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## SCALING THEORY OF POLYMER ADSORPTION

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**Résumé.** — On discute les propriétés d'équilibre de chaînes flexibles adsorbées sur une surface plane, en supposant que *a*) l'adsorption est faible (d'où des épaisseurs de couche adsorbées  $D$  relativement grandes), *b*) les chaînes sont longues, *c*) le solvant est bon, d'où des effets de volume exclu qui s'avèrent importants, contrairement à une opinion ancienne de Hovee.

Les répulsions entre monocouches sont incorporées ici dans des lois d'échelle qui vont plus loin que les théories habituelles de champ moyen (Flory-Huggins). On trouve trois régimes :

(i) Dans la limite diluée (chaînes séparées)  $D$  est indépendant de l'indice de polymérisation  $N$ , et varie comme  $\delta^{-3/2}$  (où  $\delta$  mesure la force de l'attraction effective vers la surface). Avec l'approximation de champ moyen, on aurait  $D \sim \delta^{-1}$ .

(ii) Il existe un régime semi-dilué où les pelotes commencent à se recouvrir.

(iii) Le cas principal correspond au plateau de l'isotherme d'adsorption. On montre que dans ce cas les corrélations locales dans la couche adsorbée sont analogues à celle d'une solution tridimensionnelle. L'épaisseur  $D$  varie comme  $N\delta(\ln c_B)^{-1}$  où  $c_B$  est la concentration de la solution en volume. La dépendance prévue pour  $D(N)$  est plus forte que en champ moyen (où  $D \sim N^{1/2}$ ) mais pas incompatible avec certaines données expérimentales.

**Abstract.** — We discuss the equilibrium properties of flexible chains adsorbed on a flat surface, assuming that *a*) adsorption is weak, resulting in large thicknesses  $D$  for the adsorption layer, *b*) the chains are very long, *c*) the solvent is good, so that excluded volume effects become important (contrary to an early opinion of Hovee).

The repulsion between monomers are incorporated through a scaling theory which goes beyond the usual mean field (Flory-Huggins) approximations. The central assumption is that polymer concentrations in the first layer and in the next layers scale in the same way, (although they do differ by a constant factor). We can then predict the surface exponents of interest in terms of standard exponents for self avoiding walks ; for the latter we use the Flory values.

One then finds three regimes of adsorption :

(i) In the *dilute* limit (separate coils)  $D$  is independent of the polymerization index  $N$ , and varies with the strength of the effective monomer surface attraction (measured by a small parameter  $\delta$ ) according to  $D \sim \delta^{-3/2}$  instead of  $D \sim \delta^{-1}$  in mean field.

(ii) There is a semi dilute regime where the coils begin to overlap, but where  $D$  remains essentially the same.

(iii) The most important case corresponds to the *plateau* in the adsorption isotherm : here we show that the correlations inside the layer are similar to those in a three dimensional system. Then  $D \sim N\delta(\ln c_B)^{-1}$  where  $c_B$  is the bulk concentration. The dependence on  $N$  is stronger than in mean field ( $D \sim N^{1/2}$ ) but not incompatible with existing data.

**1. Introduction.** — 1.1 EXPERIMENTAL BACKGROUND. — Polymer adsorption at a solid liquid interface is of considerable practical interest for various surface treatments, for stabilization of colloids, and for chromatography. It is also an important effect for certain flows inside porous rocks (and in particular for oil recuperation).

In spite of this interest, and of a vast body of exper-

imental literature [1], the processes involved are only poorly understood. Most usually what is measured is an adsorption isotherm ; this reveals the adsorbed chain conformations only indirectly (through dependences on the molecular weight  $M$ ).

More local information is obtained from ellipsometry [2] and from the *hydrodynamic barrier thickness* measured in porous structures or on polymers

adsorbed on colloidal particles [3]. Usually these data are taken mainly on the plateau of the isotherm — i.e. when a certain competition between surface attraction and steric repulsion between monomers has established a saturated surface concentration  $\Gamma$ . Then the thickness  $D$  of the adsorbed layer is often found to be an increasing function of  $M$  (or of the polymerisation index  $N$ ), varying for instance like  $M^a$  where  $a \sim 0.5$  in  $\Theta$  solvents, and  $a$  can be even larger in good solvents [4].

A significant theoretical effort has been devoted to this problem. Unfortunately many of the papers involve a significant amount of mathematical formalism, which masks their real content. We shall first present a simplified version of these theories in the next paragraphs; their essential common feature is their dependence on certain mean field (or self consistent field) arguments. We shall then show in section 2 that the deviations from mean field are important for this problem, and that they lead to somewhat different power laws.

1.2 ADSORPTION OF IDEAL CHAINS [5a]. — This is the simplest problem on the theoretical side, and it has been treated very early. The results are the following :

a) There is a well defined threshold — (in interaction strength at fixed temperature, or in  $(\text{temperature})^{-1}$  at fixed interactions) below which no adsorption takes place. For instance, in the notation of Hoeve [7] we may define a number  $\sigma$  as the ratio of the statistical weight for one monomer in the chain on the first contact layer, to the weight for one monomer in a chain floating in the bulk. Low temperatures or high surface attractions increase  $\sigma$ . Estimates of  $\sigma$  for specific lattice models can be found in ref. [5, 6, 8]. The threshold corresponds to  $\sigma = 1$ .

b) The region of main theoretical interest corresponds to  $\sigma = 1 + \delta$  where  $\delta$  is positive and small. This defines what we shall call the *weak adsorption regime* where the chain is expected to adhere at the surface by a small fraction of its monomers (Fig. 1). This is the region where the adsorption thickness  $D$  is large when compared to the monomer size  $a$ , and where a universal description is feasible. These universality features were emphasized in ref. [9] together with various analogies :

(i) The similarity between the adsorption problem and natural DNA denaturation was already noticed by many authors [7].

(ii) More profoundly, what we are dealing with in both cases is the appearance of a *bound state* in a certain equation of the Schrödinger type [9] : this bound state can be treated quite generally by a scattering length approach familiar in low energy scattering of quantum particles [10].

c) For any (small but positive)  $\delta$  (i.e. beyond threshold) the thickness  $D$  is *independent of  $N$* . This can be understood as follows : for a single ideal chain

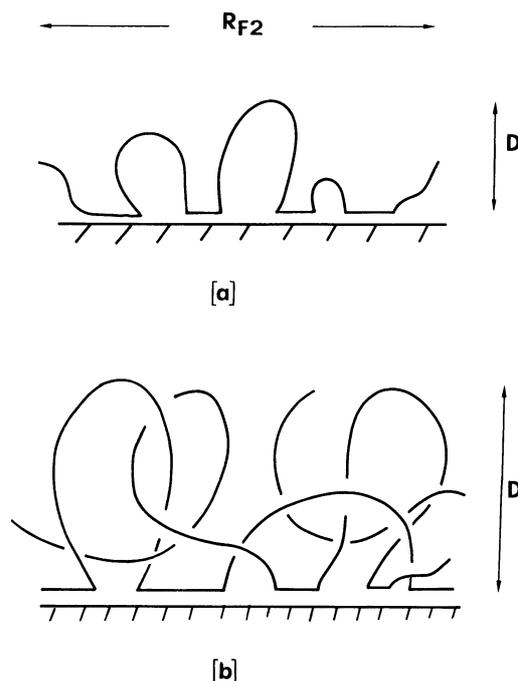


FIG. 1. — Polymer chains weakly adsorbed on a flat surface : a) The single chain case : for large molecular mass  $M$  the thickness  $D$  is independent of  $M$ . b) The many chain case : repulsion between monomers counteract the surface attraction. The layer thickness is now larger and  $M$  dependent.

confined in a thickness  $D$  the chemical potential (divided by  $k_B T$ ) has the following form

$$\mu \cong \mu_0 + \frac{Na^2}{D^2} - \delta \frac{aN}{D} + \mu_{\text{translation}} \quad (1.1)$$

where  $\mu_0$  is the potential for a free chain with a fixed center of gravity; The second term is due to the loss of entropy resulting from confinement :  $Na^2 = R_0^2$  is the ideal mean square radius and we assume  $D < R_0$ . The precise coefficient can be found in ref. [11] but here we purposely ignore all coefficients. The third term in eq. (1.1) states that of the  $N$  monomers only a fraction  $a/D$  is in the first layer and benefits from the effective attraction measured by  $\delta$ . Finally

$$\mu_{\text{trans.}} = \ln(\Gamma/N) + \text{Const.},$$

is the standard term for a dilute two dimensional gas of coils (with concentration  $\Gamma/N$ ). Optimizing (1.1) with respect to  $D$  one finds (always ignoring coefficients)

$$D_{\text{single chain}} \cong a\delta^{-1}. \quad (1.2)$$

Thus  $D$  is large (for small  $\delta$ ) and independent of  $N$ . This independence is at variance with most experimental results : clearly the one chain picture is not sufficient.

1.3 REAL CHAINS IN A GOOD SOLVENT : FLORY HUGGINS APPROXIMATION [7, 8]. — Here we have a repulsion interaction between monomers, and as

soon as the surface concentration  $\Gamma$  is finite, there is competition between this repulsion and the monomer-surface attraction. In the spirit of a mean field theory we may now write

$$\mu = \mu_0 + \frac{Na^2}{D^2} - \frac{\delta aN}{D} + Nv \frac{\Gamma}{D} + \mu_{\text{trans.}} \quad (1.3)$$

where the *excluded volume parameter*  $v$  is related to the celebrated Flory parameters [12] by

$$v = a^3(1 - 2\chi) \quad (1.4)$$

In what follows we shall mainly consider the case  $\chi = 0$  (good solvent limit). The basic reason is that changes in the solvent react simultaneously on *two* parameters ( $v$  and the adsorption strength  $\sigma$ ): thus data on solvent effects appear too complex to be unraveled at present.

The term  $Nv\Gamma/D$  in eq. (1.3) expresses that each monomer sees a repulsive potential proportional to the local concentration  $c$  (monomer/cm<sup>3</sup>). This is related to the surface concentration  $\Gamma$  (monomers/cm<sup>2</sup>) by

$$\Gamma = cD \quad (1.5)$$

from which the form (1.3) results.

Minimizing (1.3) with respect to  $D$  we get (always ignoring coefficients)

$$\frac{a}{D} \cong \delta - \gamma \quad (1.6)$$

where  $\gamma = \Gamma a^2$  is a dimensionless surface concentration. The chemical potential is

$$\mu = \mu_0 + \mu_{\text{trans.}} - N(\delta - \gamma)^2 \quad (1.7)$$

Equating this to the chemical potential  $\mu_B$  of a bulk solution (concentration  $c_B$ )

$$\mu_B \cong \ln(c_B/N) \quad (1.8)$$

we obtain the isotherm in the form

$$\gamma \cong \delta - N^{-1/2}[\ln(\gamma/c_B a^3)]^{1/2} \quad (1.9)$$

This gives a plot  $\gamma(c_B)$  with a high initial slope, followed by a flat plateau where the  $\ln$  factor is not very large, and where  $\gamma$  becomes close to  $\delta$ . Another essential result concerns the thickness  $D$ : comparing (1.6) and (1.9) we have

$$D_{\text{plateau}} \sim aN^{1/2}[\ln(\gamma/c_B a^3)]^{-1/2} \quad (1.10)$$

Thus (apart from numerical factors of order unity) the adsorption layer is found here to be comparable to the ideal coil size.  $D_{\text{plateau}}$  is larger than  $D_{\text{single chain}}$ . The *plateau* corresponds to a nearly exact cancellation between attractive forces (towards the surface) and repulsive forces (due to monomer interaction):

the overall attraction is very small and this is the source of the large thickness  $D$ .

Qualitatively the result (1.10) is in reasonable agreement with some of the experiments [3-4] and it has thus been accepted as being basically correct. However, a closer examination of the data reveals that the dependence of  $D$  on  $N$  can differ widely from an  $N^{1/2}$  law. In another direction, it has been recognized recently (through neutron experiments, and through rigorous theoretical analysis) that bulk polymer solutions show qualitative deviations from the Flory-Huggins theory [13-15]: there are delicate (concentration dependent) correlations between monomers which allow them to avoid each other and modify the power laws for the osmotic pressure  $\pi(c)$ , etc. In three dimensions, for *semi dilute* solutions,  $\pi(c) \sim c^{2.25}$  instead of  $\pi(c) \sim c^2$  as expected from the Flory-Huggins approach. In two dimensional systems, the deviations from mean field theory are still much more drastic. Recently, we have discussed the behaviour of chains, confined in slits or capillaries, from the point of view of scaling laws [16]. In ref. [16] we had restricted our attention to non adsorbing walls. The present paper represents an extension of this discussion to the case of one single adsorbing wall. As we shall see, the power laws for adsorption which emerge from the scaling analysis are rather different from those of the mean field theory. The relation with more general scaling theories is described finally in an appendix.

2. Scaling theory in the weak adsorption regime. —

2.1 THE SINGLE CHAIN PROBLEM. — Let us consider one flexible chain, weakly adsorbed as in figure 1, and confined to a layer of thickness  $D$  much smaller than its natural size  $R_F$  in the bulk solution. The free energy (in units of  $k_B T$ ) for such a chain has the following form (to be explained below)

$$\mu - \mu_0 = N \left( \frac{a}{D} \right)^{5/3} - \delta \frac{aN}{D} + \mu_{\text{trans.}} \quad (2.1)$$

(a) The first term on the r.h.s. of eq. (2.1) represents the work which is necessary to confine a self excluded chain in a slit of thickness  $D$ , and has been discussed in ref. [16]. The reader may also rederive directly the form of this term if he imposes that it be simultaneously

- (i) a function of  $R_F/D$  only (where  $R_F \cong aN^{3/5}$  is the Flory radius in a good solvent).
- (ii) an extensive function of  $N$  (as it clearly should be from figure 1).

Note the difference between this confinement energy (proportional to  $D^{-5/3}$ ) and the confinement energy of the conventional theory (the second term in eq. (1.1)) — proportional to  $D^{-2}$ .

(b) The second term on the r.h.s. of (2.1) represents the attraction energy towards the surface and retains

the structure which it had in eq. (1.1). Near the adsorption threshold, the density profile varies smoothly in the thickness  $D$ , and has but a finite jump in the first layer : for these reasons we may still say that the fraction  $p$  of monomers in direct contact with the surface is  $p \sim a/D$ . This leads to the form written.

From a conceptual point of view, however, there is a hidden difference in the second term between the ideal chain situation and the present situation : namely when we restrict ourselves to self avoiding walks, this renormalizes the entropy of both free and adsorbed segments, and the threshold itself is shifted. The quantity  $\delta$  in eq. (2.1) is measured *from the renormalized threshold*.

We emphasize once more that all numerical coefficients in eq. (2.1) are ignored. Proceeding now to minimise (2.1) with respect to  $D$  we find an optimum

$$D_{\text{single chain}} \cong a\delta^{-3/2} \quad (2.2)$$

very strikingly different from the conventional result (1.2). The resulting potential is

$$\mu = \mu_0 - N\delta^{5/2} + \mu_{\text{trans.}} \quad (2.3)$$

and this allows to derive the initial slope of the adsorption isotherm

$$\gamma \cong c_B a^3 \exp(N\delta^{5/2}). \quad (2.4)$$

If in the future a system is found where the vicinity of the threshold can be systematically explored — i.e. where one can vary  $\delta$  by acting on pH, or temperature, or controlled grafting on the surface — then the law (2.4) could become of interest.

Another parameter of interest is the size of the chain measured parallel to the adsorbing surface : this can be taken directly from ref. [16] and is

$$R_{F_2} \cong aN^{3/4} \left(\frac{a}{D}\right)^{1/4} \cong aN^{3/4} \delta^{3/8} \quad (2.5)$$

Finally we should recall that our discussion assumed  $D$  smaller than the coil radius  $R_F$  in bulk solution. We have  $D/R_F \sim \delta^{-3/2} N^{-3/5}$  and we are thus led to the inequality

$$N\delta^{5/2} \equiv K \gg 1. \quad (2.6)$$

**2.2 THE PLATEAU REGIME.** — Let us assume now that many chains are adsorbed, and that they build up a layer of thickness  $D$  — large enough so that the local behaviour inside the layer is similar to the local behavior in a *bulk solution* (of local concentration  $c = \Gamma/D$ ). The chemical potential (per chain, in units of  $k_B T$ ) is then expected to have the form

$$\mu - \mu_0 \cong N \left(\frac{a}{D}\right)^{5/3} - N\delta \frac{a}{D} + N(ca^3)^{1.25} + \mu_{\text{trans.}} \quad (2.7)$$

The novelty is in the third term : as stated earlier the osmotic pressure scales like  $k_B Tc(ca)^{1.25}$  in bulk solutions. The resulting contribution to the chemical potential scales like  $\pi/c$  — hence the result. For our discussion of adsorption, we shall find it more convenient to use the total coverage  $\Gamma$  as our variable, and we shall thus write

$$(ca^3)^{1.25} = \left(\frac{\Gamma a^2}{D}\right)^{1.25} = \left(\frac{\gamma a}{D}\right)^{1.25}. \quad (2.8)$$

It will turn out that in the present regime the first term in the r.h.s. of (2.7) is dominated by the third term : interchain repulsions are more important than the confinement energy. Assuming this for the moment, and minimizing the resulting  $\mu$  at fixed  $\Gamma$ , we find

$$D \cong a \frac{\gamma^5}{\delta^4} \quad (2.9)$$

and

$$\mu - \mu_0 \cong -N \left(\frac{\delta}{\gamma}\right)^5 + \mu_{\text{trans.}} \quad (2.10)$$

Equating this to the chemical potential of the bulk solution (concentration  $c_B$ ) we reach an adsorption isotherm of the form

$$\gamma \cong \delta N^{1/5} l^{-1/5} \quad (2.11)$$

where  $l$  is a short hand notation for the logarithm

$$l = \ln \left( \frac{\gamma}{c_B a^3} \right).$$

The isotherm has a flat *plateau* when  $l$  becomes not much larger than unity (the limits on  $l$  will be discussed later in eq. (2.15)). We have :

$$\gamma_{\text{plateau}} \cong \delta N^{1/5}.$$

This has only a very weak dependence on  $N$ , and is thus not very different from the prediction of the mean field theory. More interesting differences appear if we consider the layer thickness : from eq. (2.9, 11) we have

$$D(c_B) \cong aN\delta l^{-1}. \quad (2.12)$$

Eq. (2.12) is the central result of this paper. In the *plateau* regime where  $l$  behaves essentially as a constant,  $D$  is linear in the molecular mass. Note however that  $D/Na \sim \delta$  is small : the chains are far from being fully stretched. A few comments are appropriate at this point.

a) We treated the interaction energy in the adsorbed layer as if we were dealing with a three dimensional solution. This requires that the three dimensional correlation length  $\xi_3(c)$  be smaller than  $D$ . The scaling form of  $\xi_3$  is [14] :

$$\xi_3 = a(ca^3)^{-3/4} \cong a \left(\frac{D}{\gamma a}\right)^{3/4}. \quad (2.13)$$

Inserting the values ((2.11), (2.12)) for  $\gamma$  and  $D$  we arrive at

$$\frac{\xi_3}{D} \cong \left(\frac{l}{K}\right)^{2/5} \quad (2.14)$$

Thus our analysis holds provided that

$$l \ll K. \quad (2.15)$$

This coincides in fact with the definition of the *plateau* regime. We shall see in a later paragraph that when  $l \sim K$  one expects a different (semi dilute) regime.

b) We neglected the confinement energy in eq. (2.7). Taking the ratio  $x$  between this energy and the overall potential (of order  $\delta \frac{a}{D}$  per monomer) we find

$$x \cong \left(\frac{a}{D}\right)^{2/3-1/4} \gamma^{-5/4} \cong \left(\frac{l}{K}\right)^{2/3} \quad (2.16)$$

Since  $l \ll K$  this ratio is indeed small and the approximation is valid.

c) We already pointed out that the chains are far from being totally stretched outwards. It is of interest to compare the layer thickness  $D$  with the size  $R_F$  of a single coil in the bulk solution. The result is

$$\frac{D}{R_F} \cong K^{2/5} l^{-1} \quad (2.17)$$

At the onset of the *plateau*  $l$  is of order  $K$  and  $D/R_F$  is small. At higher concentrations  $c_B$ ,  $l$  is smaller and  $D$  may become comparable to  $R_{F3}$ .

d) It is also (at least conceptually) interesting to estimate the *lateral size*  $R$  of one coil, in the present regime where different coils are strongly overlapping. From ref. [14, 16] we know that

$$R \cong N^{1/2} a(ca^3)^{-1/8} \cong N^{1/2} a\left(\frac{N}{l}\right)^{1/10} \quad (2.18)$$

In practice the last factor will be very close to unity :  $R$  is very close to the ideal chain size. It may be helpful to note that

$$\frac{R}{D} \cong l^{9/10} K^{-2/5} \quad (2.19)$$

At the onset of the *plateau* regime ( $l \sim K$ ) we have  $R/D \sim K^{1/2} > 1$ . The coils are flat. At higher concentrations  $D$  increases slowly while  $R$  is nearly constant, and the coils are slowly changing from oblate to prolate ellipsoids.

2.3 THE SEMI DILUTE REGIME. — From ref. [16] we know that coils confined in a slit show a third regime in between the dilute limit and the three dimensional limit. A similar *semi dilute* intermediate regime is expected in the adsorption problem. However, as we shall see, the laws for  $\gamma(c_B)$  and  $D(c_B)$  are not

very different from what we have already described in the dilute limit : thus the semi dilute regime will not manifest itself very conspicuously in the experiments, and we shall discuss it only very briefly.

Starting from the dilute end, we expect the chains to overlap when the surface concentration exceeds a certain limit

$$\Gamma_1 \cong N/R_{F2}^2 \quad (2.20)$$

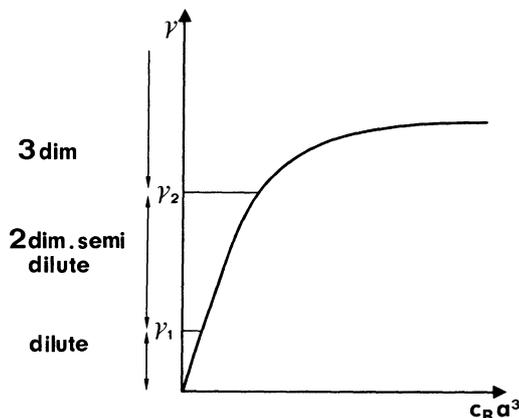


FIG. 2. — Various regimes in the adsorption isotherm.  $\gamma$  is a dimensionless measure of the surface excess. The limits are  $\gamma_2 \sim \delta^{1/2}$  and  $\gamma_1 \sim \gamma_2 K^{-1/2}$  where  $\delta$  measures the effective attraction of one monomer to the surface, and  $K$  is a large number defined in eq. (2.6).

where  $R_{F2}$  is the lateral size of a single adsorbed coil (eq. (2.5)). For  $\Gamma > \Gamma_1$  (but  $\Gamma$  still much smaller than the *plateau* values) the correct form of the thermodynamic potential is

$$\mu - \mu_0 = N\left(\frac{a}{D}\right)^{5/3} + N\frac{a}{D}(\gamma^2 - \delta) + \mu_{trans.} \quad (2.21)$$

The repulsion between coils is described by the  $\gamma^2$  term, for which a full justification can be found in ref. [16]. Qualitatively, the essential property is that the osmotic pressure  $\pi(c)$  goes like  $c^3$  in two dimensional solutions (as opposed to the Flory-Huggins value  $c^2$ ). The interaction potential scales like  $\pi/c$  and is thus proportional to  $c^2$  (or  $\gamma^2$ ).

After minimization of (2.21) with respect to  $D$  we find

$$\frac{D}{a} \cong (\delta - \gamma^2)^{-3/2} \quad (2.22)$$

and

$$\mu \cong -N(\delta - \gamma^2)^{5/2} + \mu_{trans.} \quad (2.23)$$

from which we derive an adsorption isotherm of the form

$$\gamma^2 \cong \delta - \left(\frac{l}{N}\right)^{2/5} \quad (2.24)$$

Note that eqs. ((2.22) (2.24)) require  $l \leq K$  in the semi dilute regime. The thickness is :

$$D \cong a \left( \frac{N}{l} \right)^{3/5} . \quad (2.25)$$

Although correct, the formulas (2.24-25) are misleading. Eq. (2.25) for instance, if we ignore the logarithmic factor  $l$ , resembles the Flory radius  $R_{F3}$  for one single coil in the bulk. However, for the concentrations of interest,  $l$  is in fact large, and  $D$  is smaller than  $R_{F3}$ .

This can be made more precise if we consider the upper concentration limit of the semi dilute regime : the form (2.21) for the free energy holds only when the system is strongly two dimensional, i.e. when  $\xi_3 > D$ . We can estimate the ratio  $\xi_3/D$  from eqs ((2.14), (2.24)) and we find

$$\left( \frac{\xi_3}{D} \right)^4 \cong \left( \frac{l}{K} \right)^{3/5} \left[ 1 - \left( \frac{l}{K} \right)^{2/5} \right]^{-3/2} \quad (2.26)$$

(again omitting all numerical coefficients). This ratio is larger than unity only in a narrow span of values for  $l/K$  (roughly between  $l = 0.5 K$  and  $l = K$ , but the coefficients quoted are only illustrative). Thus in practice we always  $l \sim K$  in the semi dilute regime and eq. (2.25) then leads us back to thicknesses  $D$  of order a  $\delta^{-3/2}$ , i.e. similar to those in the dilute limit.

**3. Concluding remarks.** — Comparing now the results of the mean field theory with those of the (slightly more refined) scaling theory we find the following features :

1) The mean field picture does give us, as usual, a correct idea of the general trends : *a*) in the very dilute limit the layer thickness  $D$  is independent of molecular mass ; *b*) as soon as we get near the *plateau* of the adsorption isotherm, the attraction towards the surface is nearly cancelled by monomer-monomer repulsions ;  $D$  becomes then much larger, and  $N$  dependent.

2) However, the power laws deduced from mean field theory are completely wrong, when we look either at dependances on adsorption strength (on  $\delta$ ) or on molecular mass (on  $N$ ). This conclusion is at variance with certain qualitative remarks of Hoeve [7] who did not appreciate the possible existence of a weak adsorption regime in the presence of excluded volume effects.

Returning now to the data, as reviewed in ref. [4], we find that the law for  $D(N)$  in the *plateau* regime can vary rather widely depending on the system under study — even if we restrict our attention to good solvents. With polystyrene in cyclohexane the data give  $D \sim N^{1/2}$ . But with vinyl acetate or methylmethacrylate in benzene the increase with  $N$  is stronger. Finally with PS in benzene the dependence is weaker than  $N^{1/2}$ .

One major source of discrepancy is the following : all theorists have assumed reversible adsorption, and this is rarely found in practice. Indeed, theoretical studies on entangled polymers attached at one end [17] suggest strongly that entanglement times may become prohibitively long in certain adsorption experiments. A more elaborate — *kinetic* — theory of polymer adsorption may be required for the future.

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## APPENDIX

**Relation between single chain adsorption and the problems of surface magnetism.** — Relations between the statistics of polymer solutions and those of magnetic critical points have progressively emerged in the past few years [18, 13]. The most clear and simple presentation of these relations — due to G. Sarma — is contained in an appendix to ref. [15]. The result can be stated as follows :

Consider a set of atoms ( $i, j, \dots$ ) occupying a set of fixed positions in space (on a periodic lattice or even more general arrangements). Each atom carries a spin  $S_i$  of square length  $S_i^2 = n$ . The vector  $S_i$  has  $n$  independent components ( $n = 1$  corresponds to the Ising model,  $n = 3$  to the Heisenberg model). Neighboring spins are coupled by a ferromagnetic interaction of the form

$$\mathcal{H} = - \sum_{s < i} J_{ij} S_i \cdot S_j . \quad (A.1)$$

In the paramagnetic (disordered) state realised at high temperatures  $\tau$  we can define a susceptibility  $\chi_i(\tau)$  as the ratio  $\overline{S_i}/H$  of the average moment  $\overline{S_i}$  on site  $i$  to the external field  $H$  (in the limit of small  $H$ ). The high temperature series expansion for  $\chi_i(\tau)$  is related to the generating function for self avoiding walks on the network ( $i, j, \dots$ ) by the following law

$$\sum_{N=0}^{N=\infty} \sum_{j,k,l,\dots} J_{ij} J_{jk} \dots J_{st} \frac{1}{\tau^N} = \tau \chi_i \Big|_{n=0} . \quad (A.2)$$

The product of  $J$  factors on the left hand side contains  $N$  factors : each choice of a set ( $i, j, \dots, t$ ) corresponds to a walk of  $N$  steps : *only self avoiding walks are included*. On the right hand side, the suffix  $n = 0$  means that after calculating  $\chi_i$  for a physical magnet with arbitrary  $n \geq 1$ , one must perform an analytic continuation of the result to the (non physical) value  $n = 0$ . By this trick the generating function for

self avoiding walks, when the weight for each step ( $ij$ ) is a constant  $J_{ij}$ , is related to a magnetic problem.

In the case of interest here we shall have *magnetic atoms* located on a periodic lattice — for instance a simple cubic lattice with a unit cell length  $a$ . This lattice is limited to a half space, the boundary being for instance a (100) plane. The last layer of atoms will describe the possible sites of adsorption of the polymer chain. We choose :

$$J_{ij} = J$$

for all internal bonds between nearest neighbours,

$$J_{ij} = J_s > J$$

for all surface bonds between nearest neighbours,

$$J_{ij} = 0$$

for all pairs which are not nearest neighbours.

(In the polymer language, the second condition will ensure that links which stay on the surface are energetically favored.)

For the magnetic problem we know that the susceptibility  $\chi_i$  is finite at high temperatures  $\tau$ , but that it diverges when  $\tau$  goes down to the critical point  $\tau_c$ . More precisely we have

$$\tau\chi_i(\tau) = \sum_{N=0}^{\infty} \varphi_i(N) (\tau_c)^N \tag{A.3}$$

where  $\varphi_i(N)$  is a *slow* function of  $N$  (in practice a power of  $N$ ). After taking  $n = 0$ , each term on the r.h.s. of (A.3) gives us the partition function  $Z_N$  for a self avoiding walk of  $N$  steps (with the weight factors  $J_{ij}$ )

$$Z_N = \varphi_i(N) \tau_c^N \tag{A.4}$$

The chemical potential (for a chain of  $N$  units starting from point  $i$ ) is thus, in units of  $k_B T$  :

$$\mu = - N \ln \tau_c - \ln \varphi_i \tag{A.5}$$

The dominant term in the r.h.s. of (A.5) is the first term. Thus the study of the one chain chemical potential is reduced to a study of the transition temperature  $\tau_c$  for the ferromagnet. In the present problem, with enhanced surface couplings, we know from various theoretical studies [19] that the following properties hold :

a) When  $J_s/J$  is smaller than a certain critical value,  $r$ , the material shows a single transition at the bulk transition point  $\tau_B$ .

b) When  $J_s/J > r$ , or when the parameter

$$\sigma = \frac{J_s}{rJ} \tag{A.6}$$

is larger than unity, there is a temperature regime

$$\tau_B < \tau < \tau_s$$

where the vicinity of the surface orders magnetically while the bulk stays paramagnetic. The quantity  $\sigma$  in (A.6) is the exact analog of the ratio introduced by Hoeve *et al.* [7] for the chain problem and defined in section 1.

c) What is of particular interest for us is the behaviour of the surface transition temperature  $\tau_s$ , as a function of  $\sigma$ , when  $\sigma$  is just above the threshold value ( $\sigma = 1 + \delta$ ).

Mean field behaviours for this regime have been discussed in detail by Lubensky and Rubin [19]. More generally, for small  $\delta$ , one expects a variation of  $\tau_s$  with  $\delta$  of the form :

$$\tau_s = \tau_B + \delta^{m(n)} \tag{A.7}$$

In mean field,  $m(n) = 2$ ; beyond mean field, there are some numerical studies on  $\tau_s(\delta)$  both for the Ising case ( $n = 1$ ) [20] and for the chain problem ( $n = 0$ ) [21]. But they are not yet precise enough to give us a definite value of  $m(n)$ . Our discussion (eq. (2.3)) leads to the prediction :

$$m(0) = 5/2 \tag{A.8}$$

Note that  $m(0) > 2$  and  $D \sim \delta^{1-m(0)}$  diverges more strongly when  $\delta \rightarrow 0$  than in the case of an ideal chain ( $D \sim \delta^{-1}$ ). This appears natural : repulsions increase the size of the adsorbed layer.

At first sight it may appear very surprising that we should be able to calculate such a critical exponent by elementary considerations. However, the reader should keep in mind the fact that our exponents for the adsorption problem are closely interlinked with the Flory exponents for excluded volume effects in a single chain. In the latter problem, the simple arguments of Flory do lead to exponents which are numerically excellent for all dimensionalities ( $d = 1, 2, 3, 4, \dots$ ) : this gives us confidence in the validity of eq. (A.8).

*Note added in proof.* — Pr. Silberberg pointed out that experiments by Garvey, Tadros and Vincent [22] on poly (vinyl alcohol) adsorbed on polystyrene, are in rather good agreement with the predictions of the present paper. They found that a) in the *plateau* regime, the concentration in the layer ( $\Gamma/D$ ) is comparable to that in a single coil ( $N/R_F^3$ ). This is precisely what can be found from eqs. (2;11, 12); b) the thickness  $D$  is somewhat greater than  $R_F$ , as expected (prolate ellipsoid regime). The author is greatly indebted to A. Silberberg and T. Tadros for discussions and correspondence on these points.

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