# Scaling Description of Polymer Interfaces: Flat Layers

**M. Aubouy,† O. Guiselin,‡ and E. Raphaël*,†**

*Laboratoire de Physique de la Matière Condensée, Collège de France, URA No. 792 du CNRS, 11 place Marcelin Berthelot, Paris 75005, France, and Laboratoire Léon Brillouin (CEA-CNRS), CEN-Saclay, 91191 Gif sur Yvette, France*

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ABSTRACT: We present a new scaling approach to describe an arbitrarily dense polymer interface (layer made of overlapping polymer chains). Our analysis is based on a description of the layer in terms of loops and tails. Within a simple scaling model for the behavior of the loops and tails, we are able to relate the features of the interface to the "loop density profile" $S(n)$, defined as the number (per unit area) of loops and tail having more than $n$ monomers. Our theory predicts (as functions of $S$) the variations of the monomer density, the extension of the layer, the adsorbance (per unit area), and the effective free energy for various conditions ("good" solvent, Θ solvent, or melt). We are able to recover, in an unusual and rather staightforward manner, previously known results on reversibly and irreversibly adsorbed layers; moreover, new insights into the physics of these situations emerge. New results are obtained for interfaces made of grafted chains which adsorb reversibly on the surface. Both quantitative and qualitative corrections to previous theories are obtained.

## 1. Introduction

Long polymer chains in contact with a surface can build layers with remarkable properties from both scientific and technological points of view. Consequently, many studies have been devoted to these polymer layers in the past few years.[1−6] One of the most commonly investigated situations is uniform adsorption, in which all the segments of the polymer are equally attracted to the surface. The surface can be a solid/liquid interface or the interface between two immiscible solvents. For definiteness, we assume a solid/liquid interface. When in contact with an attractive surface, the chains adsorb and build a layer which can be described as a continuous succession of loops and tails of different sizes,[6] as depicted in Figure 1. The behavior of these loops (or tails) results from a competition between monomer−monomer interactions and elastic forces: they stretch away to exploit the relatively low density at the outer edge of the layer, this elongation being counterbalanced by elastic restoring forces of entropic origin. A complete characterization of the resulting interface requires both the determination of the global properties of the structure (thickness, monomer density profile, etc.) and the loop and tail size distributions. Clearly, these quantities are not independent of each other, and, depending on the situation, theoretical studies have inferred the loop distribution from the monomer density profile, or the reverse.

For the reversible adsorption situation, scaling arguments have been used to calculate the thickness of the layer, $L$, and the variation of the volume fraction along the normal of the surface, $\phi(z)$.[6] In a "good solvent", $L$ scales as $aN^{3/5}$, where $a$ is the size of the monomer and $N$ is the polymerization index, and $\phi(z)$ varies as $z^{-4/3}$ (apart from a small region close to the surface).[7,8] These results have been deduced from the crucial assumption that the layer should be at equilibrium with a dilute solution under no constraint. The loop distribution can then be computed:[9] The number per unit surface, $S(n)$, of loops and tail having more than $n$ monomers is given by[10]

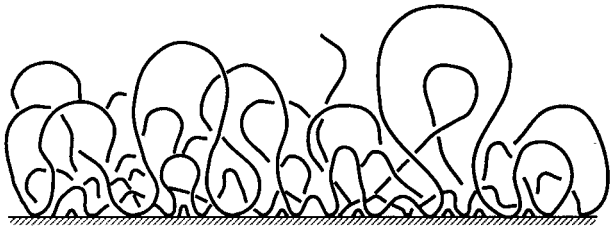

**Figure 1.** Sketch of a dense polymer layer (layer made of overlapping polymer chain).

$$S(n) \cong 1/(a^2 n^{6/5}) \tag{1}$$

For brevity, we will refer to the function $S$ as the "*loop density profile*" *of the layer*. Note that the number per unit surface of loops and tails having exactly $n$ monomers is given by $-S'(n)$, where $S'$ denotes the derivative of $S$.

Conversely, the loop and tail distribution can be used as a tool to get the global characteristics of the layer. This has been done by one of us in the case of irreversible adsorption, where the monomers are strongly bound to the surface.[11] Such behavior was first reported by Cohen-Addad *et al.*[12] for poly(dimethylsiloxane) (PDMS) adsorbed on silica wafers. The characteristic feature of this situation is that the loops and tails are "pinned" at the surface, and no rearrangement in the loop distribution can take place. The structure of the layer is thus strongly dependent on how it was assembled. One particular scenario, which has been the subject of many recent works, assumes the following sequence of operations:[11,13−17] (a) the solid surface is put in contact with a polymer melt at equilibrium, (b) the monomers adsorb instantaneously and irreversibly, and (c) the chains which are not in direct contact with the surface are washed away. The essential physics is quite simple: the loop distribution of the resulting layer is the *equilibrium* loop distribution at the melt interface which has been frozen by contact with the adsorbing surface. This leads to a power law for the loop density profile, a signature of all equilibrium situations, as

† Collège de France.
‡ CEN-Saclay.
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shown below. From a careful examination of the configuration of a single chain at the interface between the melt and the solid, one obtains[11]

$$S(n) \cong 1/(a^2 n^{1/2}) \tag{2}$$

which allows for the determination of the characteristics of the layer. In a good solvent, *e.g.*, $L \cong aN^{5/6}$ and $\phi(z) \sim z^{-2/5}$.

To date, this approach—describing a polymer layer on the basis of its loop and tail distribution—has been essentially developed in two directions. (i) A full self-consistent-field theory has been completed for arbitrary polydisperse polymer "brushes"[18] (a layer made of chains attached by one end to a surface is often referred to as a polymer brush). However, this study does not properly account for monomer−monomer interactions in good solvent conditions (a more accurate description of these interactions has been carried out, but only in the case of monodisperse polymer brushes[19,20]). (ii) A scaling description of the irreversibly adsorbed situation described above has been given. However, as emphasized above, this work assumes a complete equilibrium situation. Recent experimental studies show that, in some cases, PDMS layers on silica can rearrange on large time scales.[21] Since rearrangement should strongly affect the layer characteristics, an intermediate state should be very different from the initial situation. This provides new motivation for theoretical modeling of arbitrary polymer layers.

In this paper, we present a general scaling description of an arbitrary polymer interface. Our aim is to show that any polymer layer, whatever the solvent conditions may be, can be very simply described by its loop density profile $S$, and that, in turn, this function appears to be the proper tool for theoretical study of these interfaces. This is done in three steps.

We first give a general description of a polymer interface in terms of its loop density profile (section 2). It is assumed that (a) the polymer chains are monodisperse ($N$ monomers per chain) and (b) the chain density at the interface is high enough for the different coils to overlap. Three solvent conditions are considered: good solvent (athermal, for simplicity), $\Theta$ solvent, and melt (*i.e.*, no solvent whatsoever).

We then compute the free energy of the layer (section 3). An interesting property of these systems emerges from the consideration of their free energy if we consider an equilibrium situation: equilibrium can be understood in terms of a competition between entropy, which favors loop polydispersity, and excluded volume interactions, which favor dilute regimes corresponding to layers with few loops per unit area. As a consequence, the equilibrium profiles of eqs 1 and 2 can be directly deduced from the minimization of an effective free energy.

In section 4, we illustrate our approach with a specific example: the case of polymer chains which are simultaneously grafted and reversibly adsorbed at a solid−liquid interface. At low coverage, the structure of the layer is not much affected by the grafting constraint, and its extension for instance, is comparable with the equilibrium result: $L \sim N^{3/5}$. In contrast, at high surface coverage the chains are strongly stretched and they expand much farther from the surface: $L \sim N$. The transition is shown to be continuous.

Throughout our analysis, we will omit all the various order-unity prefactors which may appear and concentrate on scaling relations.

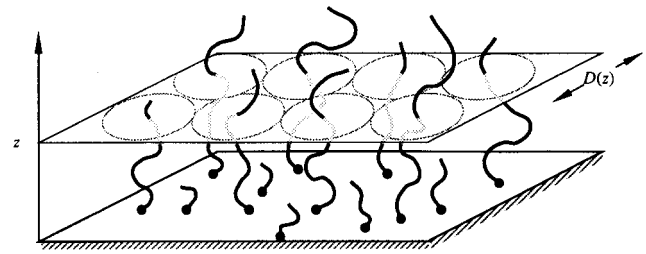


**Figure 2.** At a given altitude $z$, the areal density of pseudotails is given by $S(n(z))$.

## 2. Description of an Arbitrary Polymer Layer

In this section, we consider an arbitrary polymer layer characterized by its loop density profile $S$ (see Figure 1). We show that the extension, $L$, the variations of the volume fraction, $\phi(z)$, and the absorbance, $\Gamma$ (the number per unit surface of monomers belonging to chains in direct contact with the surface), can be simply expressed as functions of $S$. Our results are used to find very general scaling relations between $L$, $\Gamma$, and $N$.

To begin with, let us assume that *each loop of 2n monomers can be visualized as two separate "pseudotails" of size n each* (from now on, we shall make no distinction between tails and pseudotails). Ultimately, we shall appeal to the success of this model in describing a wide range of situations as a justification of this assumption, but this hypothesis is not trivial. Since independent tails are not forced to join ends, a loop of $2n$ monomers and two independent tails of $n$ monomers behave differently. The main point is whether this distinction is important enough to modify the conclusions of a simple model in which it is neglected. Recent work of Joanny and Semenov[22] on reversibly adsorbed layers suggests that the loops and the tails behave differently, but their model in which loops and tails play different roles leads to identical prediction concerning the extension of the interface or the variations of the volume fraction inside the layer. We shall return to this question in section 3.

What remains now is the problem of describing the structure of a very polydisperse polymer brush. In a way similar to the Alexander−de Gennes analysis of monodisperse polymer brushes,[23,24] *we suppose that the tails are all stretched the same way*: all $n^{\text{th}}$ monomers of every tail of size larger than $n$ are situated at the same distance $z$ from the surface. Therefore, $n$ becomes a function of $z$ (which may be inverted).

From this equal stretching assumption,[25] we can relate the average distance between two tails, $D(z)$, at a height $z$ to the average number of tails having more than $n$ monomers, $S(n)$ (see Figure 2):

$$D(z) \cong S(n(z))^{-1/2} \tag{3}$$

The conservation of monomers can be written as

$$\phi(z) \cong a^3\, S(n(z))/\dot{z} \tag{4}$$

where we have set $\dot{z} = \mathrm{d}z/\mathrm{d}n$. Finally, the adsorbance is obtained by counting monomers:

$$\Gamma \cong \int_1^N S(n)\, \mathrm{d}n \tag{5}$$

Note that eqs 3−5 are purely geometrical and, up to this point, no consideration of the behavior of the polymer chains is required. We now specify the solvent conditions.

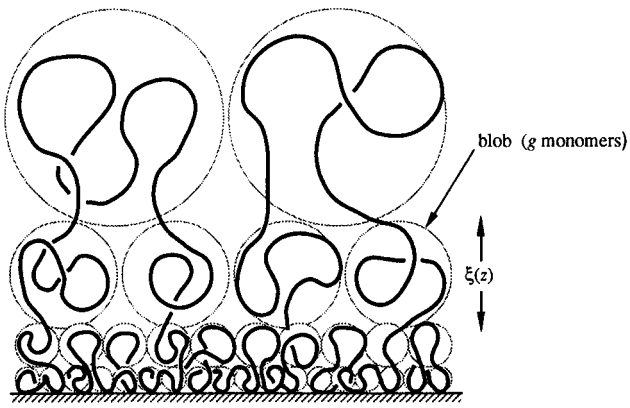


**Figure 3.** By analogy with a semidilute solution, the layer can be pictured as a close packing of blobs of size $\xi(z)$. At a scale smaller than $\xi(z)$, the pseudotails behave as isolated coils. At a larger scale, the pseudotails are extended along the normal of the surface.

In the case of a good solvent, different chains repel each other and, by analogy with a semidilute solution,[26] the layer can be pictured locally as a close packing of subunits, called "blobs", whose size is of the order of the mean distance between tails (see Figure 3): $\xi(z) \cong D(z)$. At a scale smaller than $\xi$, the chains are self-avoiding, and the number of monomers $g$ inside one subunit is $(\xi/a)^{5/3}$ (to simplify the presentation, we have considered the athermal limit where the excluded volume parameter $v \cong a^3$). At a scale larger than $\xi$, the tails are stretched away from the surface, and thus $\mathrm{d}n/g \cong \mathrm{d}z/\xi$. Combining these two relations, we find that

$$\dot{z} \cong a(a^2 S(n))^{1/3} \tag{6}$$

Substituting into eq 4, we obtain

$$\phi(z) \cong (a^2 S(n))^{2/3} \tag{7}$$

Equations 6 and 7 allow the determination of the characteristics of the layer. In particular, integrating formally eq 6 reveals the extension of the layer to be a simple functional of the loop density profile:

$$L \cong \int_1^N S^{1/3}(n)\,\mathrm{d}n \tag{8}$$

In general, the computation of the volume fraction or the extension for a given loop density profile $S$ is straightforward. To illustrate this point, consider power law distributions of the form $S(n) \sim n^{-\alpha}$, where the exponent $\alpha$ satisfies the double inequality $0 \le \alpha < 3$. This form is particularly appropriate for equilibrium layers (see Introduction), but it is interesting to realize that the monodisperse brush situation (chains of equal length, $N$, attached to a repulsive surface), with an equal density $\sigma$, is characterized by $S(n) = \sigma$, if $1 \le n \le N$, and $S(n) = 0$ otherwise. Thus, this amounts to the choice $\alpha = 0$. Equations 7 and 8 easily yield $\phi(z) \sim z^{-2\alpha/(3-\alpha)}$ and $L \sim N^{1-\alpha/3}$. Furthermore, considerable information may be obtained without ever knowing the exact form of the loop density profile. For example, if the exponent $\alpha$ lies in the range $0 \le \alpha < 1$, scaling analysis of eqs 5 and 8 leads to $L \cong aN(a^2 S(N))^{1/3}$ and $\Gamma \cong NS(N)$. By elimination of $S$ between these two relations, we find

$$L \cong aN\,(a^2\Gamma/N)^{1/3} \tag{9}$$

This is a remarkable result. While, as is expected, both the extension $L$ and the adsorbance $\Gamma$ of a given layer are strongly related to its inner structure (characterized by the loop density profile), it is surprising that there should be a scaling relation between these two quantities which is not dependent on the functional form of $S$. Equation 9 implies, in particular, that two layers, one made of grafted chains ($\alpha = 0$), and the other of irreversibly adsorbed chains—in the sense of ref 1—($\alpha = 1/2$), with the same quantity of material per unit surface, have the same extension (within an order-unity prefactor). This has been experimentally confirmed.[16] Another interesting aspect of this analysis comes from the appearance of a critical value $\alpha = 1$ (below which eq 9 is valid). As mentioned in the Introduction, reversibly adsorbed layers are characterized by an exponent $\alpha = 6/5$ and thus *do not obey relation* 9. We see that a "natural" distinction appears between two kinds of behaviors: a brush type of behavior on one hand, and a reversibly adsorbed type of behavior on the other hand. This distinction is quite strong and holds, for example, for the response to a mechanical probe such as compression, as explained in the Appendix.

In the case of a $\Theta$ solvent, the layer can also be visualized as a close packing of blobs whose size $\xi(z)$ is of the order of the average distance between tails. In this situation, however, repulsion between tails is due to three-body interactions, and the chains are Gaussian at a scale smaller than $\xi$:[26] $g \cong (\xi/a)^2$. Exploiting again the elongation of the tails along the $z$-direction, we obtain the equation governing their behavior: $\dot{z} \cong a(a^2 S(n))^{1/2}$. Then the volume fraction inside the layer varies as

$$\phi(z) \cong (a^2 S(n))^{1/2} \tag{10}$$

and the extension of the layer may be simply expressed in terms of the loop density profile:

$$L \cong \int_1^N S^{1/2}(n)\,\mathrm{d}n \tag{11}$$

Scaling analysis of power law distributions for $S$ can be completed in the spirit of the good solvent case. For example, we find that

$$L \cong aN(a^2\Gamma/N)^{1/2} \tag{12}$$

if $S$ is of the form $S(n) \sim n^{-\alpha}$, with $0 \le \alpha < 1$.

Finally, when there is no solvent, *i.e.*, in a melt of polymer chains, the tails are stretched along the $z$-direction, but they overlap laterally. We still may picture each tail as a string of non-overlapping blobs, but the size of the subunits $\xi(z)$ is now proportional to the *square* of the average distance between tails: $\xi(z) \cong D^2(z)$. The idea is that excluded volume effects are screened, and thus, (a) two adjacent tails overlap laterally and (b) chains are Gaussian locally. The size of the "blob" (*i.e.*, the length scale above which one chain is stretched) is now determined by *packing considerations*; this leads to a quadratic dependence, as first shown in ref 27. Inside a blob, the chains are Gaussian, and thus $g \cong (\xi/a)^2$, leading to a differential equation:

$$\dot{z} \cong a^3 S(n) \tag{13}$$

As is expected, the volume fraction (eq 4) is of the order of unity, and the extension $L \cong a^3\Gamma$ (eq 5).

## 3. Energetics

We now proceed to find the free energy that is suitable for describing the layer. For this purpose, it is conve-

nient to represent the surface as a lattice, each lattice site, of size $a^2$, being occupied by one (and only one) pseudotail extremity. Let $A$ be the total area. The free energy $F$ of this system of polydisperse interacting pseudotails is the sum of four contributions: (a) the osmotic contribution, which accounts for monomer−monomer interactions, (b) the elastic energy of the tails, (c) the entropy associated with the loop distribution polydispersity, and (d) a surface energy describing the interactions between the monomers and the surface. For any given loop density profile and for any given set of positions of the pseudotails on the lattice, at equilibrium, the elasticity exactly balances the osmotic energy, and the two contributions are identical within an order-unity prefactor. It is thus sufficient to estimate one of them. In fact, the computation of contribution a, for example, remains delicate since both the locations of the pseudotails on the lattice and their conformations fluctuate. We simplify the problem by estimating the interactions between tails within the correct scaling picture (accounting for correlations of monomers location) but for their average position. This is a mean-field approximation for the locations of the different pseudotails, but we emphasis that we do properly account for monomer−monomer interactions. We first compute contributions a and b. Depending on the solvent conditions, we calculate either the osmotic term (for an athermal solvent or Θ solvent) or the elastic term (for a melt). We then successively compute the entropy and the surface terms.

In athermal solvent conditions, the osmotic pressure inside the layer obeys the des Cloiseaux law:[26] $\Pi \cong (T/a^3)\phi^{9/4}$, where $T$ is the thermal energy. Taking advantage of eq 7, the osmotic contribution to the free energy, which is the integral of Π over the entire layer, may be written

$$F_{\mathrm{osm}} \cong \left(\frac{T}{a^2}\right)\int_1^N (a^2 S(n))^\beta \,\mathrm{d}n \tag{14}$$

where $\beta = 11/6$. Equation 14 still holds for other solvent conditions but with different exponents: $\beta = 2$ for Θ solvents and $\beta = 3$ for melts. The result for Θ solvents is obtained by considering the appropriate scaling law for the osmotic pressure: since three body interactions are dominant, $\Pi \cong (T/a^3)\phi^3$. In melt conditions, we calculate the elastic energies of the different pseudotails:

$$F_{\mathrm{el}} \cong \left(\frac{1}{a^2}\right)\int_1^N (-S'(n))E_n \,\mathrm{d}n \tag{15}$$

where $E_n \cong T\int_1^n (\dot{z}/a)^2 \,\mathrm{d}m$ represents the elastic energy of a pseudotail of $n$ monomers. After some manipulations, it is easily confirmed that the elastic contribution is of the form of eq 14, with $\beta = 3$.

We now turn to find the entropy which describes how many arrangements of the layer can exist on the surface for a given loop distribution. With each given loop density profile $S$ is associated a large number $\Omega(\{S\})$ of ways to realize it. Since two pseudotails of equal sizes are indistinguishable,

$$\Omega(\{S\}) \cong \frac{\left(\sum_{n=1}^{N} -AS'(n)\right)!}{\Pi_{n=1}^{N}(-AS'(n))!} \tag{16}$$

Equation 16 leads to a simple expression for the entropic contribution to the free energy, $F_{\mathrm{ent}} = -(T/a^2)\ln \Omega(\{S\})$. In the continuum limit, $F_{\mathrm{ent}}$ is given by[28]

$$F_{\mathrm{ent}} \cong TS_0\int_1^N \left(\frac{-S'(n)}{S_0}\right)\ln\left(\frac{-S'(n)}{S_0}\right)\mathrm{d}n \tag{17}$$

Here, the Stirling approximation for computing factorials has been used, and we have set $S_0 = \int_1^N(-S'(n))\,\mathrm{d}n$. The quantity $S_0$ is the total number per unit area of pseudotails (also the number per unit area of monomers in direct contact with the surface).

Finally, we describe the interactions between the monomers and the surface by the following contribution to the free energy:

$$F_{\mathrm{s}} \cong \gamma_0 - \gamma_1 S_0 \tag{18}$$

where $\gamma_0$ is the bare solid/liquid surface tension and $\gamma_1$ is the solid/polymer surface tension (note that these two quantities do not have the same dimensionality in eq 18. This choice, which has been discussed in great detail by de Gennes,[6] involves two approximations: (1) interactions between the monomers and the surface are short range, and (ii) interactions between monomers in direct contact with the surface are weak.

Equations 14, 17, and 18 lead to the following expression for the effective free energy of the layer:

$$F \cong \gamma_0 - \gamma_1 S_0 + \left(\frac{T}{a^2}\right) \times \int_1^N \left\{(a^2 S(n))^\beta + a^2 S_0\left(\frac{-S'(n)}{S_0}\right)\ln\left(\frac{-S'(n)}{S_0}\right)\right\}\mathrm{d}n \tag{19}$$

with $\beta = 11/6$ (good solvent), $\beta = 2$ (Θ solvent), or $\beta = 3$ (melt). We now explore some of the consequences of this important equation.

Let us first consider reversibly adsorbed chains in good solvent conditions. We presume that the surface is fully covered by monomers, and thus $S_0 = a^{-2}$. In general, this quantity $S_0$, which is the density of monomers at the surface, has to be determined self-consistently by minimization of the free energy: monomers cover the surface because of favorable interactions with the solid, but the coil they belong to pays entropic penalties due to the increase of volume fraction and the proximity of an impenetrable surface.[30] However, we will assume that the strength of the interactions between the monomers and the surface is such that the density of monomers in the vicinity of the solid is of order unity. This involves practically assuming an effective gain per monomer in direct contact with the surface of the order of $T$.[6] Within this assumption, the effective free energy of the layer is given by

$$F \cong \left(\frac{T}{a^2}\right)\int_1^N \{(a^2 S(n))^{11/6} + (-S'(n))\ln(-S'(n))\}\,\mathrm{d}n \tag{20}$$

After some algebra, it is easily confirmed that the loop density profile which minimizes eq 20 is $S(n) \sim n^{-6/5}$. We therefore recover, by an unusual but rather straightforward way, the result first proposed by de Gennes in ref 9 and mentioned in the Introduction (see eq 1). Moreover, our approach sheds light on the physics of the reversibly adsorbed layer by suggesting that, at fixed $S_0$, the resulting structure can be understood as

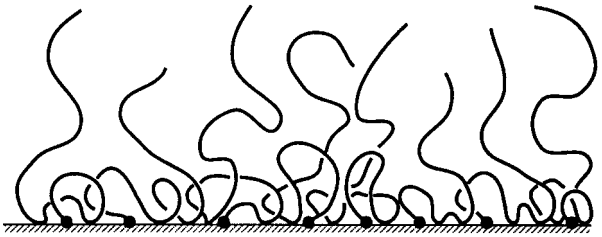

**Figure 4.** Sketch of a layer made of grafted chains which may adsorb reversibly on the surface.

the best compromise between excluded volume interactions and entropy of the set of loops.

By arguments that directly parallel those presented above, we find that the loop density profile of reversibly adsorbed layers in Θ solvent and melt are respectively given by $S(n) \sim n^{-1}$ and $S(n) \sim n^{-1/2}$. The latter result was first presented (again, using a completely different approach) in ref 11 (see the Introduction, eq 2, and the former could be deduced directly from ref 9 (see, for example, ref 31).

## 4. Reversible Adsorption of End-Tethered Polymer Chains

We now illustrate the general procedure presented above for modeling a polymer interface with a specific example: layers made of grafted chains which may adsorb reversibly on the substrate (see Figure 4). This situation may be of some relevance from both the points of view of polymer brushes (grafted chains on a *repulsive* surface) and of reversibly adsorbed layers. Since, experimentally, polymer chains are rarely strongly repelled by surfaces, preparing purely repulsive substrates (suitable for building polymer brushes) often involves a lot of physical chemistry work.[32] In view of this, one may want to know both qualitatively and quantitatively the effects of adsorption on the characteristics of a given brush. This could be used either to monitor the modifications arising from a particular treatment, or, having in mind a specific application, to check *a priori* whether any treatment at all is worthwhile.

On the other hand, one may be primarily interested in adsorbed layers. In this case, our analysis shows how the structure of a reversibly adsorbed layer of chains is modified when the chain density is increased from its equilibrium value. This may be achieved in several ways, including attaching a group of different chemistry at the end of the chains and increasing the surface chemical potential of the "anchor" with respect to that in the bulk.[33,34] To our knowledge, all previous theoretical studies of this situation (Alexander[6] and Ligoure[35]) predict a discontinuous "jump" (first-order transition) between a low-density state, where the layer has roughly the structure of an adsorbed layer, and a high-density state, where it shows the features of a brush and occurs when the chemical potential of the anchor is increased from its bulk value.

Our starting point is the effective pseudo-free energy of the layer, which may generally be written

$$F \cong \left(\frac{T}{a^2}\right)\int_1^N \{(a^2S(n))^{11/6} + (-S'(n))\ln(-S'(n)) - \mu S(n)\}\,\mathrm{d}n \quad (21)$$

where $\mu$ is a Lagrange multiplier. Equation 21 is a modification of eq 20 (which, as explained above, assumes that the density of monomers close to the surface

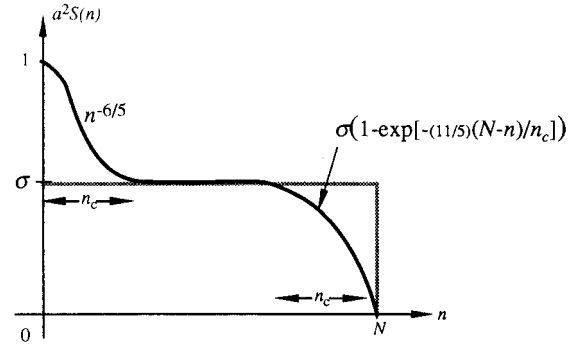


**Figure 5.** Loop density profile of the layer made of grafted and adsorbed chains. The gray line shows the result in the simple case of grafted chains without adsorption (polymer brush).

is of order unity) to include the constraint that the areal density of chains, $\sigma$, is fixed:

$$\int_1^N S(n)\,\mathrm{d}n = N\sigma \quad (22)$$

(As usual, an alternative point of view for eq 21 is to consider $\mu$ as the effective chemical potential of a chain in the layer, and the pseudopotential can then be identified with the Gibbs function.) After minimization, we obtain a second-order Euler−Lagrange differential equation of the form

$$\frac{S''(n)}{S(n)} = \mu - ({}^{11}/_{5})(a^2S(n))^{5/6} \quad (23)$$

which can later be solved for $S$ to give

$$\begin{aligned} S(n) &\cong 1/(a^2n^{6/5}) && \text{if } 1 < n < n_c \\ S(n) &\cong \frac{\sigma}{a^2}(1 - \mathrm{e}^{-(11/5)(N-n)/n_c}) && \text{if } n_c < n < N \end{aligned} \quad (24)$$

In eq 24,

$$n_c \cong \sigma^{-5/6} \quad (25)$$

$$\mu \cong ({}^{11}/_{5})\sigma^{5/6} \quad (26)$$

The solution (eq 24) was based on the hypothesis that $N^{-1} \ll \sigma \ll 1$.

The interpretation of eq 24 is quite simple (see Figure 5): the equilibrium loop density profile of a layer made of grafted and adsorbed chains follows the profile of the "purely" adsorbed layer close to the adsorbing surface (eq 1), indicating that locally the layer is very similar to an adsorbed layer. Then it saturates for a value $\sigma$, indicating that locally the layer is brushlike, with an areal chain density $\sigma$. Finally, it is truncated exponentially. In physical terms, this last region accounts for the polydispersity introduced in the pseudotail distribution through the formation of small adsorbed loops near the surface (Figure 4). Although their structures are very different (as shown by the difference in their loop density profiles), both the adsorbed-like region and the "polydisperse edge" have the same "size", $n_c$, in terms of the arclength coordinate $n$. It is interesting to note that $n_c$ is such that $D \cong an_c^{3/5}$, where $D = a\sigma^{1/2}$ is the average distance between chains. In other words, from the brush point of view, reversible adsorption affects the structure of the layer in two marginal regions of same size, roughly $D$: close to the surface, through the formation of small adsorbed loops, and in the outer edge

of the layer, by introducing some polydispersity in the tails lengths.

An interesting physical point emerges if one considers formally the limit $\sigma \cong N^{-1}$, which can be interpreted as the "purely" adsorbed situation: the polymer coverage is equal to its value at equilibrium, and we do not expect any effect related to the grafting constraint. In this limit, we find that $n_c \cong N^{5/6}$. This characteristic index defines a characteristic length $H \cong a n_c^{3/5}$, which scales as

$$H \cong N^{1/2} \tag{27}$$

In the spirit of the interpretation given above, this characteristic length separates a region dominated by loops ($z \leq aN^{1/2}$) and a region where we essantially find tails ($aN^{1/2} \leq z \leq aN^{3/5}$). This result was first found in ref 22, using a completely different approach.

To find the variations of the volume fraction $\phi(z)$ along the normal to the plane, one has first to solve eq 6 to get $n(z)$. Substitution of this result into eq 7 yields $\phi(z)$. Specifically,

$$\begin{aligned} &\phi(z) \cong (a/z)^{4/3} && \text{if } a < z < D \\ &\phi(z) \cong \sigma^{2/3} && \text{if } D < z < L_0 - D \\ &\phi(z) \cong \sigma^{2/3}\,(1 - \mathrm{e}^{-(11/5)((L-z)/uD)^{3/4}})^{2/3} && \text{if } L_0 - D < z < L_0 - (1-u)D \end{aligned} \tag{28}$$

where $0 < u < 1$ is a factor whose precise value is dependent on all the various prefactors omitted above, and $L_0 = a\sigma^{1/3}\,N$ is the extension of the layer in the absence of adsorption. To make things clearer, we have also displayed in Figure 5 the result of our theory in the absence of adsorption. In this situation, $S \cong \sigma/a^2$ is constant, and the volume fraction is thus a step function: $\phi \cong \sigma^{2/3}$ for $0 < z < L_0$. These correspond to the results of Alexander and de Gennes.[23,24] (This is not surprising, since eqs 6 and 7 are the generalization of their corresponding results to an arbitrary polydispersity.) The quantity $L \cong L_0 - (1 - u)D$ is the height of the layer made of grafted and adsorbed chains, and the correction due to reversible adsorption of the chains is thus of order $D$. In the outer fringe of the layer, the volume fraction decreases like a parabola, as shown by a Taylor expansion of eq 28:

$$\phi(z) \cong (11/5)^{2/3}\sigma^{2/3}((L - z)/uD)^{1/2} \tag{29}$$

As is clear from the calculation, the structure of the layer is modified continuously as the density of chain $\sigma$, or equivalently the chemical potential $\mu$, is varied. If the chain areal density is increased from $1/(a^2N)$ (its value in a layer made of reversibly adsorbed chains, as shown by performing integral 5 with $S$ being given by eq 1, a kink progressively appears in the equilibrium loop density profile for $S(n) \cong \sigma/a^2$. This kink becomes a plateau at higher areal chain densities, reflecting the progressive transition to a brush type of layer. This prediction of a smooth transition is in contrast with previous models which predict a discontinuous behavior (first-order transition), at a chain density $\sigma_c \cong N^{-6/5}$ in ref 6, and at $\sigma_c \cong N^{-0.93}$ in ref 35. Our approach is somewhat similar to the one used by Ligoure,[35] but this author postulates the loop density profile of the grafted and adsorbed layer to be as follows: $S(n)$ is constant if $n < n^*$, and $S(n) \sim n^{-6/5}$ if $n > n^*$ is a parameter chosen such that the free energy of the layer is minimum. This postulated function is significantly different from the solution 24 and is thus not likely to describe correctly the behavior of the layer.

Of course, our approach ignores the possibility that two tails of the same size behave differently, and the resulting picture may be affected by the relaxation of this constraint. This is particularly true in the high-density regime, where the layer is very "brushlike". But the present scenario is quite rich, and some features may survive more accurate modeling. In particular, the smoothness of the transition seems robust. This is because, around the "transition point" ($\sigma \cong N^{-1}$), the layer is still very polydisperse, and, as argued in section 2 (see ref 25), our approximations are stronger in this limit.

## 5. Conclusions

We have given a full scaling approach appropriate for treating theoretically dense polymer layers (layers made of overlapping chains). Within the framework of simple approximations for the behavior of different loops and tails, we have shown that the main features of dense polymer layers can be very easily computed in terms of the loop density profile $S$, such that $S(n)$ is the number (per unit surface) of loops and tails having more than $n$ monomers. In principle, our theory predicts (as functions of $S$) the variations of the density, the height, the adsorbance, and the effective free energy for various solvent conditions ("good", $\Theta$, or melt).

In addition, we have shown that this approach may be the basis of a unified picture of the existing models for the properties of various polymer interfacial layers. Indeed, both the results for reversibly and irreversibly adsorbed layers can be recovered in a straightforward manner from our theory. Furthermore, new insight into the physics of these interfaces appears. An important result is that, at fixed surface coverage, the structure of equilibrium layers can be understood in terms of a balance between excluded volume interactions and entropy of the set of loops. Efforts are under way to explore the consequences of these results, in particular in the important case where the coverage is not fixed.

Another new result concerns the clear understanding of the differences and analogies between reversibly adsorbed layers, irreversibly adsorbed layers (as defined in ref 11), and brushes. All these layers are characterized by loop profiles which are power laws, but their features are very different. We have shown that, depending on the comparison of the loop profile exponent $\alpha$ with 1, we may distinguish between a brush type of behavior ($0 \leq \alpha < 1$) and a reversibly adsorbed type of behavior ($\alpha > 1$). Irreversibly adsorbed layers are characterized by $\alpha = 1/2$, and thus exhibit a "pseudo-brush" behavior.

That practical calculations are possible by using our general method was shown by treating in detail the case of layers made of grafted chains which may also adsorb in good solvent. The features of this layer, such as the softening of the density profile (by comparison with the step function in the equivalent brush), have been obtained, and a continuous variation of these features is predicted as the chain coverage is increased. These offer both qualitative and quantitative corrections to the previous models and could be of some relevance from an experimental point of view.

Several extensions of this work are envisaged in the near future. Spherical geometries (polymers coating

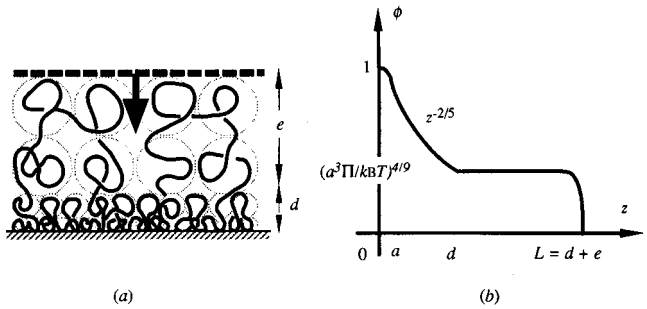


**Figure 6.** (a) Schematic representation of a polymer layer under compression. (b) We simplify the problem by assuming that there is one unperturbed region (close to the surface) and one region of constant density (at the edge).

spherical particles), which in applications to colloid stabilization are perhaps the most important cases,[2] can be treated in the spirit of this article. This has been done.[29] The corresponding results will be reported elsewhere. The force required to compress an arbitrary layer is an important matter which deserves more attention than what is given in the Appendix. By analogy with other features, we expect a complete model of the layer's deformation under compression at fixed $S$ to be simply expressed as a function of $S$. Thus, an interesting further study would concern situations where $S$ is not fixed but instead can very under compression. This could be relevant for reversibly adsorbed layers, for example, since some chains may detach during mechanical probing.

We have given little attention to the experimental side of the problem. Since the loop density profile is our main tool, one should ask whether this quantity is experimentally accessible. A possible direct measure of the loop distribution was suggested by di Meglio[36] and involves an AFM. If one approaches an adsorbing tip close enough to a coated interface, chains from the layer may adsorb reversibly on the tip. If then the tip is slowly removed from the surface, these bridging chains will stretch and eventually detach. A careful record of the variations of the force acting on the tip versus distance should keep track of each individual detachment as sudden "jumps" of the force. Within a simple model relating the size of the loop to its characteristics at the onset of detachment, one may then be able to deduce the loop density profile of the layer. In the near future, this technique could become a very useful and elegant probe of clothed interfaces.

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## 6. Appendix

In this Appendix, we show that an irreversibly adsorbed layer (as defined in ref 11) also exhibits a brush type of behavior under compression. We consider the situation depicted in Figure 6, where an external agent compresses a polymer layer with a neutral plate. *We presume that the presence of the plate only results in imposing a pressure at the edge of the layer.* Due to several possible interactions between the chains and the bare surface, it is more likely that this somewhat ideal situation may be achieved by bringing two identical layers into contact, rather than approaching one bare surface to a polymer layer.[3,37]

A usual rule of the thumb is to decompose the layer into an unperturbed region, near the surface, and a region of constant density, at the edge (see Figure 6). The idea is to compare the pressure induced at the edge of the layer, $\Pi_{op}$, with the osmotic pressure which exists in the *unperturbed* layer, $\Pi(z)$. Roughly speaking, if $\Pi_{op} \ll \Pi(z)$, then locally the layer is not affected by the compression; if $\Pi_{op} \gg \Pi(z)$, the pressure is imposed by the operator, and the volume fraction is constant. In doing so, we neglect the elasticity of the loops, and the result is thus a crude approximation of the response of the layer, but the essential physics remains, as shown by more sophisticated calculations.[38] The size of the unperturbed region $d$ is obtained by setting $\Pi_{op} = \Pi(d)$. Using the results of section 2 for loop profiles of the form $\sim n^{-\alpha}$, we easily obtain (for good solvents)

$$d \sim \Pi_{op}^{-2(3-\alpha)/9\alpha} \tag{30}$$

Implicit in eq 30 is the hypothesis that $S$ is not modified during compression and the layer is at equilibrium. The thickness of the compressed region is given by the conservation of monomers and scales as follows:

$$\begin{aligned} e &\sim \Pi_{op}^{-4/9} && \text{if } 0 \le \alpha < 1 \\ e &\sim \Pi_{op}^{-2(3-\alpha)/9\alpha} && \text{if } \alpha > 1 \end{aligned} \tag{31}$$

Turning to the overall thickness of the layer, $L = e + d$, we obtain

$$L \sim \Pi_{op}^{-2(3-\alpha)/9\alpha} + \Pi_{op}^{-4/9} \tag{32}$$

for small exponents ($0 \le \alpha < 1$). The underlying physics of eq 32 is that any *increment of pressure* in two type of works: (a) exposing some initially unperturbed monomers to a state of higher density (first term), and (b) increasing the density in the perturbed region (second term). As is clear, however, from the comparison of the two exponents, for moderate compression the second term can soon be neglected, and we see that the response of the layer becomes independent of $\alpha$:

$$L \sim \Pi_{op}^{-4/9} \tag{33}$$

This means, in particular, that brushes and irreversibly adsorbed layers exhibit the same behavior under compression.

When $\alpha > 1$, both contributions are comparable (eqs 30, 31), and we obtain

$$L \sim \Pi^{-2(3-\alpha)/9\alpha} \tag{34}$$

which is dependent on the inner structure of the layer. Setting $\alpha = 6/5$ in eq 34 gives the relation $\Pi_{op} \sim L^{-3}$, first proposed by de Gennes to model the response of reversibly adsorbed layers to compression.[37]

In this Appendix, we have shown that, depending on the density of the layer, compressing the layer may not always result in probing the inner structure of the layer. The idea is that the perturbed region of the layer, whose structure is independent of the characteristics of the layer, may screen this contribution and become the dominant response of the interface. In the case of layers whose loop density profiles are power laws, the critical value of the exponent is 1, and the distinction between a brush type of behavior and a reversibly adsorbed type of behavior emphasized in section 2 still holds. It should be noted that this distinction *cannot* be generalized to curved interfaces. Reference 14 shows, for example, that two colloidal particles coated with polymer layers

and brought into contact display different behavior when the layer is made of grafted chains or irreversibly adsorbed chains. This is because, in spherical geometry, the perturbed loops can take advantage of the unperturbed side of the particle to rearrange and thus are not forced to stay in the region of high density. As a consequence, the contribution of the perturbed region to the response is weaker, and, in effect,[29] can be neglected in the case of irreversibly adsorbed layers.

Clearly, the calculations presented in this Appendix remain at the level of arguments, but we believe it may offer some useful qualitative insights into the full problem.

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(28) Clearly, the form of the result (eq 17) for the entropy is based on our simplification that one loop behaves as two independent pseudotails. A more accurate estimate would involve considering two different size distributions (one for the loops and one for the tails) and does not reduce to the simple form of eq 17. Such an approach has been explored (Guiselin O., unpublished results): the result is a set of equations which may be solved in some favorable cases (to give, *e.g.*, the equilibrium loop distribution in reversibly adsorbed layers, see below) but leads to unphysical predictions. A possible explanation for this failure is the following (see ref 29). If one loop is treated as two independent tails, some extra configurations of the loop are allowed (those where the tails' free-ends do not join), and, from this point of view, the entropy is *overestimated*. But simultaneously, the relative orientation of the loop with respect to the surface becomes irrelevant. Due to this degree of freedom which is now ignored, the entropy is also *underestimated*. The form (eq 17) for the entropy may benefit from partial cancelation of these two approximations, and thus any improvement of only one of these may result in a poorer description of the behavior of the layer.
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