

Adsorption of Polymers

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ABSTRACT. We discuss some recent results about the scaling approach to polymer adsorption. The various concentration regimes are discussed, as well as the concentration profile in the plateau range. These are compared with experimental results. We briefly discuss surface imperfections such as regular or fractal roughness and chemical impurities.

KEYWORDS: Adsorption / Interface / Concentration Profile / Neutron Reflection / Surface Roughness / Random Impurities.

Polymers have important applications¹ when they are located at interfaces. They are used as glues or paints for instance. Their adhesive and elastic properties may then be important. They are also used for colloidal stabilization, or separation such as for instance water purification. The important property here is the adsorption of the polymer on the colloidal particles. But they are also traditionally used as emulsifiers. Then their interfacial properties are important and the fact that they eventually decrease the surface tension between immiscible fluids. Finally, they may also be grafted on surfaces for protection for instance. This short overview is intended to show that already many applications exist in every day life. Still, the fundamental properties of the polymers at interfaces are not fully understood. In what follows, we would like to review some properties of linear polymers at interfaces. More specifically, we will consider the conformation of linear macromolecules at interfaces. Polymers are usually either strongly attracted or repelled by surfaces, even though the interaction of each monomer may be weak. This is of course related to the fact that several units are interacting with the surface. We will focus our attention on the attractive case, that is on polymer adsorption. We will first consider the case of a single chain at the surface of a good solvent. Then the (bulk) concentration effects will be discussed. The surface is assumed to be regular and flat. Then, we will discuss briefly the effects of surface roughness and impurities. We stress that only the scaling approach is used below, even though other theories were given^{2,3}.

1. ADSORPTION OF A LINEAR CHAIN

1.1. Ideal chain.

Consider a linear polymer made of N monomers in a good solvent. We assume that every unit has an attractive interaction with the free interface, assumed to be flat. Let δ be the (dimensionless) free energy gain per monomer on the surface. We assume it to be small. We first consider the case of an ideal chain, with one end grafted on the surface. It was shown⁴ that when the conformation is isotropic, the chain has N_s monomers on the surface, with

$$\text{The energy gain } F_g \text{ is } N_s \sim N^{1/2} \quad (1)$$

$$F_g \sim \delta N^{1/2} \quad (2)$$

and tends to localize the chain on the surface. This competes with an entropy loss if this localization occurs. A slightly different expression will be used below for the excluded volume case. The ideal chain case may be solved exactly by considering the Schrödinger type of equation introduced by Edwards⁵ some years ago. We have then to solve the following equation

$$\frac{\partial \psi}{\partial N} = \epsilon \psi = -\frac{a^2}{6} \frac{\partial^2 \psi}{\partial z^2} + \frac{V(z)}{kT} \psi \quad (3)$$

with ψ the eigenfunction, z the direction normal to the interface, $V(z)$ the attractive potential, and ϵ the lowest eigenvalue. When N is very large, the ground state dominates, and the local concentration C is directly related to ψ . De Gennes⁴ showed some years ago that it is equivalent to solve the problem in the absence of potential, but with a boundary condition on the surface:

$$\frac{1}{y} \frac{\partial \psi}{\partial z} = -\frac{1}{D} \quad (4)$$

where D is the adsorption length and gives the width of the region where the chain is confined. If we assume that the potential is localized, $V(z) = -kT \delta(z)$, D varies as

$$D \sim \delta^{-1} a \quad (5)$$

and the concentration falls off exponentially from the wall with a characteristic length D .

1.2. Good solvent.

Let us now consider a polymer at the interface of a good solvent. The number N_s of monomers on the surface⁶ when the polymer is not adsorbed is, generalizing relation (1):

$$N_s \sim N^\phi \quad (1')$$

The value of the cross-over exponent ϕ depends on the exact problem one is considering: As a matter of fact, two different versions⁷ may be considered, depending on the nature of the surface. The latter may be either impenetrable, which is the case for instance for a solid surface, or penetrable, which is the case for instance for the interface between two immiscible good solvents. In the latter case, it was shown by Bray and Moore that the cross-over exponent⁸ is related to the excluded volume exponent ν

$$\phi = 1 - \nu \quad (\text{surface of defects}) \quad (6')$$

In the former case, ϕ is, in principle, independent of v , although for the three dimensional case that we will consider exclusively, the numerical values of both exponents happen to be very close to each other:

$$\phi \approx 3/5 \text{ (impenetrable; } d=3) \tag{6}$$

In all the following, we will consider exclusively the latter case. Studies of the surface of defect case implies the change from (6) to (6') in the cross-over exponent. The value of ϕ in the two dimensional case was calculated by computer simulations by Ishinabe⁹ and by Kremer¹⁰. It is possible to make a scaling assumption concerning the characteristic distance L by noting that the scaled energy for a chain is δN^ϕ and has to be compared to unity. If it is less than unity, the chain is not adsorbed. In the opposite case, it is. Thus we have¹¹, for the impenetrable case in three dimensions:

$$L \sim N^{3/5} f(\delta N^{3/5}) \tag{7}$$

where the unknown function $f(x)$ has known limits: for $x \ll 1$, $f(x) \sim 1$, and $f(x \gg 1) \sim x^a$ where the exponent a is determined by the condition that the chain adopts a pancake shape with width D independent of N . One finds

$$D \sim \delta^{-1/a} \tag{8}$$

Note that we may define surface blobs, made of g_s monomers, that are on the verge of being adsorbed: $\delta g_s^{3/5} \sim 1$. The size of such blobs is D . The chain is a two dimensional arrangement of surface blobs. Using the Flory value v_2 for the excluded volume exponent in two dimensions, we find for the radius $R_{||}$ of the pancake

$$R_{||} \sim \left(\frac{N}{g_s}\right)^{3/4} D \tag{9}$$

2. CONCENTRATION EFFECTS

2.1. The profile.

When the bulk concentration is increased, the surface concentration Γ_s also increases. Different regimes¹⁰ are then met. The dilute regime that we discussed above is valid as long as the various polymers do not overlap each other. This is realized as long as $\Gamma_s \ll \Gamma_s^*$, with

$$\Gamma_s^* \sim \frac{N}{R_{||} D} \sim N^{-1/2} \delta^{1/2} \tag{10}$$

For $\Gamma_s \gg \Gamma_s^*$, the characteristic distances may be obtained by scaling arguments. Assuming

$$R_{||} \sim N^{3/4} d^{-1/4} f(\Gamma_s/\Gamma_s^*) \tag{10a}$$

and

$$R_{\perp} \sim D g(\Gamma_s/\Gamma_s^*) \quad (10b)$$

we find

$$R_{\parallel} \sim N^{1/2} \Gamma_s^{-1/2} \quad (11a)$$

$$\xi_{\parallel} \sim \Gamma_s^{-3/2} \delta^{-1/2} \quad (11b)$$

and

$$R_{\perp} \sim N^{3/5} (\Gamma/\delta)^{1/3, 6/5} \quad (11c)$$

The N dependence in (11c) is related to the progressive appearance of loops. These are related to the squeezing of the polymers and to the existence of the excluded volume interaction, so that the profile extends to distances larger than D . Note that these loops do not exist in the ideal chain case: Because there is no interactions, the surface concentration may become very high.

For still higher bulk concentrations, $\Gamma \gg \delta^{1/3}$, a plateau regime is reached, where the surface concentration basically remains constant. Note that the surface may be saturated while the bulk is still in a dilute regime: One can show that the partitioning of the chains is roughly described by a Boltzmann factor, with $\Gamma_s \sim \frac{D}{a} C_b \exp(-N\delta^{5/3})$. Extending relations (11) into the plateau regime, we find

$$R_{\parallel} \sim N^{1/2} \delta^{-1/6} \quad (12a)$$

$$\xi_{\parallel} \sim \delta^{-1} \quad (12b)$$

$$R_{\perp} \sim N^{3/5} \quad (12c)$$

Thus the two dimensional blob reaches the size of the surface blob, relation (8), and the profile extends to distances of the order of the radius of a chain in the bulk. This is directly related to the special loop structure that was introduced by de Gennes¹³. The resulting phase diagram is rather complicated¹¹⁻³³. In what follows, we will be interested only in the latter plateau regime. Because of the Boltzmann weights, the first regimes correspond to very dilute bulk concentrations. Note that this regime extends to the semi dilute bulk range without changes in the parallel dimensions. The orthogonal extension R_{\perp} becomes then the blob size $\xi \sim C_b^{-3/4}$. We consider now the concentration profile $\Phi(z)$ from the surface. Because the surface is saturated with blobs of size D , the surface concentration Φ_s is

$$\Phi_s \sim g_s/D^2 \sim \delta \quad (13)$$

Three different regimes were discussed by de Gennes and Pincus¹⁴ and Eisenriegler¹⁵. Far from the surface, in the distal range, for $z \gg R$ (or ξ), the profile falls off exponentially. Closer to the surface, in the central region, for $D \ll z \ll R$ (or ξ), the profile is self similar. Moreover, in this distance range, the local concentration is in the semi-dilute range. Thus there is locally a screening length $\xi(z) \sim \Phi(z)^{-3/4}$. Because there should be only one length, the latter has to be identified to the distance z to the surface. Thus we find

$$\Phi(z) \sim (a/z)^{4/3} \quad (\text{central}) \quad (14)$$

Close to the surface, in the proximal region, for a $\ll z \ll D$, the profile decreases as a power law

$$\Phi(x) \sim \Phi_s (a/z)^m \quad (15')$$

The exponent m is found by continuity of relations (14) and (15) for $z = D$:

$$\Phi(x) \sim \Phi_s (a/z)^{1/3} \quad (15)$$

Adsorption of polymer mixtures is discussed by Lipatov, in this conference.

Although there is a continuing effort to find a monomer-solvent pair such as δ is small, this parameter is usually large for most of the systems. Thus in what follows, we will neglect the proximal region and consider only profiles essentially made of the the central, self-similar region, relation (14).

2.2. Experimental tests.

It has to be realized that the experimental determination of the preceding profiles, in the presence of a bulk phase, is experimentally difficult. It has been attempted by several techniques, including ellipsometry, hydrodynamical widths, and radiation scattering and reflectometry. The first two techniques measure moments, while the last ones provide the Fourier transform of the profile $\Phi(z)$.

Ellipsometric measurements were performed by Kawaguchi, Takahashi and coworkers¹⁶⁻¹⁸ and found that in a good solvent, the ellipsometric width L_e varies as

$$L_e \sim N^{0.4} \quad (16)$$

this is directly interpreted as the first moment of the profile:

$$L_e \sim \int z \Phi(z) dz \sim R_F^{2/3} \quad (17)$$

where $R_F \sim N^{3/5}$ is the Flory radius of a chain in the bulk.

Hydrodynamic thickness e_h was also measured¹⁹ by these authors, with reasonable agreement.

Neutron small angle scattering was performed by Auvray et al.²⁰ on polymer adsorbed on a porous medium. The scattered intensity is related to the Fourier transform of the profile, and was found to be in agreement with the above discussion. Note however that these results are challenged by Cosgrove et al.²¹ who did similar experiments on polyoxyethylene on polystyrene latex spheres and could not fit their results by any power law. Thus there does not seem to exist a general consensus about the results at the present time.

Neutron reflectometry was also used, and we discuss briefly the results obtained by Farnoux and coworkers^{22,23} on polydimethylsiloxane adsorbed at the free surface of a solution in toluene. The variation with incidence angle (or wavelength) of the reflected intensity close to total reflection is related to the concentration profile. Various profiles were assumed for the data treatment, for instance a decomposition into several step profiles. These were ruled out very recently by Guiselin²⁴ using a series of measurements with several molecular weights, and it seems that the reflectivity results are in good agreement with the scaling predictions.

3. SURFACE IMPERFECTION

So far, we considered only flat ideal surfaces. Clearly, those are very difficult to get experimentally. Natural imperfections appear as soon as one deals with real surfaces. One may think at least about two different types of imperfections, namely surface roughness and chemical impurities.

3.1. Surface roughness.

Two types of roughness were considered, either regular or fractal, which we discuss briefly now.

3.1.1. Regular.

Hone, Ji and Pincus²⁵ considered the adsorption of an ideal chain on a penetrable surface when the height z of the latter is modulated in one dimension, that is if

$$\begin{aligned} z(x_0, y) &= \text{const.} \\ z(x, y_0) &= z_0 \cos(2\pi x/l) \end{aligned}$$

with x_0, y_0 being constants, and l the wavelength of the modulation. Their result is that the length D is merely decreased except when the wavelength is very short: for $l \ll z_0 \ll D_R$, the adsorption length D_R is

$$D_R \sim D l/z_0 \quad (18a)$$

where D is the length for a flat surface, relation (8). In the opposite case of very large amplitudes, $l \ll D_R \ll z_0$, they find

$$D_R \sim D \left(\frac{l}{D}\right)^{1/2} \quad (18b)$$

More generally, the ratio D_R/D is proportional to the ratio of the actual adsorbing surface inside of a sphere of radius D_R to that of the sphere. This is found by writing down the following dimensionless Flory free energy:

$$F = \left(\frac{R_0}{D_R}\right)^2 + \delta N \frac{a}{D_R} \frac{A}{D_R} \quad (19)$$

where the first term is the entropy loss because of confinement, and the second one the energy gain by the monomers on the surface. For a flat surface, the last fraction would be absent. Its presence corresponds to the increased surface area available to the monomers in the rough case with respect to the planar one. Minimizing relation (19) with respect to D leads

$$D_R \sim A/D \quad (20)$$

The reader may check easily that $A \sim z_0 D^2/l$ for $l \ll z_0 \ll D$, and $A \sim D^3/l$ for $l \ll D_R \ll z_0$. These results are easily generalized by incorporating the excluded volume interaction term in the above relation for the good solvent case. Let us stress that the above results are valid only for a penetrable surface that is not folded. This is the case for a self affine fractal surface, as opposed to a fractal surface, to be discussed below, that has multiple overhangs.

3.1.2. Fractal.

We consider now a fractal surface, that has many overhangs and is self similar on a linear scale $a \ll r \ll L$. This case was considered recently²⁶⁻²⁸ for an impenetrable surface. The latter is defined by a fractal dimension D_S with value between 2 and 3 such that its measure on scale r is

$$\Sigma(r) \sim (L/r)^{D_S} r^2 \quad (21)$$

The number dn of monomers in the volume $d\Omega(r) \approx dr\Sigma(r)$ within a distance dr from the surface is, using relation (14), valid on the plateau for strong adsorption, i.e. for $\delta \approx 1$

$$dn \sim \Phi(r)d\Omega(r) \sim \left(\frac{a}{r}\right)^{4/3} \left(\frac{L}{r}\right)^{D_S} r^2 dr \quad (22)$$

Integrating, we get the total number n_{tot} of adsorbed monomers:

$$n_{\text{tot}} \sim (L/a)^{D_S} \quad (23)$$

The latter relation shows that the polymer adopts a flat configuration, of width a , that is the size of a monomer on the rough surface. These geometrical effects are discussed by Kawaguchi and Arai in this conference²⁹.

3.2. Surface impurities.

Another source of surface imperfection is the fact that impurities may be located on the surface, preventing monomers to be adsorbed on the corresponding sites. Their average effect is to decrease the energy gain per monomer on the surface. For small values of d , if we assume that adsorbing sites are present only with probability p , and thus that a fraction $(1-p)$ of the sites are forbidden and correspond to impurities, the average energy gain per site is pd and is smaller than for a "clean" surface. Thus the effect of the impurities in this case is to delocalize the polymer and to make adsorption more difficult. On the other hand, for large energy gains, $d \gg 1$, the effect is not clear: competing with the previous effect, there is a change in the quality of the solvent, as discussed recently by Edwards³⁰, Muthukumar, and coworkers³¹⁻³² in the bulk. This may be discussed in the following way: Because of the presence of loops, the structure of the polymer in the adsorbing plane without impurities may be considered as a Levy flight with distribution of step sizes $P(l) \sim l^{-1-\sigma}$. One may write down a Flory free energy for such flight.

$$F = \left\{ \frac{R^\sigma}{N} \right\}^{1/(\sigma-1)} + \left\{ \frac{N}{R^\sigma} \right\}^{1/(\sigma-1)} + w \frac{N^2}{R^2} - v N \ln R \quad (24)$$

where we used $d=2$ for the adsorption plane, and where w is the excluded volume parameter on the plane, v is the pseudo-potential for the impurities, and takes into account their concentration, and $\sigma = 2$. When v is large, minimization leads to

$$R \sim v^{-1/2} \quad (25)$$

Thus the size of the polymer becomes independent of its mass. It is not clear however whether this corresponds to a collapse of the chain or to a local adsorption of part of it, with a hairpin structure of the remaining part. Such hairpin would then have a somewhat elongated structure in the direction orthogonal to the adsorbing plane.

We conclude by mentioning that the case of poor solvents was considered very recently by Johner and Joanny³⁴, who showed that wetting may occur in these systems. Finally copolymer systems were also studied, both in the melt to see the influence of surfaces on the ordering transition, and in dilute solutions in selective solvents, that are good for one of the blocks and bad for the other one. In this case, there is an interesting competition between micellization and adsorption. When the attraction by the surface is sufficiently strong, structures similar to grafted polymers are obtained. This is discussed by Wu³⁵ in this conference.

REFERENCES

1. D. H. Napper, "Polymeric Stabilization of Colloidal Dispersions". Academic Press, 1983. See also Colloïdes et Interfaces, A. M. Cazabat, M. Veyssié eds., Ed. de Physique, 1984.
2. J. M. H. Scheutjens, G. J. Fleer, *J. Chem. Phys.*, **84**, 178 (1980).
3. M. A. Cohen-Stuart, this conference.
4. P. G. de Gennes, "Scaling Concepts in Polymer Physics", Cornell University Press, 1979.
5. S. F. Edwards, *Proc. Phys. Soc.*, **285**, 65 (1965).
6. P. G. de Gennes, *J. Phys. France*, **37**, 1445, (1976).
7. K. Binder, in "Phase Transitions and Critical Phenomena", vol. 8, C. Domb and J. Lebowitz eds., Academic Press, 1983.
See also E. Eisenriegler, K. Kremer, K. Binder, *J. Chem. Phys.* **77**, 6296 (1982).
8. A. J. Bray, M.A. Moore, *J. Phys.* **A11**, 1927 (1977).
9. T. Ishinabe, *J. Chem. Phys.*, **76**, 5589, 1982. *J. Chem. Phys.* **77**, 3171 (1983).
10. K. Kremer, *J. Phys.* **A16**, 4333 (1983).
11. E. Bouchaud, Thesis, University Paris 11, 1988.
12. E. Bouchaud, M. Daoud, *J. Phys. Paris*, **48**, 1991, (1987).
13. P. G. de Gennes, *Comptes Rendus Ac. Sci. (Paris)II*, **294**, 1317 (1982).
14. P. G. de Gennes, P. Pincus, *J. Phys. Lett. (Paris)*, **44**, 241, (1983).
15. E. Eisenriegler, *J. Chem. Phys.* **79**, 1052 (1983).
16. A. Takahashi, M. Kawaguchi, H. Hirota, T. Kato, *Macromolecules*, **13**, 884 (1980).
17. M. Kawaguchi, A. Takahashi, *Macromolecules*, **16**, 1465 (1983).
18. K. Nagata, M. Kawaguchi, this conference.
19. M. Kawaguchi, M. Mikura, A. Takahashi, *Macromolecules*, **17**, 2063, 1984.
20. L. Auvray, J.P. Cotton, *Macromolecules*, **20**, 202, 1987.
21. T. Cosgrove, T. G. Heath, K. Ryan, T. L. Crowley, *Macromolecules*, **20**, 2879 (1987).
22. X. Sun, E. Bouchaud, A. Lapp, B. Farnoux, M. Daoud, G. Jannink, *Europhys. Lett.* **6**, 207 (1988).
23. X. Sun Thesis, University Paris 11, 1988.
24. O. Guiselin, L.T. Lee, B. Farnoux, A. Lapp, *Macromolecules*, to be published.
25. D.Hone, H. Ji, P. Pincus, *Macromolecules*, **20**, 2543 (1987).
26. P.G. de Gennes, *Comptes Rendus Ac. Sci. (Paris)*, **II**, **299**, 913 (1984).
27. F. Brochard, *J. Phys. Paris*, **46**, 2117 (1985).
28. M. Blunt, W. Barford, R. Ball, *Macromolecules*, **22**, 1458 (1989).
29. M. Kawaguchi, T. Arai, this conference.
30. A. Baumgartner, M. Muthukumar, *J. Chem. Phys.*, **87**, 3082 (1987).
31. S.F. Edwards, Y. Chen, *J. Phys.* **A21**, 2963 (1988).
32. S.F. Edwards, M. Muthukumar, *J. Chem. Phys.*, **89**, 2435 (1988).
33. C. Marques, Thesis, University Louis Pasteur, Strasbourg, 1989.
34. A. Johner, J. F. Joanny, preprint.
35. D. T. Wu, this conference.