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Polymers at interfaces: from a quasi self similar adsorbed layer to a quasi brush first order phase transition

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Abstract. — We discuss the adsorption of polymer chains, where all monomers are weakly attracted by the surface, except an endgroup which is strongly attracted by the surface. The equilibrium structure of the adsorbed layer is described using scaling arguments. This structure is intermediate between a self similar adsorbed layer and a brush. A first order phase transition is predicted from a quasi-self similar adsorbed layer to a quasi brush regime. The model is compared with some recent experimental results.

1. Introduction.

Adsorption of polymer chains from a good solvent onto an interface can occur for two different reasons. When all monomers of the chain, although still soluble have a finite affinity to the surface, the chains are essentially uniformly adsorbed, leading to a self similar form for the concentration profile [1]; we shall refer to it as the self similar adsorbed layer (SSAL). On the other hand, the surface attraction may be due to a specific segment of the chains, which adsorb strongly to the surface: adsorption of endfunctionnalized chains or block copolymers exemplifies a tethered surface layer. In this case, the stickers of the chains (the insoluble block for copolymers or the endgroup for the endfunctionalized chain) anchor to the surface, whereas
the other soluble monomers are forced to stretch into the solution to form brushes [2]. The properties of such a brush are quite different from those of a SSAL. For instance, the thickness of a SSAL is on the order of magnitude of the radius of gyration of a free chain in solution, whereas it is much higher in the case of a brush. Both structures (SSAL and brush) have been extensively, theoretically as well as experimentally studied in recent years. References are given in three review articles [3, 4].

So far relatively less attention has been paid to the case of weakly adsorbing homopolymers carrying strongly adsorbing terminal monomers [2, 5]. Ou-Yang and Gao [5] have studied the adsorption of A-B-A triblocks copolymers (with hydrophobic small A blocks: the stickers and an a weakly adsorbing backbone: PEO block) on PS microspheres in aqueous solution. They have measured the hydrodynamic layer thickness as a function of the number of polymers per latex sphere by dynamic light scattering technic. The layer thickness built up gradually at low concentration, but over a narrow concentration range it increases sharply and then reaches a plateau. The adsorption curves are very different from those of both the homopolymers and grafted polymers with surface repelling backbones [6]. They have interpreted their results as a first order phase transition from a pancake to a brush configuration [2].

Alexander considered the “pancake-cigar” transition in his pioneering paper on tethered chains [2]. It is expected to occur in brushes comprising of chains capable of uniform adsorption. The Alexander analysis utilizes a highly simplified model. The adsorbed layer is modeled as a concentration step function and the fraction of monomers is identified with the ratio (monomer size/layer thickness). This oversimplification is only to be expected, since this paper predates the modern notions of self-similar adsorption layers. A clear summary of his analysis can be found in a recent review article [7]. Alexander predicts the existence of three regimes of adsorption: a two-dimensional (dilute or semi-dilute) regime, a three-dimensional semi-dilute regime of unstretched chains, and finally, a three-dimensional semidilute regime of stretched chains (the brush state). Using a grand canonical approach, Alexander shows that the chemical potential of adsorbed chains is not an increasing monotonic function of the surface coverage. It exhibits a maximum in the two-dimensional regime and a minimum at the crossover between the unstretched three-dimensional regime and the brush regime. Consequently the three-dimensional regime of semidilute unstretched chains is unstable and a first order phase transition is expected to occur around $\sigma \equiv R_P^2$. $\sigma$ denotes the number of adsorbed chains per unit area, and $R_P$ is the three-dimensional radius of gyration of the chains. Indeed, the transition occurs as soon as the external chemical potential equals the minimal value of the chemical potential of adsorbed chains: it should correspond to a very low surface coverage in the vicinity of the two-dimensional regime.

The purpose of this paper is to give a theoretical description of the structure of adsorbed layers of such weakly adsorbing homopolymers carrying a strongly adsorbing terminal monomer, in order to investigate the adsorption isotherm of these polymers and the possible existence of a transition from a SSAL configuration to a brush configuration. To perform this study we use a very elegant approach due to Guiselin [8]. Using scaling arguments like Alexander’s [2], Guiselin has shown that a SSAL can be viewed as a very polydisperse brush [9]. This analogy allows us to give a unified description of a SSAL and a brush and is a convenient framework for describing the intermediate expected structure.

The paper is organized as follows: in section 2 we review the approach of Guiselin [8] and apply it to the case of weakly adsorbing polymers with a strongly adsorbing endgroup. Section 3 is devoted to the study of the equilibrium structure of these adsorbed layers both in the canonical and grand canonical approaches. The existence of a first order phase transition from a quasi SSAL to a quasi brush structure will be shown. In section 4 we compare the model with some experimental results of reference [5].
2. The model.

Let us consider chains with polymerization index \( N \) terminally anchored to a flat surface. The chains are constituted by \( (N-1) \) monomers which have a weak interaction (\( \delta kT \) per monomer) with the surface. The last monomer (the sticker) has a high attractive interaction (\( \Delta kT \)) with the surface. In the limit \( \Delta \gg \delta \) we can suppose that all stickers of the adsorbed chains are grafted to the surface. We denote by \( \sigma \) the number of adsorbed chains per unit area: \( \sigma = a^2 / \Sigma \), where \( \Sigma \) is the average surface per adsorbed chain and \( a \) is the Kuhn statistical length; \( \Phi_s \) denotes the volume fraction of polymers at the adsorbing surface. It is very important to notice that the thickness on which \( \Phi_s \) is defined is not the monomer length \( a \), but the correlation length at the surface \( \zeta \); \( \zeta \) is always larger than the monomer length \( a \). For simplicity we put \( a = 1 \) and \( kT = 1 \) in the following.

2.1 "GUISELIN MODEL". — The polymer layer can be characterized by its loops and tails distribution [8]. Let us call \( D'_1(n) \) and \( D'_2(n) \) the number per unit area of loops and tails made of \( n \) monomers respectively, and \( D'(n) = D'_1(n) + 2D'_2(2n) \) is the number per unit area of pseudotails made of \( n \) monomers. Guiselin [8] defines \( D(n) = \int_1^n D'(n)dn \), \( D(n) \) is then the number per unit area of pseudotails made of more than \( n \) monomers.

Guiselin [8] assumes that the adsorbed layer is analogous to a polydisperse brush and that the pseudotails are all stretched in a similar way. This approximation corresponds to the step profile approximation of Alexander for the case of a polymer brush [2]. Using this analogy, he obtains the following relations:

\[
\frac{dz}{dn} = D(n)^{1/3} \\
\Phi(z) = D(n)^{2/3}
\]  

(1)

where \( z \) denotes the distance from the surface (the \( n \)-th monomers of all pseudotails larger than \( n \) are at the same distance from the surface), and \( \Phi(z) \) is the volume fraction of polymer at distance \( z \) perpendicular to the surface. The Guiselin model refers to three-dimensional states of adsorbed layers, since the correlation length \( \zeta(z) \) and the volume fraction of polymer \( \Phi(z) \) are related through the relation \( \zeta(z) = \Phi(z)^{-3/4} \).

We have the following conservation relation:

\[
\int_1^n nD'(n)dn = N\sigma
\]  

(2)

The thickness of the layer is given by:

\[
h = \int_1^n D(n)^{1/3}dn
\]  

(3)

All these equations are valid in the overlapping regime, i.e. \( D(n) > N^{-6/5} \) The validity of equations (1-3) can be verified for the case of a brush and a SSAL. In the brush case \( \Phi(z) = \sigma \) and \( h = N \sigma^{1/3} \) [2]; equations (1-3) give the same result. In the SSAL case, the volume fraction profile \( \Phi(z) \) varies as \( z^{-4/3} \), and the thickness \( h \) scales as \( N^{3/5} \) [1]. \( D(n) \) has been calculated in reference [10]: \( D(n) \sim n^{-6/5} \) and corresponds to the limit of the overlapping regime. Putting this expression for \( D(n) \) in equations (1,3) leads to the correct result for \( h \) and \( \Phi \).

The free energy of the layer can be expressed as a functional of the \( D(n) \) distribution. In principle, the equilibrium structure can be obtained by the functional minimization of the free energy, which gives a Euler-Lagrange equation. However, this method supposes that the
distribution of pseudotails $D(n)$ is an analytical function of $n$. We shall show that it is certainly not the case. Our purpose is to postulate a given form of the pseudotails distribution and to verify that it leads to a smaller equilibrium value of the free energy of the layer, than for both a brush or a SSAL.

2.2 POSTULATED PSEUDO-TAILS DISTRIBUTION. — We postulate the following distribution of pseudotails $D(n)$

$$D(n) = \Phi_s^{3/2}$$

$$D(n) = \Phi_s^{3/2} \left( \frac{n}{n^*} \right)^{-\alpha} \quad 1 \leq n \leq n^*$$

$$D(n) = \Phi_s^{3/2} \left( \frac{n^*}{n^*} \right)^{-\alpha} \quad n^* \leq n \leq N$$

where $\alpha = 6/5$, and $n^*$ is a parameter characterizing the distribution $D(n)$.

$D(n)$ obeys all physical requirements: it is a continous and decreasing function of $n$. By substituting $n^* = 1$ or $n^* = N$ respectively in equation (4), one gets the structure of a SSAL or a brush respectively. The expected structure of the layer is a combination of the SSAL and the brush ($1 \leq n^* \leq N$). The proximal region ($n < n^*$) has the inner structure of a brush with a grafting density $\Phi_s^{3/2}$. The external region ($n > n^*$) has the structure of a SSAL. This choice for the distribution of pseudotails $D(n)$ is not arbitrary: it mimics the scenario proposed by Ou-Yang and Gao [5]: at low surface coverage $\sigma$, because backbones can absorb, polymers assume low profiles and the structure of the layer is a SSAL. By increasing the surface coverage $\sigma$, the stronger adsorbing endgroups (the stickers) will start to displace the weakly adsorbed backbones from the surface, because backbones cannot overlap very much in a good solvent. This competition between the stickers and the backbones will continue to “pop” the polymers backbones into the solution, by anchoring more chains onto the surface. Consequently small loops and tails are destroyed by increasing $\sigma$.

It is convenient to define an order parameter $\eta = \sigma/\Phi_s^{3/2}$. From equations (2, 4) one gets:

$$\eta = \alpha/(\alpha - 1)x \left( 1 - \frac{x^{\alpha-1}}{\alpha} \right)$$

where $x = n^*/N$ ($1/N \leq x \leq 1$).

As a matter of fact, the physical parameter $\eta$ describes the degree of “disorder” of the layer. The ordered state corresponds to the brush ($\sigma = \Phi_s^{3/2}$) [2] and $\eta = 1$ (putting $x = 1$ in Eq. (5) leads to $\eta = 1$). The disordered state corresponds to the SSAL (putting $x = 1/N$ in Eq. (5) leads to $\eta = 6/N$; in the thermodynamical limit $N = \infty$, $\eta$ equals strictly 0 in the disordered state).

2.3 FREE ENERGY OF THE LAYER. — In order to evaluate the free energy of the layer, we use scaling arguments, which do not give precise estimate of prefactors in the free energy of adsorbed chains. Consequently, we omit all these prefactors. Still the scaling arguments predict a correct order of magnitude and correct scaling laws, we expect that the model describes well the essential features of the adsorbed layer. However, it should be noticed than an exact but quite complex mean field calculation in the strong segregation limit could be performed using the model of reference [9] and the analogy of Guiselin.

For a given surface coverage $\sigma$ and a given pseudotails distribution $D(n)$, the free energy of the adsorbed layer per unit area $F$ reads:

$$F = F_v + F_s + F_{\text{conf}} + F_{\text{ads}} + F_{\text{tr}}$$
$F_\nu$ denotes the excluded volume interaction energy of the layer per unit area:

$$F_\nu = \frac{1}{2} \int_0^h \Phi(z) \frac{3\nu-1}{2} \, dz = \frac{1}{2} \int_1^N D(n) \frac{1+\chi}{2} \, dn \quad (7)$$

The second and third terms of equation (6) are entropic contributions to the Helmholtz energy. $F_s$ is the stretching energy of chains per unit area. Using the trick of Milner et al. [11], it is evaluated as the stretching energy of a dense (and therefore ideal) melt of chains of blobs of dimension $\xi(z) = D(n)^{-1/2}$ [8]:

$$F_s = \frac{1}{2} \int_1^N D'(n) \, dn \int_1^n D(n')^{5/6} \, dn' = F_\nu \quad (8)$$

The equality $F_s = F_\nu$ in equation (8) is obtained by a simple integration per part; it seems to be surprising, but it is a noteworthy consequence of the equality $\xi(z) = D(n)^{-1/2}$. However, Guiselin [12] has shown that this relation between the local correlation length and the local stretching of the adsorbed chains minimizes the free energy of the layer.

$F_{\text{conf}}$ takes into account the variation of the number of configurations of an adsorbed chains as a function of the pseudotails distribution. It has been shown in the case of a SSAL [12] that this contribution cannot be omitted. $F_{\text{conf}} = -\log(\Omega)/A$, where $\Omega$ is the number of configurations of tails and $A$ is the area of the adsorbing surface. There are $AD(1) = \sum_{n=1}^N AD'(n)$ pseudotails, but all tails of same length are indiscernable; one deduces the number of possible configurations $\Omega[12]$:

$$\Omega = \frac{(AD(1))!}{\prod_{n=1}^N (AD'(n))!} \quad (9)$$

Using the Stirling approximation, the contribution $F_{\text{conf}}$ reads:

$$F_{\text{conf}} = -\Phi_s^{3/2} \log \left( \Phi_s^{3/2} \right) + \int_1^N D'(n) \log(D'(n)) \, dn \quad (10)$$

The fourth term in equation (6) is the energy gained by adsorption of the weakly adsorbing monomers and the strongly adsorbing stickers.

$$F_{\text{ads}} = -\delta(\Phi_s - \sigma) - \Delta \sigma \quad (11)$$

The last term in equation (6) denotes the translational entropy of the polymers in the layer:

$$F_{\text{tr}} = \sigma \log(\sigma) \quad (12)$$

All the contributions of the free energy of the layer can be now expressed as a function of the internal variable $x$ and the extensive one $\sigma$. 
3. Thermodynamical equilibrium.

3.1 Canonical Ensemble: Fixed Surface Coverage. — We assume that the averaged surface coverage \( \sigma \) and therefore the area per polar head is fixed. Using the postulated distribution \( D(n) \) (Eq. (4)), the free energy per unit area of a homogeneous layer can be explicitly calculated from equations (6, 7, 10-12) as a function of \( x \) and \( \sigma \). It reads:

\[
\begin{align*}
F &= \gamma N \Phi^3 \left( x + x^\alpha \right) - \delta \left( \Phi - \sigma \right) - \Phi^{3/2} \log \left( \Phi^{3/2} \right) + \\
&\quad \Phi^{3/2} \left( 1 - x^\alpha \right) \left[ \log \left( \alpha \Phi^{3/2} \right) - \log \left( N + 1 + 1/\alpha \right) \right] - (1 + \alpha x^\alpha) \log(x) \right) - \Delta \sigma + \sigma \log(\sigma) 
\end{align*}
\]

(13)

where \( \Phi \) is given by equation (6) and \( \alpha = 6/5, \gamma = 11/6 \).

The equilibrium state is obtained by the minimization of \( F \) with respect to \( x = n^*/N \) \( (1/N \leq x \leq 1) \). The minimum corresponds to the value \( x = x_{eq} (\sigma) \). The order parameter \( \eta(\sigma) \) and the thickness of the layer \( h(\sigma) \) can be then calculated by putting the value \( x = x_{eq} (\sigma) \) in equations (3 and 5) respectively.

The expression (13) of the free energy \( F \) does not allow for an analytical treatment of the thermodynamical equilibrium; nevertheless the numerical calculations are easy to do. The variation of the free energy per adsorbed chain \( f_{\text{chain}} = F/\sigma \) is illustrated in figure 1 where \( f_{\text{chain}} \) is plotted on the parameter \( x \) characterizing the pseudotails distribution \( D(n) \), for the following set of parameters: polymerization index \( N = 10000 \), adsorbing energy per monomer \( \delta = 1 \), sticking energy \( \Delta = 30 \), and different values of the surface coverage \( \sigma \).

![Dependence of the free energy per adsorbed chain](image)

Fig. 1. — Dependence of the free energy per adsorbed chain \( f_{\text{chain}} \) on the internal parameter \( x \) characterizing the pseudotails distribution \( D(n) \) for the following set of parameters: polymerization index \( N = 10000 \), adsorbing energy per monomer \( \delta = 1 \), sticking energy \( \Delta = 30 \), and different values of the surface coverage \( \sigma \).

The value \( x_{eq} \) increases by increasing the surface coverage. For small values
of $\sigma$, $x_{eq}$ is very small (for instance for $\sigma = 10^{-3}$, $x_{eq} = 9 \times 10^{-4}$), and the structure of the homogeneous layer is very close to a SSAL: only small loops are forbidden ($n < 10$). At higher values of $\sigma$ (for $\sigma = 2 \times 10^{-3}$, $x_{eq} = 0.175$), the structure of the layer is intermediate between a SSAL and a brush (quasibrush). The transition from a quasi SSAL to a quasi brush is rather sharp. In figure 2 the order parameter $\eta$ corresponding to the equilibrium value $x_{eq}^{(\sigma)}$ is plotted as a function of $\sigma$ for different sets of parameters $(N, \delta)$. The transition is abrupt for high values of $N$ or small values of $\delta$, whereas it is smoother for smaller values of $N$ and larger values of $\delta$. The position of the transition $\sigma_t$ depends strongly on the polymerization index $N$ and on the energy gained by adsorption of a monomer $\delta$. One finds from numerical calculations (see Fig. 3), for $100 < N < 10^5$ and $0 < \delta < 8$, that $\sigma_t \sim \delta N^{-0.93}$

![Graph showing dependence of $\eta$ on $\sigma$](image)

Fig. 2. — Dependence on the order parameter of the adsorbed layer $\eta = \sigma / (\Phi_s)^{3/2}$, on the surface coverage $\sigma$ for different set of parameters (---) $N = 10^5$, $\delta = 1$; (---) $N = 10^4$, $\delta = 1$; (---) $N = 10^4$, $\delta = 4$; (...) $N = 10^4$, $\delta = 8$; (---) $N = 10^3$, $\delta = 1$.

In order to determine the thermodynamical equilibrium in the canonical ensemble, the free energy $F(x_{eq}, \sigma)$ must be now minimized, subject to the constraint that the total amount of adsorbed polymers is fixed ($x_{eq}$ has been numerically calculated for each value of $\sigma$: it is the value of $x$ which gives the absolute minimum of $F(x, \sigma)$). In figure 4, the free energy $F(x_{eq}, \sigma)$ is plotted as a function of $\sigma$ for the following set of parameters: $(N = 10000; \delta = 1; \Delta = 10; \Delta = 250; \Delta = 500)$. In all cases, the curves present a first minimum at low values of $\sigma$ and an inflexion point. Increasing the value of the sticking energy $\Delta$ leads to the existence of a second minimum for high values of $\sigma$. Two phases can coexist if it is possible to construct a tangent line that touches the free energy curve at two points $\sigma_1$ and $\sigma_2$ ($\sigma_1 < \sigma_2$), but otherwise lies everywhere below it (common tangent construction). Common tangency at each of the two points of the free energy curve is then found by demanding that at point $\sigma_1$ each of the following two quantities is equal to its value at point $\sigma_2$:

$$F(x_{eq}, \sigma) = \sigma \frac{\partial F(x_{eq}, \sigma)}{\partial \sigma}$$

At very low surface coverage (but still larger than the overlapping surface coverage), i.e. $\sigma < \sigma_1$, the adsorbed layer is monophasic; it is a quasi SSAL with a small order parameter
The surface coverage at the transition (inflexion point of the curves in Fig. 2) $\sigma_t$ is plotted on the polymerization index $N$ (for $\delta = 1$) and on the adsorbing energy $\delta$ (for $N = 10000$).

Dependence on the free energy per unit area of the adsorbed layer $F(x_{eq}, \sigma)$ on the surface coverage $\sigma$ for the following set of parameters ($N = 10000$; $\delta = 1$) and three different values of the sticking energy $\Delta$.

$\eta$ referred to as the “disordered state”. At $\sigma = \sigma_1$, a first order phase transition occurs: the adsorbed layer separates in two phases: a quasi SSAL ($\sigma < \sigma_1$) coexists with a quasi brush ($\sigma > \sigma_2$) the quasi brush is the ordered state with a finite order parameter $\eta$ (it is not strictly speaking a brush, because $\eta$ is smaller than 1). The proportion of each phase follows the rule of momenta. For $\sigma > \sigma_2$, the layer is monophasic again: the single phase being a quasi brush. The range domain of coexistence of two phases ($\sigma_1 < \sigma < \sigma_2$) depends on the polymerization index $N$ as well as the energy $\delta$, but it depends only very weakly on the sticking energy $\Delta$, as can be shown in figure 4 whereas the proportion of each phase depends evidently strongly on $\Delta$. 
3.2 Grand canonical ensemble: equilibrium with a reservoir. — Generally, the
total amount of adsorbed polymers is not fixed. The adsorbing surface is in contact with a
solution of free chains in a good solvent, and the surface coverage \( \sigma \) depends on the chemical
potential of free chains in solution \( \mu_{\text{ext}} \), and on the osmotic pressure in the reservoir \( \pi_{\text{ext}} \). We
restrict our attention to the case of a dilute solution of polymers in the reservoir: in this case,
the osmotic pressure \( \pi_{\text{ext}} \) acting on the adsorbed layer can be neglected. When the chains
in the reservoir do not form micelles: \( \mu_{\text{ext}} \approx 1 + \log \left( \phi_0 / N \right) + N v \phi_0 \), where \( \phi_0 \) denotes the
polymer volume fraction in the reservoir and \( v \), the excluded volume parameter. At equilibrium,
the surface coverage can be determined from the equality of chemical potentials of free and
adsorbed chains:

\[
\mu_{\text{ext}} = \mu_0 = \frac{\partial F(x, \sigma)}{\partial \sigma} \bigg|_{x=x_{\text{eq}}}.
\]  

(14)

It is more convenient to include the sticking energy \( \Delta \) in an effective external potential:

Equation (14) can be rewritten: \( \mu'_{\text{ext}} = \mu' \) where \( \mu'_{\text{ext}} = \mu_{\text{ext}} + \Delta \) and \( \mu' = \mu + \Delta \)

In practice, one needs to calculate numerically the dependence of the chemical potential
\( \mu'(\sigma) \). Figure 5 illustrates the dependence of the chemical potential \( \mu'(\sigma) \) on the surface coverage
\( \sigma \) for the typical set of parameters (\( N = 10000; \delta = 1 \)). It is important to notice that \( \mu' \) is not a monotonic function of \( \sigma \). It has a maximum in the quasi-SSAL regime and a minimum in the
quasi brush regime. Therefore, there are no stable solutions in the intermediate regime and a
first order phase transition is predicted. For \( \mu'_{\text{ext}} < \mu'_{\text{min}} \), a single quasi-SSAL phase is expected.
For \( \mu'_{\text{min}} < \mu'_{\text{ext}} < \mu'_{\text{max}} \), two phases should coexist: a quasi-SSAL and a quasi-brush. Finally,
for \( \mu'_{\text{max}} < \mu'_{\text{ext}} \), a single quasi-brush is expected. It should be noticed, that, after passing
the point of transition, polymers should quickly saturate the interface. Experimentally, this
corresponds to the case that after reaching the quasi-brush phase, adding more polymers to
solution will slightly increase the number of surface chains and most of chains will go to the
solution. In figure 6 the dependence of the value of the external chemical potential \( \mu'_{\text{ext}} \)
corresponding to the change in the majority phase (from quasi-SSAL to quasi-brush) is
plotted as a function of \( N \) and \( \delta \). It appears that: \( \mu'_{\text{ext}} \sim \delta N^{-0.54} \)
Fig. 6. — The value of the external effective chemical potential $\mu'_\text{ext}$ corresponding to the change of the majoritary phase (quasi-SSAL to quasi brush) is plotted on $N$ (for $\delta = 1$) and $\delta(N = 10000)$ respectively.

4. Discussion.

Alexander predicts the existence of a first order phase transition for weakly adsorbing polymers carrying a polar head [2]. However, he predicts that the transition should occur from a low density regime to a high density regime. The low density regime corresponds to a structure of “pancakes”, i.e. the adsorbed chains are two-dimensional; the high density regime is the brush state. This transition is referred to as “pancake to brush” transition. It should occur around $\sigma \cong R_F^{-2}$ [7]. The model developed in this paper disagrees with this interpretation. It suggests that the transition should occur from a quasi-SSAL to a quasi-brush regime. It means that even at surface coverage still larger than the overlapping regime, the layer thickness remains rather thin ($\cong R_g$), but stable. Moreover, the ordered state is not a perfect brush, but an intermediate structure between a brush and SSAL (the order parameter $\eta \sim 0.6 < 1$).

Ou-Yang and Gao [5] have interpreted their experimental results in terms of this Alexander’s “pancake to brush” transition. But there is no experimental evidence that the transition occurs around $\sigma \cong R_F^{-2}$. For instance, they have shown that the inflexion point of the transition $\sigma_t$ decreases with the molecular weight and goes like $\sigma_t \sim N^{-1}$. This implies that the pancakes should be formed by ideal chains at the surface; but there is no physical reason for which chains in good solvent should become ideal near an interface.

The present model predicts that $\sigma_t \gg \sigma_{\text{overlap}}$, that $\sigma_t$ goes like $\delta N^{-0.94}$ and the adsorbed chains remain swollen as the free ones do in good solvent. The exponent 0.94 is very close to the experimental one $-1$.

Ou-Yang and Gao have also shown that the transition regions are almost overlapping for both C12 and C16 endgroups. It means that the transition region depends very weakly on the sticking energy $\Delta$. Our model agrees with this experimental fact (see Fig. 4).

The same authors have noticed that in the brush configuration, the polymers are stretched to about four or five times that of $R_g$ in solution. Using a large set of parameters ($10^2 < N < 10^5$; $0 < \delta < 8$), the present model predicts that in the quasi-brush regime, the chains are stretched to about two times that of $R_g$. This discrepancy indicates probably that our model is too crude: the absence of precise estimates of the prefactors in the free energy of the layer, as
well as the rough calculation of the entropy of the pseudotails configurations does not allow
to predict quantitatively the $n^*$ of the quasi-brush structure (see Eq. (4)). The calculated value
$x_{eq}$ at the transition ($x_{eq} \sim 0.3$) is certainly underestimated. A more sophisticated model [9]
could perhaps be used.

5. Conclusion.

In this paper we have theoretically discussed the equilibrium of a layer formed by weakly
adsorbing polymers carrying a strongly adsorbing sticker. We have shown that the structure
of the adsorbed layer is intermediate between a SSAL [1] and a brush [2]. The model predicts
the existence of a first order phase transition from a quasi-SSAL to a quasi-brush regime. The
transition occurs at surface coverage larger than the overlapping one. This theory is in good
agreement with the experiments of Ou-Yang and Gao [5]. This transition is quite different
from this one predicted by Alexander more than fifteen years ago. Recent experiments [13] could
be possibly reinterpreted by using the present model. However small angle neutron scattering
techniques should be performed in order to investigate the inner structure of the adsorbed
layers and the lateral heterogeneities in the two phases coexistence domain.

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