AA}$, excluded volume parameter $v = 8 \text{ \AA}^3$ [3], energy gained when a terminal group is fixed $\Delta = 9 kT$, the polymerization index N).

by Tauton *et al.* [2]). The strong dependence of σ on concentration at low concentration regime implies also a rapid variation of brush thickness with concentration (Fig. 3). At higher concentrations, a plateau regime for which h is almost constant is attained. This corresponds to the solution dominated regime for which $\alpha \approx 1$ and $h = (N\sigma/\phi_0) a$. Since in this regime $\sigma \sim \phi_0$, we get $h = \text{const}$. The crossover between the brush and solution dominated regimes depends on the molecular weight of chains and the value of Δ . The role of the energy gain Δ is clearly illustrated in figure 4 where we plotted the dependence of the brush height on

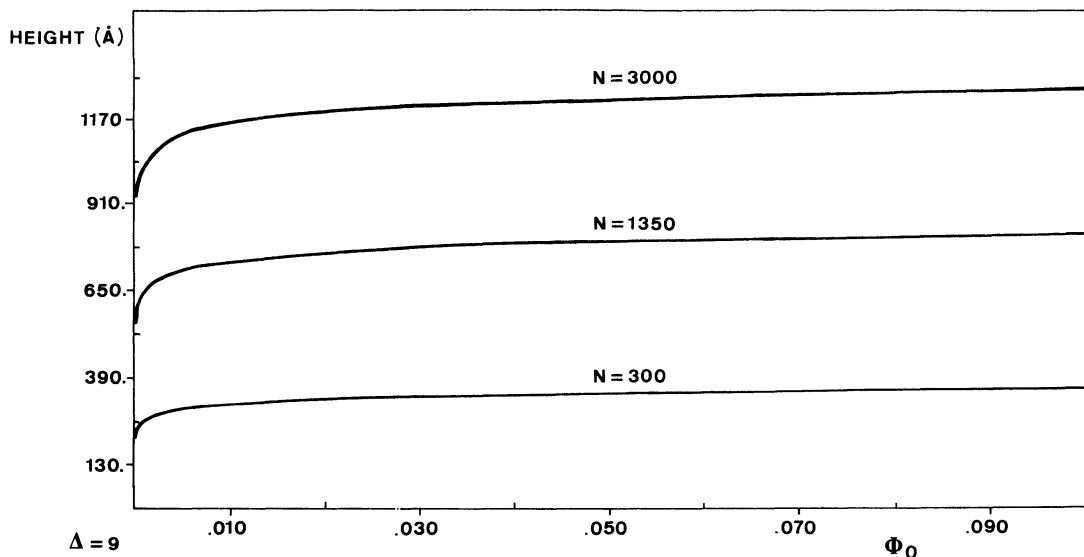


Fig. 3. — Dependence of the brush thickness h (Å) on the solution monomers volume fraction ϕ_0 for the same typical set of molecular parameters, and for different values of the polymerization index N .

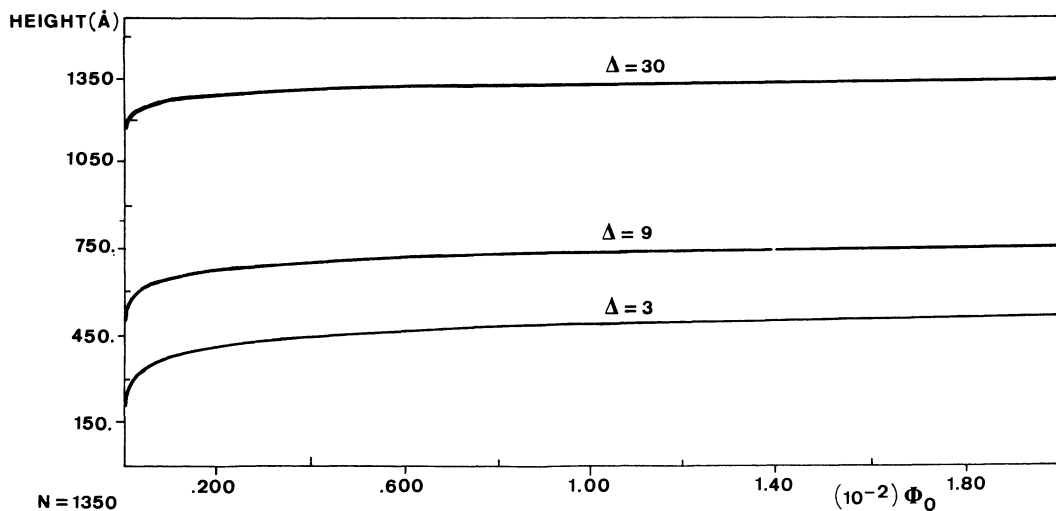


Fig. 4. — Dependence of the brush thickness h (Å) on the solution monomers volume fraction ϕ_0 for different values of the energy gain Δ .

ϕ_0 for different values of Δ . As Δ is increased, the stronger is the tendency to adsorb, the higher is the surface coverage σ and thus the thickness of the brush.

In conclusion, we expect that at equilibrium the surface coverage σ depends on the concentration of polymer solution ϕ_0 . This leads to a nonlinear dependence of the brush height h on the polymerization index N (Fig. 5). From plots $\text{Log } h$ versus $\text{Log } N$, the non linear dependence of brush height h in N may be approximated by a power law : $h \sim N^{0.6}$ for reasonable values of ϕ_0 . For high concentrations ϕ_0 we expect the brush to be relatively dense so that entropic terms $\ln(\phi_0/\sigma)$ can be neglected in equation (10). Then, one gets from (2) and (11) $h \sim N^{1/2}$ [15]. Numerical calculations confirm this result, but for high ϕ_0 for which, unfortunately, the model is no longer valid as the penetration of free chains to the brush cannot be neglected.

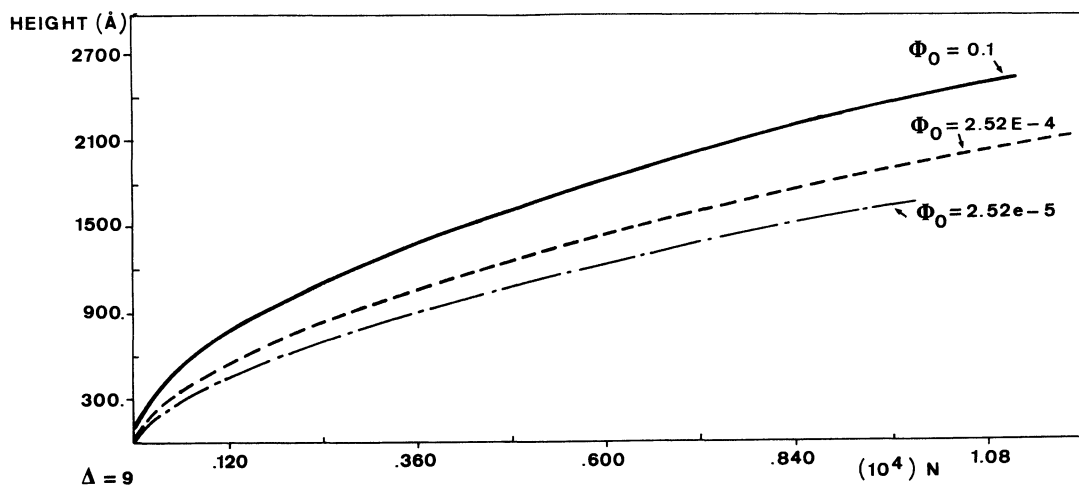


Fig. 5. — Dependence of the brush thickness h (Å) on the polymerization index N for different values of the solution monomers volume fraction (energy gain $\Delta = 9 kT$).

3. Grafting and desorption kinetics.

In this section, we study the adsorption kinetics for the brush dominated regime when the concentration in the brush at equilibrium is much higher than in the solution. We consider the solution below the critical micelle concentration (c.m.c.). We also assume that a functionalized chain end in contact with the interface is adsorbed very rapidly. Then, the kinetics of grafting is controlled by the diffusion in the solution and penetration of chains through the brush protecting the wall.

It is important to realize that the time τ_1 required to build a brush in which the chains just start to overlap ($\sigma = \sigma^* \approx N^{-1}$) is usually very short compared to the time τ_c necessary to reach $\sigma \approx \sigma_{eq}$. Indeed, below σ^* , there is essentially no activation barrier and the adsorption is controlled by chain diffusion in the solution :

$$\sigma(t) \sim \left(\frac{Dt}{a^2} \right)^{1/2} (\phi_0/N) \quad (13)$$

where D is the chain diffusion coefficient. Hence, the overlapping brush is attained after the cross-over time

$$\tau_1 \simeq \frac{a^2}{D\phi_0^2}. \quad (14)$$

Typically for chains considered in section 2, $N \simeq 10^3$, $D \simeq 3 \times 10^{-7}$ cm²/s and $\phi_0 \simeq 10^{-3}$ we get $\tau_1 \simeq 0.3$ s.

Above the overlap concentration, a further adsorption requires some stretching of the chains and there is a potential barrier which opposes the penetration of the chains. Very rapidly (for high Δ or N) the barrier becomes an essential obstacle and the diffusion of free chains does not control anymore the adsorption kinetics. In fact, the transition between the two regimes is smooth. There is an intermediate regime in which the two processes are relevant.

We define a cross-over surface coverage σ' by the requirement :

$$e^{\gamma N \sigma'^{2/3}} = \frac{N^{8/5} \sigma'^{12}}{\phi_0}.$$

It will be shown later that the kinetics of grafting is controlled by the Brownian diffusion in the solution for $\sigma < \sigma^*$ and by the activation barrier for $\sigma > \sigma'$. For $\sigma^* < \sigma < \sigma'$ we are in the intermediate regime.

We consider the penetration of a chain into the brush with the surface coverage $\sigma(t) < \sigma_{eq}$ and the thickness $h(t)$ (Eq. (11)). The chain penetration can be characterized by the position of the end-functionalized group x (Fig. 6). Only this part of the chain is stretched and the potential energy of the chain (the barrier height at point $h(t) - x$) is

$$kTU(x) = \int_0^x \frac{d\mu_{el}(h)}{dh} dh = \mu_{el}(x) - \mu_{el}(0) \quad (15)$$

where $\mu_{el}(x) = \left. \frac{\partial(F_{el} Q)}{\partial Q} \right|_{Q/\sigma = \text{const}}$. Note that the penetration by one end is energetically favored. Equation (6) yields

$$U(x) = \frac{\pi^2}{8Na^2} x^2. \quad (16)$$

When $x = h(t) - a$, the chain is rapidly adsorbed and it gains the energy Δ (Fig. 6).

The kinetics of adsorption in this regime is governed by conservation equation :

$$\frac{d\sigma}{dt} = a^2(J_{in} - J_{out}) \quad (17)$$

where J_{in} and J_{out} are the flux from solution to the interface and from the interface to the solution respectively. The flux J_{in} obeys a generalized diffusion equation

$$J_{in}(x) = -D(x) \left[\frac{\partial(\phi/Na^3)}{\partial x} + \frac{\partial U}{\partial x} (\phi/Na^3) \right]. \quad (18)$$

As the chain penetrates the brush, its diffusion coefficient changes, so $D(x)$ denotes the diffusion coefficient of the end of the chain at point x in the brush.

It is reasonable to assume that the diffusion in the solution and the penetration in the brush are decorrelated when the diffusion time τ_1 is much smaller than the characteristic time of brush construction with an activation barrier τ_c .

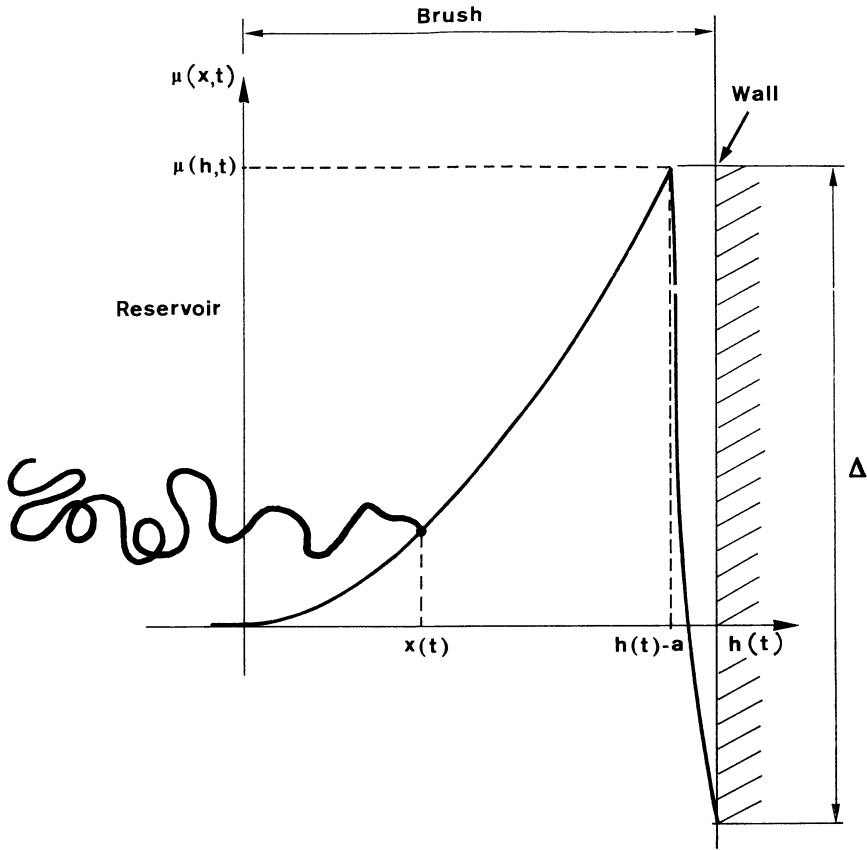


Fig. 6. — Schematic profile of the potential energy acting on a chain penetrating the grafted layer at time t .

In such a case, the flux $J_{in}(x)$ practically does not depend on x

$$J_{in}(x) = J_{in}(0) = J_{in} \approx - \frac{D(x)}{N^3 a} e^{-U(x)} \frac{\partial}{\partial x} (e^U \phi) . \quad (18a)$$

The integration of (18a) gives with a boundary condition $\phi(x = h - a) = 0$

$$J_{in} = \frac{(\phi_0/a^3 N)}{\int_0^{h-a \approx h} \frac{e^{U(x)}}{D(x)} dx} . \quad (19)$$

After linearization of $U(x)$ near its maximum $U(h - a)$, we integrate the denominator of the right-hand side of equation (19) and get :

$$J_{in} = \frac{a^{-2} m \phi_0 D(h)}{N} \sigma^{1/3} e^{-\gamma N \sigma^{2/3}} \quad (20)$$

where

$$\gamma = \frac{3}{2} (\pi^2/12)^{1/3} (v/a^3)^{2/3} \quad \text{and} \quad m = (3 \pi^4/4)^{1/3} (v^{1/3}/a^3) .$$

Note that m^{-1} represents the microscopic surface occupied by a monomer and $\gamma N \sigma^{2/3}$ the stretch energy of a chain. $D(h)$ is the effective diffusion coefficient at the interface. Thus $D(h)$ may be found explicitly.

Following Halperin and Alexander [16], we assume that the chain penetrates the barrier by a reptation-type diffusion. This picture is consistent with the fact that the penetration by one end is energetically favored [17]. Thus the relevant diffusion coefficient D is that of a chain in a tube. By analogy with semi-dilute solutions

$$D_1 = (kTg(h))/(6 \pi \eta_0 \xi N) \quad \text{where} \quad \xi \approx a \sigma^{-1/2} \approx \Sigma^{1/2},$$

$g = \xi^3(\phi(0)/a^3)$ is the number of monomers per blob, and $\mu_0 = (1/6 \pi \eta_0 \xi N)$ is the blob mobility, with η_0 denoting the solvent viscosity. Hence, we get

$$D = \left(\frac{2}{3 \pi} \right)^{1/3} \frac{kT}{\eta_0 v^{1/3} N} \sigma^{-1/3} = \frac{D_0}{N} \sigma^{-1/3}.$$

The flux from the interface to the solution reads $J_{\text{out}} = \nu_0 a^{-2} \sigma e^{-\Delta}$, where ν_0 denotes a microscopic frequency. The conservation equation (17) relates ν_0 to the macroscopic parameters at equilibrium $[d\sigma/dt]_{\sigma = \sigma_{\text{eq}}} = 0$ leading to

$$\nu_0 = \frac{m D_0 \phi_0}{N^2 \sigma_{\text{eq}}} e^{(\Delta - \gamma N \sigma_{\text{eq}}^{2/3})}. \quad (21)$$

Equation (17) now reads

$$\frac{ds}{dT} = e^{-\gamma N \sigma_{\text{eq}}^{2/3} s^{2/3}} - s e^{-\gamma N \sigma_{\text{eq}}^{2/3}} \quad (22)$$

which is the differential equation governing the brush construction. $s = (\sigma/\sigma_{\text{eq}})$ and $T = (t/\tau_2)$ are reduced variables, where $\tau_2 = (N^2 \sigma_{\text{eq}}/D_0 m \phi_0)$ is a short characteristic time.

Equation (22) can be easily solved numerically. Figure 7 illustrates the dependence of reduced surface coverage s on the reduced time T , for a characteristic set of molecular parameter s : $a = 7.6 \text{ \AA}$; $v = 8 \text{ \AA}$; $\Delta = 20$; $\phi_0 = 10^{-2}$; $N = 3210$.

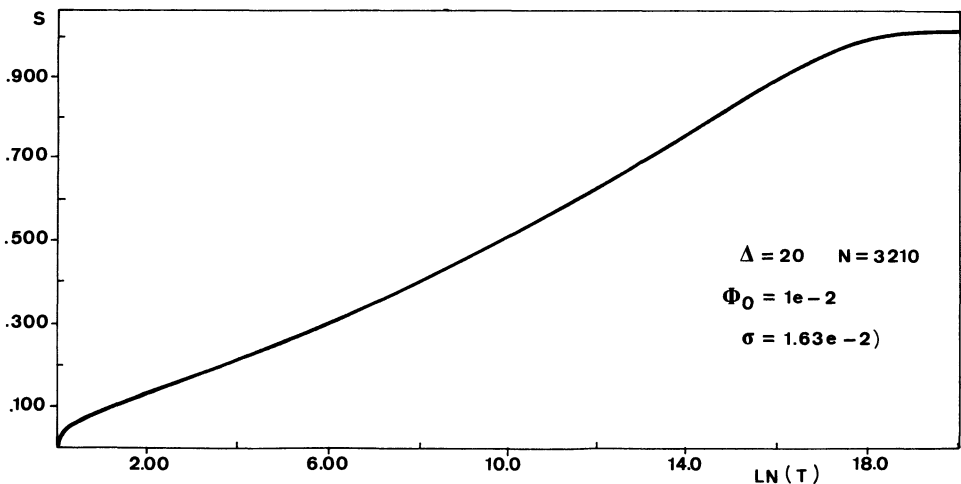


Fig. 7. — Dependence of the reduced surface coverage $s = \sigma/\sigma_{\text{eq}}$ on $\ln(T)$, where $T = t/\tau_2$ is the reduced time and $\tau_2 = N^2 \sigma_{\text{eq}}/D_0 m \phi_0$ is a short characteristic time. Molecular parameters are $\Delta = 20 kT$, $N = 3210$, $\phi_0 = 10^{-2}$, $\tau_2 = 5.6 \times 10^{-5}$ s. The construction time is $\tau_c \approx 15.4 \times 10^3$ s.

To get some qualitative insight into the construction dynamics, we can distinguish two regims. In the first « quasi-logarithmic » regime, the retrodiffusion is very weak, so that J_{out} can be neglected in equation (22). Under such conditions, the integration of equation (22) yields :

$$s^{1/3} e^{+\gamma N \sigma_{eq} s^{2/3}} \approx \frac{2}{3} \gamma N \sigma_{eq} T. \tag{23}$$

In this regime the time dependence of σ is essentially logarithmic.

Using equation (23) with $s = 1$, one can evaluate the construction time

$$\tau_C \sim \frac{2}{3} \tau_2 \exp \{ \gamma N \sigma_{eq}^{2/3} \} / (\gamma N \sigma_{eq}). \tag{24}$$

It is important to remark that τ_2 is not the relevant construction time. The construction time τ_C is much longer due to the exponential factor. This justifies the use of the blob model which gives τ_1 up to a numerical prefactor.

The hypothesis that the diffusion of free chains in the solution does not control the adsorption kinetics is justified, only if $\tau_C \gg \tau'_1$ where $\tau'_1 = [(N/\phi_0) \sigma_{eq}]^2 a^2/D$ which would be the time to reach the equilibrium without activation barrier with D being the Zimm diffusion coefficient : $D = kT/(6 \pi \eta_0 N^{3/5} a)$.

This condition is equivalent to the requirement

$$e^{\gamma N \sigma_{eq}^{2/3}} \gg \frac{N^{8/5} \sigma_{eq}^2}{\phi_0}.$$

Typically for $N = 1\ 350$, $\Delta = 30$, $\phi_0 = 10^{-3}$, which leads to $\sigma_{eq} = 8.6 \times 10^{-2}$ and the solvent viscosity $\eta_0 = 0.59$ cp at 30°C , we expect the construction time τ_C to be about $\tau_C \sim 9 \times 10^6$ s compared with diffusion time ($\tau'_1 \sim 1.2 \times 10^3$ s).

Near the equilibrium, both fluxes are of the same order of magnitude, and equation (22) can be linearized around $s = 1$, yielding :

$$\sigma = \sigma_{eq} \left[1 - \exp \left(- \frac{t}{\tau_{ex}} \right) \right]. \tag{25}$$

This is the second regime (exponential relaxation regime), where

$$\tau_{ex} = \tau_2 \exp \{ \gamma N \sigma_{eq}^{2/3} \} / \left(1 + \frac{2}{3} \gamma N \sigma_{eq}^{2/3} \right)$$

denotes the characteristic exchange time of adsorbed and free chains close to equilibrium

$$\tau_{ex} \sim \tau_C \sigma_{eq}^{+1/3}.$$

For the same set of parameters, we estimate $\tau_{ex} \sim 4 \times 10^6$ s.

Unfortunately, the crossover between both regimes cannot be expressed by a simple analytical form.

But putting $t = \tau_C$, which would be the time to reach the equilibrium without retrodiffusion, in equation (23), one gets

$$\frac{\Delta \sigma}{\sigma_{eq}} \sim \exp \left(- \sigma_{eq}^{-1/3} \right) \ll 1.$$

This result means that the equilibrium is practically reached, without retrodiffusion, when the solution is not too concentrated (equilibrium brush dominated regime).

Using equations (11), (12), we get

$$\tau_C \sim \frac{N e^{\Delta}}{\sigma_{\text{eq}}}.$$

This result seems paradoxal : the stronger is Δ , the longer is the construction time, but in fact, the stronger is Δ , the higher is the surface coverage at equilibrium and then the higher is the activation barrier. Because of the exponential term, the characteristic formation times of the films vary over a wide range when the chemical nature of the end group is changed.

When a brush formed by terminally absorbed chains in equilibrium with a solution, is put in contact with the pure solvent, the flux from solution to the interface J_{in} vanishes. Then the kinetics of the brush destruction is governed by equation (17) with $J_{\text{in}} = 0$ and one gets

$$\sigma = \sigma_{\text{eq}} e^{-\frac{t}{\tau_w}},$$

where $\tau_w = \tau_2 e^{\gamma N \sigma_{\text{eq}}^{2/3}}$ is the « washing time », i.e. a characteristic time of the brush destruction.

It is important to notice that $\tau_w > \tau_C$ in all cases. This shows that as for the adsorption of the entire chains the strong adsorption of end-functionalized chains is practically irreversible. (For the same typical microscopic parameters as above, we estimate the « washing time » to be about $\tau_w \sim 5.5 \times 10^7$ s).

Conclusion.

In this paper, we have theoretically discussed the equilibrium of a layer formed by strongly stretched end functionalized chains anchored to a surface, in contact with a solution of the same chains in good solvent. We used the theory of Milner *et al.* [8], slightly modified to take into account the existence of a reservoir of free chains in the bulk. We have shown that the parameters such as surface coverage and thickness of the layer depend strongly on the energy Δ gained by absorbing the terminal group, and on the solution concentration especially at low concentrations. The dependence of the grafted layer structure on the chemical potential of the reservoir leads to a non power law variation of the layer thickness h with the polymerization index N , at fixed solution concentration. The model enables one to determine easily the free energy gain for a given surface coverage σ_{eq} or the brush height h . The determination of the equilibrium brush parameters is an essential step to understand the kinetics of formation of a brush. We distinguished two kinetic regimes. As long as the surface coverage is lower than a critical value (the anchored chains do not overlap and are not stretched). The kinetics is governed by the Brownian diffusion of free chains in the solution, which induces a dynamic depletion layer near the extremity of the film. Above this critical value of surface coverage, an activation barrier is created and governs the kinetics. The surface coverage increases essentially logarithmically with time with a characteristic building time depending exponentially on the chain deformation energy.

It should be stressed, that for moderate adsorption energy gain, or sufficiently low solution concentration, the grafted chains can be strongly stretched, without big energy cost. This is because the energy is minimized when some chain ends do not extend up to h . Thus the activation barrier is rather soft, and the Brownian diffusion remains often the dominant kinetics factor. Even in this case, however, the kinetics may be still controlled by an eventual chemical adsorption reactivity. This is the situation when the corresponding activation energy is higher than the physical barrier due to chain stretching, on which we focused our attention in the present article.

In the case of high physical activation barrier, we estimated the time to reach the equilibrium surface coverage (Eq. (24)). The time evolution of σ is given by a differential equation, which can be numerically solved. The dependence of surface coverage σ on the time is « quasi logarithmic », except nearby the equilibrium, where σ relaxes exponentially to σ_{eq} . The characteristic construction and exchange times are about the same order and vary over a wide range of magnitude, as they exponentially depend on the energy gain and polymerization index N .

We have also calculated the destruction or « washing » time of the brush in contact with a pure solvent. This time turns out to be always longer than the construction time, and the brush formation should be irreversible in most practical cases.

The eventual existence of micelles above the critical micelle concentration should limit the equilibrium coverage density and reduce the construction time, because the micelles form a reservoir of chains for the adsorption. Hence, the construction time should not exceed the one we predict in equation (24) with ϕ_0 being the critical micelle concentration.

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Appendix.

Depletion layer.

The local volume concentration of free chain monomers $\psi_f^2(z)$ outside the layer ($z > h$) may be found using Edwards' ground-state dominance method [18] :

$$-\frac{a^2}{2} \frac{d^2 \psi_f}{dz^2} + v |\psi_f|^2 \psi_f(z) = v c_0 \psi_f(z) . \tag{A.1}$$

Evidently $(c_0 - \psi_f^2(z))$ is positive and decays to zero on the outside of the layer (Fig. 1) with some length ξ which characterizes the depletion layer's thickness.

Our assumption $c_f(h) = a^{-3} \phi_f(h) \sim c_0$ is correct if the depletion layer free energy per unit surface

$$f_{dl} = \frac{F_{dl}}{kT} = \int_h^{+\infty} + \frac{1}{2} v (\psi_f^4(z) - c_0^2) dz$$

is much smaller than (σf_{el}) , the elastic energy per unit surface of the brush.

$$f_{dl} \ll \sigma f_{el} . \tag{A.2}$$

In view of equation (A.1), one expects on dimensional grounds [19]

$$\xi \sim a / (v c_0)^{1/2}$$

and

$$f_{dl} \sim \xi v c_0^2 \sim a c_0 (v c_0)^{1/2} . \tag{A.3}$$

In the brush dominated regime ($\alpha \gg 1$)

$$h \sim N v^{1/3} \sigma^{-1/3}$$

and

$$\sigma f_{\text{el}} \sim \frac{v^{2/3}}{a^4} N \sigma^{5/3}. \quad (\text{A.4})$$

Using equations (A.3), (A.4) we get

$$\frac{f_{\text{dl}}}{\sigma f_{\text{el}}} \ll \frac{N}{\alpha^{3/2}} \left(\frac{a}{h} \right)^2 \ll 1$$

because $\alpha \gg 1$ and the chains are stretched, and our assumption is valid.

In the solution dominated regime ($\alpha \sim 1$)

$$h \sim \frac{N \sigma}{a^2 c_0}$$

and

$$\sigma f_{\text{el}} \sim N v c_0 a^{-2} \sigma. \quad (\text{A.5})$$

Using equations (A.3), (A.4) and the condition ($\alpha \sim 1$), we get

$$\frac{f_{\text{dl}}}{\sigma f_{\text{el}}} \sim \frac{N a^2}{h^2} \ll 1 \quad \text{because the chains are significantly stretched.}$$

Penetration length.

The normalized condition (4) reads

$$N \sigma = \left(\frac{h}{a} \right) \phi_0 \left(1 + \frac{2}{3} \alpha \right) - \frac{1}{a} \int_0^h \phi_f(z) dz.$$

We have neglected the last term $J = \frac{1}{a} \int_0^h \phi_f(z) dz$.

This approximation is correct only if

$$J \ll (h/a) \phi_0 \left(1 + \frac{2}{3} \alpha \right). \quad (\text{A.6})$$

In this case, we can assume that the concentration profile of anchored chains is parabolic.

The local volume concentration of free chains monomers in the brush obeys an Edwards ground state dominance equation too :

$$(z < h) \quad - \frac{a^2 d^2 \psi_f}{2 dz^2} + (A - Bz^2) \psi_f(z) = v c_0 \psi_f(z). \quad (\text{A.7})$$

Near the extremity of the layer, (A.6) is linearized

$$- \frac{a^2 d^2 \psi_f}{2 du^2} + 2 Bhu \psi_f(u) = v c_0 \psi_f(u) \quad (\text{A'.7})$$

with $z = h - u$.

In view of equation (A'.7), one expects one dimensional grounds :

$$2 Bhd - \frac{a^2}{d^2} = \nu c_0 \tag{A.8}$$

where d characterizes some penetration length of free chains in the brush (Fig. 1).

In the brush dominated regime ($\alpha \ll 1$), two cases may be discussed.

If $\nu c_0 \ll a^2/d^2$, (A.8) reads

$$d \sim \left(\frac{N^2 a^4}{h} \right)^{1/3}$$

(A.4) provides

$$\frac{a^2}{d^2} \sim \left(\frac{h}{N^2 a^4} \right)^{2/3} \cdot a^2.$$

This case exists only if

$$\nu c_0 \ll \left\{ \left(\frac{h}{a} \right)^2 \cdot \frac{1}{N^4} \right\}^{1/3}. \tag{A.9}$$

Thus

$$\frac{J}{N\sigma} \sim \left(\frac{a}{h} \right)^{10/3} N^{8/3} \nu c_0$$

(A.9) implies

$$\frac{J}{N\sigma} \ll \left(\frac{a^2 N}{h^2} \right)^{4/3} \ll 1 \quad (\text{the chains are stretched})$$

and the approximation is correct.

If $\nu c_0 \gg a^2/d^2$, (A.8) reads

$$d \sim \nu c_0 \frac{N^2 a^2}{h}.$$

This case exists only if

$$\left(\left(\frac{h}{a} \right)^2 \cdot \frac{1}{N^4} \right)^{1/3} \ll \nu c_0 \ll \frac{h^2}{N^2 a^2} \tag{A.10}$$

and

$$\frac{J}{N\sigma} \sim (\nu c_0)^2 \frac{N^4 a^4}{h^4} \ll 1.$$

The approximation is correct.

In the solution dominated regime ($\alpha \sim 1$), two cases should also be discussed.

If $\nu c_0 \ll \frac{a^2}{d^2}$, (A.8) reads

$$d \sim \left(\frac{N^2 a^4}{h} \right)^{1/3}.$$

Both conditions $\alpha \sim 1$ and $vc_0 \ll \frac{a^2}{d^2}$ are incompatible because the chains are stretched, and this case doesn't exist.

$$\text{If } vc_0 \gtrsim \frac{a^2}{d^2}$$

$$d \sim vc_0 \frac{N^2 a^2}{h} \sim h$$

and

$$\frac{J}{N\sigma} \sim \frac{d}{h} \sim 1$$

and the approximation is incorrect.

So our treatment is a good approximation only in the brush dominated regime ($\alpha \gg 1$).

In the solution dominated regime, we must take into account the penetration of the free chains into the layer, and the concentration profile of attached chains is not parabolic. This regime corresponds to a concentrated solution.

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