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Résumé. — Nous considérons les différents régimes d'adsorption de polymères flexibles en bon solvant, qui apparaissent lorsqu'on augmente la concentration loin de la paroi attractive. On traverse d'abord un régime très dilué en volume, pour lequel le taux de couverture Γ augmente rapidement. Suit un régime « de plateau » où Γ croît beaucoup plus lentement, la solution étant toujours diluée en volume. Dans le cas d'une solution semi-diluée en volume, nous considérons l'adsorption des blobs. Pour de hautes fractions en volume, $\varphi_b > \delta^{4/3}$, où δ désigne l'énergie supplémentaire, adimensionnée par monomère sur la surface, les blobs ne sont pas adsorbés. La tension interfaciale est calculée dans les différents régimes. Nous suivons la théorie d'échelle de de Gennes et Pincus.

Abstract. — We consider the various adsorption regimes of flexible polymer chains in a good solvent when the bulk concentration is changed. As the latter is increased, first we find a very dilute bulk regime where the surface coverage increases fast. This is followed by a plateau with much slower increase for Γ, the bulk solution being still dilute. In the bulk semi-dilute regime, we consider the adsorption of blobs. For high bulk volume fraction, $\varphi_b > \delta^{4/3}$, where δ is the dimensionless excess energy per monomer on the surface, the blobs are not adsorbed. The interfacial tension is calculated in the different regimes. Our approach closely follows the scaling theory of de Gennes and Pincus.

1. Introduction.

When the surface tension γ_p of a polymer melt is lower than the surface tension γ_0 of a pure solvent, the macromolecules in a solution are adsorbed on the surface in order to minimize the surface tension [1]. Because both γ_p and γ_0 are temperature dependent, it is possible to change the effective interaction between the polymer and the surface by varying the temperature. In principle, it might even be possible to invert the inequality between the surface tensions of the pure species and thus to have a repulsion of the polymer by the surface.

In this paper, we would like to look at the influence of the bulk concentration C_b on these surface effects in the attractive case. We only consider flat surfaces. Thus, possible curvature effects which may be present in a porous medium for instance are neglected. The typical experiments we have in mind are the adsorption of flexible chains on a solid surface or at a solvent/air interface. In the latter case local rugosity is neglected. Adsorption of macromolecules on a porous solid may also be included when the diameter of the pores is much larger than the radius of the polymers.

Polymer adsorption has been studied for a long time, mainly in a mean field approximation [1]. Recently, an analogy was made between polymer adsorption and surface effects in magnetic systems close to a critical point [2-4]. In this analogy, one considers the configurations of a flexible chain constrained in the vicinity of a surface, and more particularly of a polymer with one end attached on the wall. Among other results, it was shown that in the limit of an infinite chain, the adsorption threshold is related to the so-called *special* transition of the magnetic system, where both the surface and the bulk order simultaneously.

Another important result is that one has to distinguish two different cases [5-7], depending on the nature of the adsorbing surface, namely impenetrable (e.g. solid substrate) or surfaces of defects where the polymer may have configurations extending on both sides of the surface simultaneously

(e.g. interface between two immiscible good solvents). The exponent φ, to be defined below, describing the cross-over from non adsorbed to adsorbed behaviours is different for both cases. In the following we will focus on the impenetrable case, but changing the value of φ allows us to extend the results to the other case.

The knowledge of the bulk behaviour and of φ is sufficient to determine the conformation of the chains in the vicinity of the surface by scaling arguments. These were already applied to the single chain case and to semi-dilute solutions [3, 4, 8, 9]. We wish here to extend this discussion to regimes that were not considered so far to our knowledge. In section 2, we shall recall the formal case of a single chain, and of dilute bulk solutions. Depending on the strength of the attraction, the surface may be dilute or semi-dilute. Section 3 is devoted to bulk semi-dilute regimes. Here the problem is the adsorption of blobs rather than chains. We find an upper bulk concentration $\tilde{C}_b$ above which there is no adsorption. The surface tension is discussed for all the previous regimes in section 4.

2. The dilute bulk regimes.

In this section we consider the various surface regimes occurring when the bulk is dilute, that is when the bulk volume fraction $\varphi_b \equiv c_b a^3$ is smaller than the overlap fraction $\varphi_b^* \sim N^{-4/5}$, where c_b, a and N are the bulk monomer concentration, the step length and the number of units per polymer, respectively, we first recall briefly some results relative to the single chain case [3, 4, 9, 14]. Then we look at two different regimes where although the solution is still dilute, the surface fraction is semi-dilute. These regimes were already pointed out by de Gennes [2], with somewhat different conclusions. In each regime, we describe the structure of the chain on the adsorbing wall, and we compute the monomer volume fraction profile $\Phi(z)$ at a distance z from the surface.

2.1 THE SINGLE CHAIN. — We first consider a single chain made of N monomers of length a each, in the vicinity of a surface [2, 3, 9]. This may be realized for instance by attaching one end of the polymer to the surface. We assume the solvent to be good, and the surface to be impenetrable. Moreover every monomer on the surface is assumed to get an excess attractive energy $(-kT\delta)$. For δ smaller than δ_c to be defined below, it has been shown that [2, 3] the number of monomers actually on the surface is N^{φ}, where φ is a cross-over exponent [5-7], and $\varphi \approx 3/5$ for three dimensional systems [10] to which we restrict our attention. Therefore, the attractive energy per chain is $kT\delta N^{\varphi}$. The actual conformation of the chain is obtained from the balance between

the attractive energy which tends to bring the polymer on the surface and the corresponding loss in entropy. It was shown that for an infinite chain there is an adsorption threshold for $\delta = 0$. For finite chains there is a cross-over between a three-dimensional and a two dimensional behaviour for

$$\delta_c \sim N^{-3/5} . \tag{1}$$

When the dimensionless energy parameter is smaller than δ_c, entropic effects dominate, and the conformation of the polymer is basically isotropic. The dimensions of the coil parallel and orthogonal to the surface remain of the same order as the Flory radius [11, 12]

$$R_F \sim N^{3/5} a .$$

In the opposite limit, $\delta \gg \delta_c$, the chain is adsorbed and expands on the surface. Two characteristic distances appear and may be obtained by scaling arguments :

i) the thickness D of the adsorbed layer is derived by assuming a scaled form for the distance :

$$D = R_F \, f(\delta N^{\varphi}) \tag{2}$$

where $f(x)$ is an unknown function which may be expanded in x for small x, and $f(x = 0) = 1$. In the adsorbed regime, $x \gg 1$, $f(x)$ has a power law behaviour which is determined by noting that D should be independent of N and should depend only on δ. This leads to

$$D \sim \delta^{-\nu/\varphi} a \approx \delta^{-1} a . \tag{3}$$

A possible interpretation for D is to assume that for shorter distances the chain is still isotropic and behaves as a free coil, i.e. as a self avoiding walk in an infinite volume. Let g_a be the number of monomers in such portion of chain (blob), our assumption is

$$D \sim g_a^{\nu} a . \tag{4}$$

Using (3) and (4), we find that

$$\delta g_a^{\varphi} \sim 1 . \tag{5}$$

Thus the adsorption blobs may be considered as subunits of the polymer at the adsorption cross-over.

ii) The parallel extension $R_\parallel$ of the polymer in the adsorbing plane may be derived in the same way as above. We assume

$$R_\parallel = N^{3/5} a h(\delta N^{3/5}) . \tag{6}$$

Noting that in the adsorbed range $\delta N^{3/5} \gg 1$, the parallel radius is two-dimensional [11, 12], so that we have

$$R_\parallel \sim N^{3/4} a \tag{7}$$

and assuming a power law behaviour for $h(x)$ in equation (6), we find

$$R_\parallel \sim N^{3/4} \, \delta^{1/4} \, a \qquad (8)$$

in good agreement with numerical simulations [3, 13].

Actually, a more precise description of the conformation of the chain is to consider the concentration profile in the direction z orthogonal to the plane of adsorption. Let $\Phi(z)$ be the number of monomers per area D^2 at a distance z from the wall. Two different regions are found [8, 9] :

a) The *proximal* region, $a \ll z \ll D$ has a characteristic adsorption behaviour :

$$\Phi(z) \simeq \Phi_s \left(\frac{z}{a} \right)^{-m} \qquad (9)$$

where $m = \dfrac{\nu + \varphi - 1}{\nu} \approx 1/3$ is calculated by continuity at the cross-over with region (2) below for $z = D$. Φ_s is the monomer fraction per unit area on the surface. It is known at the cross-over $\delta = \delta_c$

$$\Phi_s = \frac{N^\varphi a^2}{R^2} \sim N^{\varphi - 2\nu} \approx N^{-3/5} \quad (\delta \ll \delta_c) . \qquad (10)$$

Assuming a scaled form similar to (6) for Φ_s leads, in the adsorbed regime, to

$$\Phi_s \sim \delta^{(2\nu - \varphi)/\varphi} \approx \delta \quad (\delta \gg \delta_c) . \qquad (11)$$

Note that relation (11) may also be interpreted in a term of adsorption blobs, (equations (4) and (5)), as

$$\Phi_s \sim g_a^\varphi \, \frac{a^2}{D^2} . \qquad (12)$$

The exponent m is determined at the cross-over $\delta \sim N^{-3/5}$ by the condition

$$\int^{R_F} \phi(z) \, \mathrm{d}z \sim N^{1-2\nu} .$$

Inserting (9) and (10), we find

$$m = \frac{\phi + \nu - 1}{\nu} \approx 1/3 .$$

b) In the *distal* region, $z \gg D$, the concentration profile falls off exponentially. .

2.2 THE ADSORPTION ISOTHERM. — As soon as the bulk volume fraction φ_b is non zero, there is a partitioning of the polymers between surface and bulk. Although the actual number of polymers on the surface is much smaller than the number of polymers in the bulk, the surface fraction, defined as the number of monomers per unit *surface* may be very high. In this section, we calculate the variation

of the surface coverage Γ with bulk volume fraction φ_b in the case of dilute bulk solutions, $\varphi_b \ll \varphi_b^*$. We also show how the surface saturates in monomers with increasing φ_b. This is a central point of this paper. We consider both the dilute regimes (Sects. 1 and 2) and the plateau regime (Sect. 3) which corresponds to the saturation of the interface.

2.2.1 *The dilute surface regime.* — In order to get the partitioning of the chains, we first consider the free energy F per chain within a Flory approximation. This was done by de Gennes in the case of a surface of defects [2, 10]. For an impenetrable surface, we have

$$\frac{F}{kT} = N \left(\frac{a}{D} \right)^{1/\nu} - N \left(\frac{a}{D} \right)^{(1-m)} \delta + \frac{F_{\text{trans}}}{kT} \qquad (13)$$

where the first and second terms are respectively the confinement and surface attraction contributions. The last term corresponds to the translation of the centre of mass. Minimization of F with respect to D leads to equation (3) for D. The minimized free energy

$$\frac{F}{kT} \sim \frac{F_{\text{trans}}}{kT} - N\delta^{1/\varphi} \qquad (13a)$$

leads to the following surface chemical potential

$$\frac{\mu_s}{kT} \sim - N\delta^{1/\varphi} + \ln \left(\frac{\Gamma a}{ND} \right) \qquad (13b)$$

where Γ is the surface fraction. More precisely $\dfrac{\Gamma}{Da^2}$ is the average concentration is the adsorbed layer.

$$\frac{\Gamma}{Da^2} = \frac{1}{D} \int_0^\infty \varphi(z) \frac{\mathrm{d}z}{a^3} \sim \frac{1}{D} \int_0^D \varphi(z) \frac{\mathrm{d}z}{a^3} \qquad (14)$$

Equating μ_s to the bulk chemical potential

$$\mu_b \sim kT \ln \left(\frac{\varphi_b}{N} \right) \qquad (15)$$

we get

$$\Gamma = \frac{D}{a} \varphi_b \, e^{N\delta^{5/3}} . \qquad (16)$$

Thus for very low bulk concentration, the surface monomer fraction is proportional to φ_b. Because of the exponential factor, it may become large when $\delta \gg \delta_c$. When this happens, however, an important effect which we did not take into account comes into play : the excluded volume between different chains. It is this repulsive interaction which leads to the plateau regime in the isotherm to be described below. We have seen above that there are about N

monomers in the proximal region, that is in a volume $DR_\parallel^2$. Thus the surface layer is dilute as long as Γ is smaller than an overlap fraction Γ_1^* :

$$\Gamma_1^* \sim \frac{Na^2}{R_\parallel^2} \sim N^{-1/2} \delta^{-1/2} . \qquad (17)$$

For higher fractions, $\Gamma > \Gamma_1^*$, the surface layer is in a bidimensional semi-dilute regime. Note that if $\delta \gg \delta_c$, relation (16) shows that this may happen even when the bulk solution is dilute, $\varphi_b \ll \varphi_b^*$.

2.2.2 The bidimensional semi-dilute surface regime. — When the surface fraction is larger than Γ_1^*, the adsorbed macromolecules interact strongly with each other and a two dimensional semi-dilute regime takes place in the adsorbed layer. This regime corresponds to region (2) in figure 3. The charac-
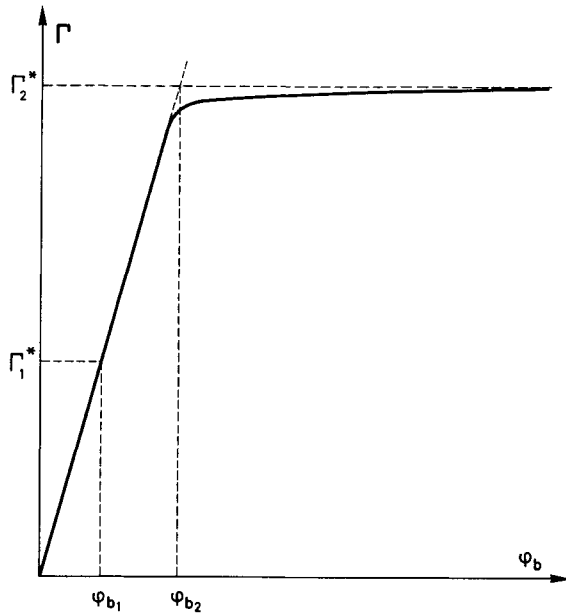

Fig. 1. — The surface coverage Γ as a function of the bulk concentration φ_b. The various regimes are discussed in the text.

$$\frac{\varphi_{b1}}{\varphi_b^*} = \left(\frac{\delta}{\delta_c} \right)^{1/2} e^{-(\delta/\delta_c)^{5/3}} ;$$

$$\frac{\varphi_{b2}}{\varphi_b^*} = \left(\frac{\delta}{\delta_c} \right)^{4/3} e^{-(\delta/\delta_c)^{5/3}}$$

teristic dimensions may be obtained by scaling arguments. The longitudinal distances may be written in the following scaled form :

$$R_\parallel, \xi_\parallel \sim N^{3/4} \delta^{1/4} f_{R,\xi} \left(\frac{\Gamma}{\Gamma_1^*} \right) \qquad (18)$$

$$R_\perp \sim Dg (\Gamma/\Gamma_1^*) . \qquad (18')$$

In the semi-dilute range, we require that the radius behaves [14] as $N^{1/2}$ and that the screening length $\xi_\parallel$ is independent of N. Assuming power law behaviours for f_R and f_ξ, we get :

$$R_\parallel \sim N^{1/2} \Gamma^{-1/2} a \quad (\Gamma \gg \Gamma_1^*) \qquad (19a)$$

$$\xi_\parallel \sim \Gamma^{-3/2} \delta^{-1/2} a \qquad (19b)$$

Similarly

$$R_\perp \sim N^{3/5} (\Gamma/\delta^{1/3})^{6/5} . \qquad (19')$$

The $N^{3/5}$ dependence of $R_\perp$ is related to the progressive appearance of larger loops. The existence of such loops with size larger than D is due to the steric hindrance of the chains which squeeze each other on the wall. When fully developed, in regime (3), they correspond to de Gennes' large loops [16]. They imply a concentration profile with a *central* region, to be discussed in regime (3), which extends to $R_\perp$, and falls off exponentially at larger distances.

Comparing equations (3) and (19b), we find that $\xi_\parallel$ is larger than D as long as $\Gamma \ll \Gamma_2^* \sim \delta^{1/3}$. Thus, in the concentration range $\Gamma_1^* \ll \Gamma \ll \Gamma_2^*$ the adsorbed chains are in a two dimensional semi-dilute regime. We now evaluate the repulsive energy due to the excluded volume interaction in this semi-dilute range. If we define surface blobs with longitudinal size $\xi_\parallel$, we know that these blobs are in contact with each other and from previous work on semi-dilute solutions [11, 28], that every blob has a contribution of the order of kT to the interaction energy. Thus, the repulsive energy per chain is proportional to the number $N/g_\parallel$ of blobs, where $g_\parallel$ is the number of monomers per blob. Assuming a single chain behaviour for a blob and taking relation (7) into account, we have

$$\xi_\parallel \sim g_\parallel^{3/4} \delta^{1/4} a . \qquad (20)$$

Comparing (19b) and (20) leads to $g_\parallel$ and therefore to the repulsive interaction energy per chain

$$\frac{F_{rep}}{kT} \sim \frac{N}{g_\parallel} \sim N\Gamma^2 \delta . \qquad (21)$$

We compare this contribution to the confinement entropy in equation (13)

$$\frac{F_{conf}}{kT} \sim N \left(\frac{a}{D} \right)^{5/3} . \qquad (21a)$$

From (21) and (21a) we get

$$\frac{F_{rep}}{F_{conf}} \sim \Gamma^2 \delta^{-2/3} . \qquad (22)$$

Thus, as long as the surface fraction Γ is smaller than $\Gamma_2^* \sim \delta^{1/3}$, the repulsive energy may be neglected with respect to the confinement energy. This implies that in the semi-dilute two dimensional surface

regime $\Gamma_2^* \gg \Gamma \gg \Gamma_1^*$, the surface coverage is still given by relation (16) and has the same variation as in the dilute surface regime of last subsection. Finally we note that the cross-over concentration Γ_2^* corresponds to a bulk concentration

$$\varphi_{b2} \sim \delta^{4/3} e^{-N\delta^{5/3}} . \tag{23}$$

2.2.3 The plateau regime.

— As discussed in the previous section, we expect two changes to occur simultaneously when Γ becomes of the same order as Γ_2^* :

i) The repulsive part in the free energy, equation (21) can no longer be neglected. All the contributions, namely confinement, surface (Eq. (13)) and repulsive, are comparable. This leads to the « plateau » in the isotherm.

ii) $\xi_\parallel$ is of the same order of magnitude as D. Thus, for larger bulk volume fractions, $\varphi_b > \varphi_{b2}$, we expect a local three-dimensional behaviour for distances smaller than D. Taking into account equations (13) and (21), when the bulk concentration is larger than the cross-over value φ_{b2}, the free energy per chain is :

$$\frac{F}{kT} = \frac{F_{trans}}{kT} + N \left(\frac{a}{D} \right)^{5/3} - N\delta^{5/3} + N\Gamma^2 \delta . \tag{24}$$

This leads to

$$\Gamma \sim \delta^{1/3} . \tag{25}$$

This corresponds to the plateau regime where the surface coverage Γ is independent of the bulk concentration. Note that although the surface is saturated, the bulk solution is still dilute : $\varphi_b \ll \varphi_b^*$. This is region (3) in figure 3. We may calculate the corrections to the constant value for Γ in equation (25) by equating the bulk chemical potential, equation (15) to the surface chemical potential, equation (15) to the surface chemical potential μ_s. From (24) we get

$$\mu_s = \ln \left(\frac{\Gamma a}{ND} \right) - N\delta^{5/3} + N\Gamma^2 \delta .$$

Assuming $\Gamma = \delta^{1/3}(1 + \varepsilon)$ with $\varepsilon \ll 1$, we find

$$\Gamma = \delta^{1/3} \left[1 + \frac{1}{N\delta^{5/3}} \ln \left(\varphi_b \delta^{-4/3} \right) \right] . \tag{26}$$

Thus there is a small negative logarithmic correction to the plateau value, $\Gamma \sim \delta^{1/3}$, which cancels for a bulk concentration $\tilde{\varphi}_b \sim \delta^{4/3}$.

In this section, we showed that when the surface is attractive enough, the surface may be semi-dilute while bulk solution is still dilute. While the excluded volume interaction may be neglected for small surface coverage, for larger values of Γ, $\Gamma \gg \Gamma_2^*$, its contribution to the free energy becomes comparable to the attractive part due to the surface interaction.

This leads to a surface coverage Γ which is nearly independent of the bulk volume fraction φ_b.

For $\Gamma \sim \delta^{1/3}$, the concentration profile extends to $R_F \sim N^{3/5}$, as shown by relation (19'). It includes, in addition to the proximal region $z \ll D$ discussed above, where

$$\phi(z) \sim \phi_s \left(\frac{z}{a} \right)^{1/3} \tag{9}$$

a central region, $D \ll z \ll R_F$, where the polymers behave in a semidilute solution. The presence of the adsorbing wall implies that $\phi(z)$ adjusts to a value such that the local screening length is identical to the distance z from the wall [8, 14].

$$\phi(z) \sim (z/a)^{-4/3} . \tag{9'}$$

Note that $\phi(z = R_F) \sim N^{-4/5} \sim \phi_b^*$, consistent with the behaviour in the central region. (ϕ_b^* is the bulk overlap volume fraction). It is very important to realize that the polymers extend to distances of the same order the Flory radius R_F, even for strong adsorption, $\delta \sim 1$, because of the presence of very large loops, as pointed out by de Gennes [16]. Let us also stress that there are about N monomers both in the proximal and in the central regions. These results are summarized in figure 2.
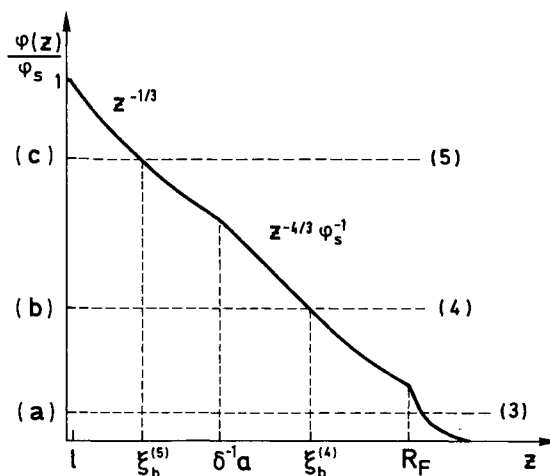

Fig. 2. — The volume fraction profile $\varphi(z)$ for the various regimes, in the direction z orthogonal to the surface. Dashed lines correspond to

a) regime (3)

b) regime (4) $(\varphi_b^* < \varphi_b < \tilde{\varphi}_b)$

c) (5) is regime SDNA $\varphi_b > \tilde{\varphi}_b$ of figure 3.

In regimes (1) and (2) the profile extends only until $R_\perp$, and decays exponentially above.

These equations however correspond to for a single chain profile. Any measurement corresponds rather to an averaging over the entire surface. Let $\varphi(z)$ be this average. In order to relate $\varphi(z)$ to the single chain profile $\Phi(z)$, it is important to stress the

difference between regimes (1) and (2) and regime (3). If one defines an adsorption blob with size D, the surface is covered with such blobs in the plateau regime (3), whereas it is not saturated in regimes (1) and (2). This leads to (see appendix A) :

$$\varphi(z) = \Gamma\delta^{-1/3}\,\Phi(z) \quad \text{[regimes 1 and 2]} \qquad (27a)$$
$$\varphi(z) = \Phi(z) \qquad \qquad \text{[regime 3]} \qquad (27b)$$

where $\Gamma\delta^{-1/3}$ is the fraction of adsorption blobs on the surface. The adsorption isotherm $\Gamma(\varphi_b)$ and the volume fraction profile $\varphi(z)$ are plotted in figures 1 and 2 respectively.

The semi-dilute regimes.

We consider now solutions with bulk concentration φ_b larger than the overlap concentration $\varphi_b^* \sim N^{-4/5}$. The concentration profile has already been studied in this regime by Eisenriegler [4] and by de Gennes and Pincus [9]. Because the bulk solution is semi-dilute, there is a screening length [17] :

$$\xi_b \sim \varphi_b^{-3/4}\,a\,. \qquad (28)$$

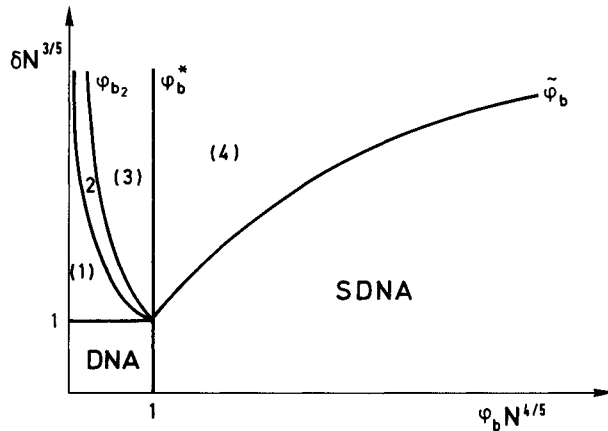This is region (4) in the phase diagram of figure 3.

Fig. 3. — The phase diagram in reduced coordinates δ/δ_c versus $\dfrac{\varphi_b}{\varphi_b^*}$.

The different regions are as follows : (1) and (2) are dilute (see text for the difference). (3) is the plateau region. (4) is bulk semi-dilute, SDNA corresponds to a non adsorbed semi-dilute. DNA is the dilute non adsorbed regime.

In the *proximal* region, the profile is unchanged. This is because as noted in previous sections, the vicinity of the surface is saturated. Thus we have

$$\varphi(z) \sim \delta\left(\frac{a}{z}\right)^{1/3} \quad (a \ll z \ll D)\,. \qquad (29a)$$

In the *central* region, self similarity still implies the same law as in previous section as long as the local screening length is smaller than ξ_b

$$\varphi(z) \sim \left(\frac{a}{z}\right)^{4/3} \quad (D \ll z \ll \xi_b)\,. \qquad (29b)$$

For still larger distances, the effect of the surface is screened out by bulk concentration, as discussed by Eisenriegler [4]

$$\varphi(z) = \varphi_b \quad (z \gg \xi_b)\,. \qquad (29c)$$

Note however that these relations cannot be extrapolated to the melt case. Then $\varphi(z) = 1$ for all values of z. In fact, we find that the adsorbed regime exists only as long as the central region discussed above exists. There is a cross-over to a non adsorbed regime when $D \sim \xi_b$. Using relations (3) and (28) we find this cross over to occur for bulk concentration

$$\tilde{\varphi}_b \sim \delta^{4/3}\,. \qquad (30)$$

A direct way to show this is to compare the adsorption energy per blob and thermal energy for $\varphi_b \sim \tilde{\varphi}_b$:

$$\frac{F_a}{kT} \sim g_b^\varphi\,\delta \sim 1$$

where g_b is related to ξ_b, relation (28), by the usual relation [11, 28]

$$\xi_b \sim g_b^\nu\,a\,.$$

Combining these two relations gives relation (30).

For higher bulk concentrations, $\varphi_b \gg \tilde{\varphi}_b$, the surface is not attractive enough for the blobs to be adsorbed. Note however that there is still a concentration profile for $z \ll \xi_b$:

$$\varphi(z) \sim \varphi_b^{3/4}\left(\frac{a}{z}\right)^{1/3} \quad a \ll z \ll \xi_b\,. \qquad (31)$$

where the prefactor $\varphi_s = \varphi_b^{3/4}$ is obtained by generalizing relation (10) to a blob :

$$\varphi_s \sim g_b^{\varphi-2\nu} \sim g_b^{-3/5}$$
$$\sim \varphi_b^{3/4}\,. \qquad (31a)$$

This is reminiscent of region DNA of figure 3 for a single chain, where although the polymer is not adsorbed, there is also a profile.

In the concentrated range $\varphi_b > \tilde{\varphi}_b$ of region SDNA of figure 3, the surface may be called neutral. For such small values of δ, even if the surface were repulsive instead of attractive, it would still be completely saturated with concentration blobs. In many respects, this region SDNA is reminiscent of a theta regime in bulk concentrated solutions [27, 28].

4. The surface tension.

The different regimes discussed above are summarized in figure 3. Note that the lines in this figure correspond to cross-over rather than to sharp transitions. An important property of adsorbed polymers is to lower the surface tension γ_0 of the solute. Let γ be the surface tension of the solution. From general considerations [1], one may write

$$d\gamma = \delta\gamma_1 + \delta\gamma_2 \qquad (32)$$

$$\delta\gamma_1 = (dW^\sigma - S^\sigma dT) \qquad (32a)$$

$$\delta\gamma_2 = -\sum n_i^\sigma d\mu_i \qquad (32b)$$

where γ_1 is a free energy per unit area. From the last term, one gets the Gibbs relation [1]

$$\left(\frac{\partial\gamma}{\partial\mu_i} \right)_{T, S, \mu_j} = -n_i^\sigma$$

where μ_i and n_i^σ are the chemical potential and the number of molecules per unit area of species i. With the notation used previously, the last equation is

$$\frac{\partial\gamma}{\partial\mu} = -\Gamma \qquad (33)$$

where μ is the monomer chemical potential.

Let us first consider the dilute regimes.

1. In regimes (1) and (2) [see Fig. 3], the free energy per unit surface is

$$\gamma_1 = -kT\delta\varphi_s a^{-2} . \qquad (34)$$

Combining (11), (16) and (34) we get

$$\gamma_1 a^2 \sim -\varphi_b \delta^{2/3} e^{N\delta^{5/3}} \sim -\Gamma\delta^{5/3} . \qquad (35)$$

In both regimes, the bulk solution is dilute. Thus we have

$$\mu = \text{Const.} + \frac{kT}{N} \ln \left(\frac{\varphi_b}{N} \right) . \qquad (36)$$

Combining (33) and (36), we get

$$\gamma_2 = \gamma_0 - \frac{kT}{N} \Gamma a^{-2} \qquad (37)$$

and, from (32), (34) and (37), we obtain

$$(\gamma - \gamma_0) \frac{a^2}{kT} \simeq -\Gamma\delta^{5/3} - \frac{\Gamma}{N} . \qquad (38a)$$

In the adsorption regime, $\delta \gg N^{-3/5}$ and the second term may be neglected :

$$(\gamma - \gamma_0) \frac{a^2}{kT} \approx -\Gamma\delta^{5/3} . \qquad \cdot (38b)$$

Note that because of equations (16) and (23), the corresponding drop in surface tension may be important, due to the exponential prefactor.

2. In the *plateau* regime, we saw that the surface free energy is kT per adsorption blob :

$$\frac{\gamma_1}{kT} \sim -D^{-2} \sim -\delta^2 a^{-2} . \qquad (39)$$

Gibbs relation (33), together with equation (15) for the *polymer* chemical potential, gives

$$\frac{d\gamma_2}{d\varphi_b} \sim -\frac{kT}{N} \frac{\delta^{1/3}}{\varphi_b} a^{-2} \qquad (40)$$

and thus we obtain

$$\frac{\gamma - \gamma_0}{kT} a^2 \sim -\delta^2 - \frac{\delta^{1/3}}{N} \ln \left(\frac{\varphi_b}{\varphi_{b2}} \right) \qquad (41)$$

where the constant $(\ln \varphi_{b2})$ term comes from the matching of surface tensions in the plateau and in regime (2) on the cross-over line $\varphi_b = \varphi_{b2}$.

3. The *bulk semi-dilute regime*, $\varphi_b^* \ll \varphi_b \ll \tilde{\varphi}_b$ was considered by de Gennes and Pincus [9]. In this regime the monomer chemical potential is

$$\mu_b \sim kT\varphi_b^{5/4} . \qquad (42)$$

This leads to

$$\frac{\gamma - \gamma_0}{kT} a^2 = -\delta^2 \left[1 - \frac{1}{N\delta^{5/3}} \ln (N\delta^{5/3}) \right] - \\ - \delta^{1/3} \varphi_b^{5/4} \qquad (43)$$

where we used Gibbs relation (33) and where we matched equations (43) and (41) at $\varphi_b \sim \varphi_b^*$ to get the constants.

Neglecting the logarithmic corrections give the de Gennes-Pincus [9] result

$$\frac{\gamma - \gamma_0}{kT} a^2 = -\delta^2 - \delta^{1/3} \varphi_b^{5/4} . \qquad (44)$$

4. In the *concentrated* range $\varphi_b > \tilde{\varphi}_b$, the concentration profile extends until ξ_b : only the surface blobs are perturbed. Because of this, the surface coverage is

$$\Gamma a \sim \int_0^{\xi_b} \varphi(z) \, dz \simeq \varphi_b^{1/4} a \qquad (45)$$

where we used equation (31) for $\varphi(z)$.

Using the Gibbs relation (33), we get

$$(\gamma - \gamma_0) \frac{a^2}{kT} \sim -\varphi_b^{3/2} \qquad (46)$$

where we used relation (42) for the monomer chemical potential. Note that the free energy contribution γ_1 to the surface tension is similar to (46). In

this concentrated regime, the main contribution to γ_1 is the repulsive energy

$$\gamma_1 a^2 \sim \int_0^{\xi_b} dz \; \varphi (z)^{9/4}$$

$$\sim kT\varphi_b^{3/2}$$

where $kT\varphi (z)^{9/4}$ is the local repulsive energy per unit volume [11] at a distance z from the wall. We note a weakness in relation (46) which does not extrapolate γ to γ_p for $\varphi_b \sim 1$: for very high volume fractions, scaling breaks down. Figure 4 summarizes the dependence of the interfacial tension with bulk volume fraction.
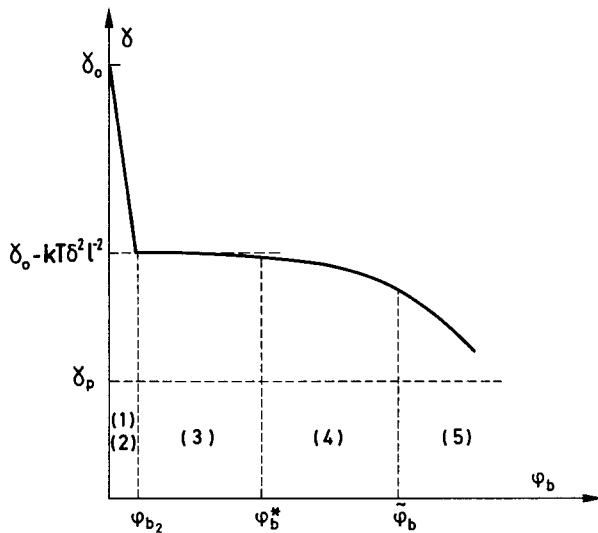

Fig. 4. — The surface tension as a function of concentration.

5. Conclusion.

We considered the adsorption of flexible polymer chains from a solution on a flat impenetrable surface. Different regimes appear when the bulk concentration is increased. They are summarized in figure 3 and are as follows :

i) In regimes (1) and (2), corresponding to very dilute bulk solutions, excluded volume effects between different polymers may be neglected. In both regimes, the chains are quasi two-dimensional. The surface coverage Γ is proportional to the bulk concentration with an exponential Bolzmann prefactor with argument $\delta N^{3/5}$, where N is the number of units of the polymer and δ the attractive energy per monomer on the surface. For large values of this argument the surface coverage may be large even if

the bulk is dilute : regime (1) is dilute, with longitudinal radius of a chain

$$R_{\parallel} \sim N^{3/4}\,\delta^{1/4}\,a$$

whereas regime (2) is semi-dilute, with

$$R_{\parallel} \sim N^{1/2}\,\Gamma^{-1/2}\,a$$

and

$$\xi_{\parallel} \sim \Gamma^{-3/2}\,\delta^{-1/2}\,a\;.$$

In both regimes, there are two characteristic normal distances

— the radius $R_{\perp} \sim \begin{cases} \delta^{-1}\,a \text{ regime (1)} \\ N^{3/5}(\Gamma/\delta^{1/3})^{6/5} \text{ regime (2)} \end{cases}$

— the thickness of the adsorbed layer

$$D \sim \delta^{-1}\,a\;.$$

ii) For bulk concentrations $\varphi_b \sim \varphi_{b2} \sim \delta^{4/3}\,e^{-N\delta^{5/3}}$, the excluded volume interaction has a contribution to the free energy of a chain similar to the attractive part by the wall, or to the confinement entropy. This corresponds to regime (3) in figure 3, which is the plateau, and where the surface coverage increases only logarithmically with bulk volume fraction φ_b, instead of linearly in regimes (1) and (2).

Whereas the surface tension drops linearly with φ_b in regimes (1) and (2), it is almost constant in the plateau regime. This region is the most interesting experimentally because :

a) there is a large difference between the bulk, which is dilute ($\varphi_b \ll \varphi_b^*$) and the surface, which is semi-dilute.

b) The concentration profile $\varphi (z)$ extends the farthest, i.e. until the radius R_F of the polymer.

iii) In the bulk semi-dilute range, $\varphi_b^* \ll \varphi_b \ll \tilde{\varphi}_b$ where $\varphi_b^* \sim N^{-4/5}$ is the overlap concentration and $\tilde{\varphi}_b \sim \delta^{4/3}$ is the bulk absorption concentration, the concentration profile $\varphi (z)$ extends until bulk correlation length $\xi_b \sim \varphi_b^{-3/4}\,a$. Although the surface coverage is basically constant, the surface tension has a concentration dependence because of the distortion of the concentration profile near the surface.

iv) In the concentrated range, $\varphi_b \gg \tilde{\varphi}_b$, the blobs do not adsorb on the surface. The adsorption energy per blob is smaller than the thermal energy. Although there is still a profile for distances $z < \xi_b$, this regime is basically similar to the melt. The surface here may be called neutral. Even for a repulsive energy of similar magnitude, the profile would be the same.

Although regimes (1) and (2) are very difficult to observe experimentally, there is a substantial drop of surface tension in these regimes. The very exist-

ence of these regimes implies that there is no abrupt (first order) phase transition for large but finite polymers. An important consequence of the smallness of φ_{b2} concerns the experimental procedure : usually, with solid surfaces, the adsorption is made with a rather concentrated solution which is subsequently washed and replaced by pure solvent. Because φ_{b2} is so small, we argue that very few polymers will be desorbed after such dilution, and thus the concentration profile will be basically unchanged, the surface being in equilibrium with an extremely dilute bulk solution.

The plateau regime (3) is the most interesting experimentally, because it provides the most substantial difference between surface and bulk. It is possible to measure these profiles with neutrons [23-25]. Finally, we stress that we discussed equilibrium properties. These are usually rather long to reach [18-22], with equilibration times of order day. A special difficulty concerns those polymers which are glassy at room temperature. Because the surface fraction is high, the superficial layer may be in a glassy state [26], implying prohibitively long equilibration times.

We end by noting that although practical uses of adsorption imply a rather large value of δ ($\delta \gtrsim 1$), the present work is relevant because of the analogy with semi-infinite magnetic systems close to a phase transition. Polymer solutions close to an interface are the only system known so far where δ may be either positive (adsorption) or negative (depletion). Thus, one may study here both sides of the special transition.

Actually this is almost possible for polymers at the interface between a solution and air, where the « adsorption temperature » T_A is within easy experimental conditions [29]. For such systems, our variable δ is just proportional to the reduced temperature difference $(T_A - T)/T_A$. Note however that, in the same way as for the theta temperature, T_A is defined in the limit of very long chains, $N \to \infty$. For large but finite polymers, we only expect smooth cross-overs, as discussed above.

Appendix A

It was shown [9] that the average number of monomers, per unit area, over a surface D^2 is $a^{-2} \varphi(z)$ with $\varphi(z)$ given by equations (9) to (12).

If we consider that the adsorption blobs form a self avoiding walk on the surface, the correlation function for a single chain is

$$g(z, \rho) = \varphi(z) \left(\frac{D}{\rho} \right)^{2/3} \quad (\rho \gg D) \quad (A.1)$$

where ρ is the parallel distance in the wall.

In the dilute regime (2.2.1), the concentration profile $\varphi(z)$ is merely the product of the single chain contribution

$$\int^{R_\parallel} g(z, \rho) \rho \, d\rho \sim N \delta^{-1/3} \Phi(z) \quad (A.2)$$

and the local chain concentration in the vicinity of the surface, $\left(\frac{\varphi_b}{N} \left(\frac{D}{a} \right) e^{N \delta^{5/3}} \right)$. We find :

$$\varphi(z) = \varphi_b \, \delta^{-4/3} e^{N \delta^{5/3}} \Phi(z) . \quad (A.3)$$

In the semi-dilute regime (2.2.2), the concentration profile is the average of the correlation function over a surface $\xi_\parallel^2$

$$\varphi(z) = \frac{1}{\xi_\parallel^2} \int^{\xi_\parallel} \rho g(z, \rho) \, d\rho$$

$$\sim \Gamma \delta^{-1/3} \Phi(z) . \quad (A.4)$$

Both (A.3) and (A.4) are equivalent to (27).

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