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Short Communication

Polymer adsorption near the surface of a polymer solution : a universal behaviour

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Résumé.— Une propriété universelle des bonnes solutions de longs polymères près d'une surface attractive est étudiée en se plaçant dans le cas où il y a saturation à la surface et où la concentration en monomères tend vers zéro à l'infini. La généralisation d'un argument présenté par P.G. de Gennes indique qu'à une distance x de la surface, la concentration *kuhnienne* (en monomères) $C_k(x)$ doit être donnée par la formule universelle $C_k(x) = A(d)x^{-d+1/\nu}$ où d est la dimension de l'espace et ν l'exposant critique de taille. On montre qu'une théorie de champ moyen est valide pour de petites valeurs de $\varepsilon = 4 - d$ et qu'elle conduit au résultat $A(4 - \varepsilon) = 2/\pi^2\varepsilon$, pour $0 < \varepsilon \ll 1$.

Abstract.— A universal property of good solutions of long polymers near an attractive surface is studied under the assumption that there is saturation on the surface and that the monomer concentration vanishes at infinity. The generalization of an argument given by P.G. de Gennes indicates that, at a distance x from the surface, the *kuhnian* concentration (monomer concentration) $C_k(x) = A(d)x^{-d+1/\nu}$ where d is the space dimension and ν the critical size exponent. It is shown that a mean field theory is valid for small values of $\varepsilon = 4 - d$ and that it leads to the result $A(4 - \varepsilon) = 2/\pi^2\varepsilon$, for $0 < \varepsilon \ll 1$.

1. Introduction.

The free surface of a polymer solution may attract the polymer which forms an adsorbed layer at the surface. Thus, the number of monomers per unit volume is a function $C(x)$ of the distance from the surface (see Fig.1). Here, we study this function assuming that :

- 1) we have very long polymers in a good solvent
- 2) the surface is strongly attractive
- 3) the solution itself is so dilute that $C(x \rightarrow \infty) = 0$.

In several articles, P.G. de Gennes has considered this situation and shown [1] that (in dimension three) $C(x)$ decreases like $x^{-4/3}$. The

argument can be presented as follows. The monomer concentration for long polymers in a good solvent (kuhnian chains [2,3]) is proportional to the number C of polymers per unit volume and in the kuhnian limit, it has to be represented by the following expression [2,3]

$$C_k = CX^{1/\nu} \quad (1)$$

where $R^2 = X^2d$ is the mean square distance between the end points of an isolated polymer and ν the well known size exponent ($\nu = 0.59$). The concentration C_k can be easily measured ; thus this kind of concentration can be considered as important from any point of view.

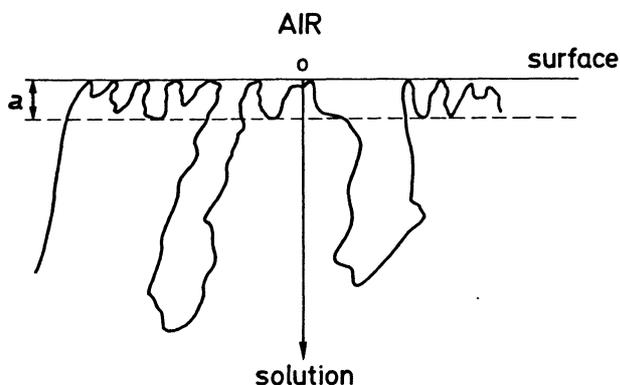


Fig. 1.— An adsorbed polymer near a surface. The length a defines the range in which the surface potential can be felt. Beyond that range, there are only repulsive forces between polymers and this repulsion creates a self-consistent potential.

Near a free surface, the quantity of interest for kuhnian chains is the concentration $C_k(x)$ which obviously has the same dimension as C_k namely $C_k \sim L^{-d+1/\nu}$. Therefore as no other length occurs in the problem, we must have

$$C_k(x) = Ax^{-d+1/\nu} \quad (2)$$

where A is a pure number.

We must emphasize the fact that, in the problem under consideration, $C_k(x)$ vanishes when $x \rightarrow \infty$, and, in the absence of any cut-off, would become infinite on the surface ; moreover the chains are assumed to be very long. This is why it is impossible to introduce any physically meaningful correlation length in the problem ; the consequence of this fact is that equation (2) is the only universal law that can be written in the present situation.

We now claim that A is a universal number which depends only on the dimension of space ($A = A(d)$). Thus $C(x)$ is not only given by a self-similar expression as was pointed out by P.G. de Gennes [1], it is also completely determined.

Actually, it may look surprising that A should not depend on the strength of the attraction but this fact can be understood as follows. The polymers that are adsorbed on the surface repel one another. Adsorption from the solution takes place until the repulsion compensates the attraction of the surface. Thus, in all cases, a polymer, that is adsorbed on the surface is only *marginally* bound. Yet, in spite of the fact that A should be universal, the quantity of polymer that is adsorbed on the surface depends on the properties of the system. This corresponds to the fact that the integral $\int_0^\infty dx x^{-d+1/\nu}$ is divergent at $x = 0$. Thus, in the vicinity of the surface, the concentration $C_k(x)$ is represented by a function of the form

$$C_k(x) = x^{-d+1/\nu} f(x/a)$$

where a is a cut-off corresponding to the range of the attractive forces. We may for instance assume that $f(x/a) = A$ for $x \geq a$. In this case, the number of monomers per unit surface is given by

$$\begin{aligned} \sigma &= \int_0^\infty dx C_k(x) = \\ &= a^{-(d-1-1/\nu)} \left[\int_0^1 dt \frac{f(t)}{t^{d-1/\nu}} + \frac{A}{d-1-1/\nu} \right] \end{aligned}$$

(for $\nu > \frac{1}{d-1}$)

In this way, we can understand why A is universal and incidentally, we note that for $d = 1$ the result is trivial. In this case, a long straight polymer starts from the surface ($\nu = 1$) and we have $C_k(x) = 1$, $A(1) = 1$.

2. A mean field method.

For small values of $\epsilon = 4 - d$, a polymer chain in solution is nearly Brownian and a mean field method might give reasonable results in this limit. Thus we may consider that the chains feel a potential $V(x)$ which is the sum of the (attractive and repulsive) surface potential and of a self-consistent potential produced by the other chains.

The weight associated with the configuration of a chain

$$W = \exp \left[-\frac{1}{2} \int_0^S ds \left(\frac{d\mathbf{r}}{ds} \right)^2 - \int_0^S ds V(\mathbf{r}(s)) \right]$$

where $\mathbf{r}(s)$ defines the position of a point of the chain and $x(s)$ the distance of this point from the surface. For $x > a$, the only contribution to $V(x)$ is the self-consistent part

$$V(x) = bSC(x) = bC(x) \tag{3}$$

where b is the interaction, S the Brownian area of the chain, $C(x)$ the number of polymers per unit volume and $C(x)$ the quantity of *Brownian area* per unit volume. We want to calculate $C(x)$ as a function of x .

The behaviour of a Brownian chain (characterized by an area S) in an external potential has been studied by many authors and the results are well known [3].

It is convenient to introduce the (renormalized) function $Z_0(\mathbf{r}_0, \mathbf{r}_1; S)$ associated with the chains that start from \mathbf{r}_0 and arrive at \mathbf{r}_1 . This partition function has the simple property that for any s

$$\begin{aligned} Z_0(\mathbf{r}_0, \mathbf{r}_1; S) &= \\ &= \int d^d \mathbf{r} Z_0(\mathbf{r}_0, \mathbf{r}; s) Z_0(\mathbf{r}, \mathbf{r}_1; S - s) \end{aligned}$$

It is not difficult to show[3] that $Z_0(\mathbf{r}_0, \mathbf{r}; S)$ is solution of the equation

$$\begin{aligned} \frac{\partial}{\partial S} Z_0(\mathbf{r}_0, \mathbf{r}; S) &= \\ &= \left[\frac{1}{2} \Delta_r - V(x) \right] Z_0(\mathbf{r}_0, \mathbf{r}; S) + \delta(S) \delta(\mathbf{r} - \mathbf{r}_0) \end{aligned} \tag{4}$$

Thus in the absence of potential

$$Z_0(\mathbf{r}_0, \mathbf{r}; S) = (2\pi)^{-d/2} \exp \left[-(\mathbf{r} - \mathbf{r}_0)^2 / 2S \right]$$

The function $Z_0(\mathbf{r}_0, \mathbf{r}; s)$ is used to calculate $C(x)$. It is not difficult to show that for N chains in a box

$$\begin{aligned} C(x) &= \\ &= \frac{N \int ds \int d^d r_0 \int d^d r_1 Z_0(\mathbf{r}_0, \mathbf{r}; s) Z_0(\mathbf{r}, \mathbf{r}_1; S - s)}{\int d^d r_0 \int d^d r_1 Z_0(\mathbf{r}_0, \mathbf{r}_1)} \end{aligned} \tag{5}$$

and we are interested in the limit where the area S and the size of the box become simultaneously infinite.

Let us now try to evaluate $Z_0(\mathbf{r}_0, \mathbf{r}; S)$. As the problem is one dimensional equation (4) can be simplified by setting

$$\begin{aligned} Z_0(\mathbf{r}_0, \mathbf{r}; S) &= \\ &= Z_0(x_0, x; S) (2\pi)^{-(d-1)} \exp(-\rho^2 / 2S) \end{aligned} \tag{6}$$

where ρ is the projection of \mathbf{r} on a plane perpendicular to Ox (i.e. parallel to the surface). We have now

$$\begin{aligned} \frac{\partial}{\partial S} Z_0(x_0, x; S) &= \\ &= \left[\frac{1}{2} \frac{\partial^2}{\partial x^2} - V(x) \right] Z_0(x_0, x; S) + \\ &+ \delta(S) \delta(x - x_0) \end{aligned} \tag{7}$$

On the other hand, equation (5) gives

$$\begin{aligned} C(x) &= \\ &= \frac{\mathcal{N} \int_0^S ds \int dx_0 \int dx_1 Z_0(x_0, x; S) Z_0(x, x_1; S)}{\int dx_0 \int dx_1 Z_0(x_0, x_1; S)} \end{aligned} \tag{8}$$

where \mathcal{N} is the number of chains per unit surface.

As the polymers are *marginally* bound, the spectrum of the operator $\left[-\frac{1}{2} \frac{\partial^2}{\partial x^2} + V(x) \right]$ must contain two parts : a continuous spectrum (starting from zero), and a discrete eigenvalue at the origin.

However, in order to avoid unessential divergences, it will be convenient to assume that the discrete state is bound with an eigenvalue $-E_0 < 0$. For this state, we have

$$\begin{aligned} \left[\frac{1}{2} \frac{\partial^2}{\partial x^2} - V(x) - E_0 \right] \varphi_0(x) &= 0 \\ \int_0^\infty dx [\varphi_0(x)]^2 &= 1 \end{aligned}$$

For the continuous spectrum, we have

$$\left[\frac{1}{2} \frac{\partial^2}{\partial x^2} - V(x) + \frac{k^2}{2} \right] \varphi(x, k) = 0 \tag{9}$$

$$\int_0^\infty dx \varphi(x, u) \varphi(x, k) = \delta(k - u) \tag{10}$$

In this case, the partition function $Z_0(x_0, x; S)$ is given by [3]

$$\begin{aligned} Z_0(x_0, x; S) &= \varphi_0(x_0) \varphi(x) e^{E_0 S} + \\ &+ \int_0^\infty dk e^{-k^2 S / 2} \varphi(x_0, k) \varphi(x, k) \end{aligned} \tag{11}$$

We may set

$$\varphi_0 = \int_0^\infty dx \varphi_0(x) \quad (12)$$

Consequently, for large values of S we have

$$\begin{aligned} Z_0(x; S) &\equiv \\ &\equiv \int dx_0 Z_0(x_0, x; S) \simeq \varphi_0 \varphi_0(x) e^{E_0 S} \end{aligned} \quad (13)$$

$$Z_0(S) \equiv \int dx Z(x; S) \simeq (\varphi_0)^2 e^{E_0 S}$$

Thus, in this limit, equation (8) gives

$$\begin{aligned} C(x) &= \frac{\mathcal{N} \int_0^S ds Z_0(x; s) Z_0(x; S-s)}{Z_0(S)} \simeq \\ &\simeq \mathcal{N} S [\varphi_0(x)]^2 \end{aligned} \quad (14)$$

Actually, at equilibrium, the polymers are marginally bound and therefore $E_0 \rightarrow 0$ when we approach this limit. In this limiting case (as we shall see later), $\varphi_0(x)$ remains the wave function of a bound state and the normalization relation

$$\int_0^\infty dx [\varphi_0(x)]^2 = 1 \quad (15)$$

is still valid.

Now let us consider the situation at equilibrium. Using equation (3), we may write equation (9), for $k = 0$ and $x \gg l$, in the following form

$$\left[\frac{\partial^2}{\partial x^2} - 2bC(x) \right] \varphi_0(x) = 0 \quad (16)$$

Since $C(x)$ and $\varphi_0(x)$ are related by equation (14), the preceding equality is the self-consistent equation that we need.

Let us look for a solution of the form

$$\varphi_0(x) = \psi/x^\alpha \quad (17)$$

Equation (16) gives

$$C(x) = \alpha(\alpha + 1)/2bx^2 \quad (18)$$

Let us now bring the expressions (17) and (18) into equation (14). We obtain $\alpha = 1$, and therefore

$$C(x) = 1/bx^2 \quad (19)$$

$$\varphi_0(x) = \psi/x \quad (20)$$

We see that equation (19) is compatible with equation (2) for $d = 4$. On the other hand, equation (20) shows that $\varphi_0(x)$ is normalizable,

in agreement with equation (15). We see that in the limit $d \rightarrow 4$, this result is compatible with the prediction made by P.G. de Gennes since for $d = 4$, we have $d - 1/\nu = 2$.

On the other hand, equation (3) gives the form of the potential for large values of x

$$V(x) = 1/x^2 \quad (21)$$

and we verify that, in this region, the potential is independent of the characteristics of the polymer, of the solvent and of the surface.

Bringing equations (19) and (20) into equation (14) also gives the value of ψ

$$\psi = 1/\sqrt{\mathcal{N}Sb} \quad (22)$$

3. The asymptotic limit $S \rightarrow \infty$, $d \rightarrow 4$.

The mean field method should be valid for large S and small values of $\varepsilon = 4 - d$, and it gives (see Eq.(19))

$$C(x) = 1/bx^2$$

We must now compare this result with equation (2).

At this point, we must remark that the mean field result, in its elementary form, cannot be right, even at $d = 4$, owing to renormalization effects. Thus, we may note that a first order calculation of the second virial coefficient gives a result proportional to b . Still, we know [3], that for $d = 4$, in the limit of long chains, the second virial coefficient vanishes. This means that, when using the mean field approximation, one should replace the true interaction b by an effective interaction which is proportional to the second virial coefficient. This amounts to changing the expansion parameter. It is a basic operation of the direct renormalization method [2,3] and we shall now apply this procedure.

Using standard notation, we may express b in terms of the dimensionless parameter z .

$$z = bS^{2-d/2}(2\pi)^{-d/2}$$

As the chains are long, z is large and has to be replaced (to first order approximation [2,3]) by the *osmotic parameter* g which defines the second virial coefficient of two chains [2,3]. In this way, we obtain

$$C(x) S^{-2+d/2} = \frac{(2\pi)^{-d/2}}{gx^2} \quad (23)$$

When $S \rightarrow \infty$, g has a definite limit g^* and for small values of $\varepsilon = 4 - d$, we know [2,3] that $g^* = \varepsilon/8$. Let us take the limit $\varepsilon \rightarrow 0$, in equation (23) : we obtain

$$C_k(x) \simeq C(x) = \frac{2}{\pi^2 \varepsilon x^2}$$

and by comparing with equation (2), we find for $0 < \varepsilon \ll 1$

$$A(4 - \varepsilon) \simeq \frac{2}{\pi^2 \varepsilon} + \dots \quad (24)$$

The result is interesting and the fact that $A(4 - \varepsilon)$ becomes infinite when $\varepsilon \rightarrow 0$ can be easily understood. When ε is very small, the chains are nearly Brownian, and they repel very weakly one another ; thus, when $\varepsilon \rightarrow 0$, more and more chains are attracted by the surface.

Unfortunately, for practical applications, the preceding result is not very useful. We have to calculate the next order in ε , and we plan to do that later.

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