Polymer adsorption on small spheres. A scaling approach

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POLYMER ADSORPTION ON SMALL SPHERES.
A SCALING APPROACH

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Résumé. — L'adsorption de chaînes polymériques sur de petits objets en solution, tels que des micelles, est étudiée en utilisant les résultats fournis par les lois d'échelles pour écrire l'énergie de confinement. Les adsorptions sur des petites sphères et des groupes de petites sphères sont discutées et les lois de puissance des énergies et des dimensions sont dérivées. Pour des objets sans interaction la ségrégation d'une phase dense, analogue à un gel, est prédite. La relation avec des solutions micellaires est considérée brièvement.

Abstract. — The adsorption of polymer chains on small objects in solution, such as micelles, is discussed using scaling results to describe the confinement energy. Adsorption on small spheres and on clusters of such spheres is discussed and appropriate power laws for the dimensions and energies are derived. For non-interacting objects the segregation of a dense, gel-like phase, is predicted. The direct relevance to solutions which can form micelles is also discussed briefly.

1. **Introduction.** — Adsorption of polymer chains on a surface is determined by a balance between the surface attraction and a repulsion resulting from the chain confinement. Scaling concepts have recently been applied to this problem by de Gennes [1]. Our purpose here is to apply the same ideas to adsorption on small objects whose surface area is too small to allow the polymer to spread to the extent corresponding to the same parameters on a free surface. Specifically we have in mind the adsorption of hydrophilic polymers on micelles which has been studied recently by Cabanne [2, 3]. To avoid the complications of the problem of micelle formation and of their equilibrium shape and size, we discuss adsorption on small spheres of given radius. To discuss an experimental situation involving micelles one would, of course, have to combine these results with some description of the micellar equilibrium itself.

Using a scaling description of the confinement energy of the chain [4] we calculate the adsorption energy and dimensions of a single chain adsorbed on a sphere as a function of the sphere radius, chain length and strength of the adsorption. The weak adsorption situation where the adsorbed layer is thick

and the average adsorption energy per monomer is small is discussed in section 2. Strong adsorption is discussed in section 3 where we also show why a long polymer adsorbed on a small sphere must still be regarded as adsorbed uniformly while configurations with only a small segment adsorbed are unstable. Contrary to the case of adsorption on a free surface [1a] it is found that both the three-dimensional and the two-dimensional regimes of reference [4] can occur. To investigate the equilibrium in a solution one has to consider the formation of clusters containing more than one sphere. This is done in section 4 for non-interacting spheres. It is found that at equilibrium the only stable solutions have the polymer adsorbed in a 2-dimensional regime with a suitable number of spheres. Smaller numbers, per polymer, can however be stabilized by repulsion between the spheres. In section 5 we discuss the segregation of a phase dense in polymers and spheres. It is found that such segregation is always favoured by the adsorption energy for non-interacting spheres. Explicit expressions for the energy and volume are derived for situations where the condensed phase can be regarded as a 3-dimensional semidilute solution.

2. **A single chain weakly adsorbed on a sphere.** — We first consider the weak adsorption limit for a single chain of length N adsorbed on a sphere of

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radius R_s. When the confined chain is in a 3-dimensional regime the free energy can be written

$$F = -4 \pi \delta R_s^2 N/V + kN\left(\frac{4 \pi N}{3 V}\right)^{5/4} \quad (2.1)$$

where δ is the net adsorption energy per monomer, k is a numerical constant (~ 1) and V is the volume to which the chain is confined as a result of the adsorption. For convenience all lengths are in units of the chain link (a) and energies in units of $k_B T$.

As in section 2 of reference [1] the first term on the r.h.s. of eq. (2.1) is the adsorption energy and the second term the repulsive confinement energy. The density ($c = N/V$) determines a coherence length :

$$\xi = \left(\frac{4 \pi}{3} c\right)^{-3/4} \quad (2.2)$$

where we have chosen the numerical constant so that $\xi = R_F(\approx N^{3/5})$ when V becomes equal to the free volume $\left(\frac{4 \pi}{3} R_F^3\right)$.

Eq. (2.1) and (2.2) assume that the adsorbed polymer can be treated as a 3-dimensional semidilute solution. The range for which this is valid will become evident below.

It is convenient to define

$$A = 5 kN/12 \delta R_s^2 . \quad (2.3)$$

Minimizing eq. (2.1) then gives

$$V_{3d} = \frac{4 \pi}{3} NA^4 \quad (2.4)$$

$$\xi_{3d} = A^3 \quad (2.5)$$

$$F_{3d} = -(kN/4) A^{-5} . \quad (2.6)$$

There are two limits for the validity of these expressions.

a) The weak adsorption limit :

$$\xi < R_F ; \qquad V < \frac{4 \pi}{3} R_F^3$$

leading to

$$A < R_F^{1/3} = N^{1/5} ; \qquad 5 k/12 < \delta R_s^2/N^{4/5} . \quad (2.7)$$

When the inequality (2.7) is violated the adsorption is too weak to confine the polymer. One then has

$$F_f = -3 \delta R_s^2/N^{4/5} = -(5 k/4) N^{1/5} A^{-1} > -5 k/4 \quad (2.8)$$

$$V = 4 \pi/3 R_F^3 .$$

b) As in the usual adsorption case discussed in reference [1] there is a transition to a confined two-dimensional regime when the adsorption becomes strong. The cross-over occurs when ξ becomes equal to the layer thickness (D). Thus

$$\xi < D \approx V/4 \pi R_s^2$$

$$A > 3 R_s^2/N; \qquad 5 k/12 > 3 \delta R_s^4/N^2 . \quad (2.9)$$

At the lower limit one has

$$A = 3 R_s^2/N = \left(\frac{5 k}{4 \delta}\right)^{1/2} \quad (2.10)$$

so that

$$\xi_{min} = D = (5 k/4 \delta)^{+3/2} \quad (2.11)$$

$$F = -kN/4\left(\frac{4 \delta}{5 k}\right)^{5/2} \quad (2.12)$$

where we have eliminated R_s and N to emphasize the equivalence with the adsorption results in reference [1].

One also notes that the two inequalities (2.7) and (2.9) can only be consistent when the spheres are small

$$1/3 \gtrless R_s^2/N^{6/5} = (R_s/R_F)^2 . \quad (2.13)$$

For larger spheres the 3-dimensional semidilute regime cannot occur for any value of δ.

In addition one obviously requires that the adsorption (i.e. δ) should be sufficiently strong to confine the chain in the first place :

$$\xi_{min} = \left(\frac{5 k}{4 \delta}\right)^{3/2} < R_F \quad (2.14)$$

where ξ_{min} is given by eq. (2.11). For very small δ the polymer is never confined and the energy is given by eq. (2.8). The adsorption energy per polymer and sphere is then of order $k_B T$ at most.

Since they describe cross-over all limits given above (eq. (2.7)-(2.14)) should obviously be regarded as qualitative. The numerical coefficients are given as derived but are not significant.

At the lower limit of the range (2.9) there is a cross-over to a 2-dimensional confined regime [4]. Assuming $D < R_s$ we can write the energy :

$$F_{2d} = -\frac{\delta N}{D} + k_1 N/D^{5/3} + k_2 N/D\left(\frac{N}{4 R_s^2}\right)^2 \quad (2.15)$$

where, as in reference [1] the second term is the repulsive energy of 3-dimensional blobs of size D and the third term is the repulsive energy of the two-dimensional chain of blobs confined to an area $4 \pi R_s^2$.

Matching to the 3-dimensional repulsive energy in eq. (2.1) requires

$$k \approx k_1 + (3/4)^2 k_2 . \quad (2.16)$$

The two-dimensional coherence length [3] is

$$\xi_2 = D^{1/2}\left(\frac{N}{4 R_s^2}\right)^{-3/2} \qquad (2.17)$$

$$D < \xi_2 < R_{F_2} = N^{3/4} D^{-1/4} . \qquad (2.18)$$

Minimizing eq. (2.15) gives

$$D = \{ 5 k_1/3[\delta - k_2(N/4 R_s^2)^2] \}^{3/2} \qquad (2.19)$$

$$F_{2d} = - (2 k_1 N/3) D^{-5/3} =$$

$$= - 2 N/5(5 k_1/3)^{-3/2} (\delta - k_2(N/4 R_s^2)^2)^{5/2} . \qquad (2.20)$$

In the relevant regime one must have

$$\left(\frac{5 k_1}{3 \delta}\right)^{3/2} < D < \left(\frac{5 k}{4 \delta}\right)^{3/2} \qquad (2.21)$$

where the upper limit is given by eq. (2.11) [5] and the lower limit by the large R_s limit. Finally :

$$- (2 k_1 N/3) \left(\frac{3 \delta}{5 k_1}\right)^{5/2} < F < - kN/4\left(\frac{4 \delta}{5 k}\right)^{5/2} . \qquad (2.22)$$

3. Strong adsorption and the possibility of inhomogeneous solutions.

— The discussion in section 2 did not involve any explicit limitations on the strength of the adsorption (i.e. the magnitude of δ). A trivial limitation is obvious. Clearly one must have

$$D > 1 . \qquad (3.1)$$

Thus, when the parameters of the system are such that eq. (2.19) would give a smaller thickness the expression we have used for the repulsive energy (the second term on the r.h.s. of (2.15)) is no longer adequate. The problem then becomes that of the 2-dimensional adsorption of a monolayer.

A more subtle point involves the assumption of a uniform density which was essential in all the discussion of section 2. Intuitively it does not seem obvious that this is justified in the present case. In particular for strong adsorption ($\delta > 1$) one is tempted to consider configurations where only a small segment of the chain is adsorbed on the sphere while the rest of the chain is essentially free. This is however misleading, because a chain cannot change its density in an important way in regions where there are no external forces. In the case we are considering we are presumably neglecting a weak radial variation of the density but no dramatic effects. It is of interest to show this explicitly. We assume strong adsorption

$$\delta > 1 . \qquad (3.2)$$

Now let the number of monomers in the strongly adsorbed first layer be N_1. The rest of the chain

($N - N_1$ monomers) does not interact with the surface directly. It will be attached to the directly adsorbed segments at n attachment points. In calculating the configuration of the *free* segments one therefore has to include the entropy associated with the distribution of the attachment points on the chain. The contribution to the free energy is

$$F_{at} = - \ln \left[\binom{N - N_1}{n} \cdot \binom{N_1}{n} \cdot (n \; !)^2\right] \approx$$

$$\approx - n \ln \left[(N - N_1) . N_1\right] \qquad (3.3)$$

where the last expression on the r.h.s. assumes that n is small :

$$n/N_1 \ll 1 . \qquad (3.4)$$

One notices immediately that (3.3) has the same form as the adsorption energy with δ replaced by $\ln (N - N_1).N_1$. Thus since

$$\delta_{eff} = \ln (N - N_1).N_1 \gg 1 , \quad N \gg N_1 \qquad (3.5)$$

the free part of the chain is very strongly adsorbed on the first layer. Moreover, in most cases

$$\delta_{eff} \gg \delta \qquad (3.6)$$

and, since n cannot be larger than N_1

$$n \approx N_1 \qquad (3.7)$$

when $N \gg N_1$. The argument is valid also for subsequent layers until the length N is exhausted and implies an essentially uniform or slowly varying density. For an ideal chain this sort of argument would indeed imply an exponential decay of the density with a very high value on the surface [5]. For real (self avoiding) chains the attractive surface adsorption energy has to be balanced against the repulsion of the monomers. This leads to the approach we have used in section 2. While the assumption of a constant density is actually quite good for real chains in a good solvent our approximation would still be valid, and qualitatively correct, if the density varied exponentially as for an ideal chain. The essential point is that the cost in entropy of separating a short segment from the chain, and allowing it to adsorb strongly, is extremely high.

It is obvious that the argument applies to weak adsorption ($\delta < 1$) just as well.

One notes that this situation is quite different from the case where the number of attachment points (n) is fixed e.g. for adsorbed copolymers as discussed in references [6] and [7]. Since n is determined self-consistently, one does not find stretched segments in the present case.

4. Equilibrium conditions and clusters.

— In practice one is of course interested in solutions with finite concentrations of spheres (c_s) and of polymers (c_p).

We shall assume that the adsorption energy of a single sphere (F_{ss}) is large

$$F_{ss} \gg 1 \qquad (4.1)$$

and concentrations such that :

$$F_{ss} \gg - \log c_s ; \quad - \log c_p . \qquad (4.2)$$

The interesting questions relate to situations where there is a surplus in one of the constituents. We shall assume that the spheres are small so that constituents with more than one polymer attached to a given sphere can be disregarded. The equilibrium conditions in solution are then :

$$\log c_n^c = n \log c_s' + \log c_p' - F_n \qquad (4.3)$$

$$c_{n+1}^c/c_n^c = c_s' \exp(F_{n+1} - F_n) \qquad (4.4)$$

where c_n^c is the concentration of polymer with n adsorbed spheres, F_n is the internal free energy of such a cluster and c_s' and c_p' are the concentrations of free spheres and free polymers respectively. These free concentrations (and the related chemical potentials) are of course in practice determined by the actual constraints on the system. For our discussion we regard them as given. The equilibrium conditions are then determined by F_n. Within the approximations we have used, the adsorption energy depends only on the surface area. Thus one has :

$$F_n^a = nF_f , \qquad A > nN^{1/5} \qquad (4.5a)$$

$$F_n^a = n^5 F_{3d} , \qquad 3 n^2 R_s^2/N < A < nN^{1/5} \qquad (4.5b)$$

$$F_n^a = - \left(\frac{2 N}{5}\right)\left(\frac{5 k_1}{3}\right)^{-3/2} [\lambda\delta - k_2(N/4 \, nR_s^2)^2]^{5/2} \qquad (4.5c)$$

where the expressions on the r.h.s. are given by eq. (2.8), (2.6) and (2.20) respectively by replacing R_s^2 by nR_s^2, and λ $(1 \leqslant \lambda \leqslant 2)$ is a geometrical factor. The regimes (4.5b) and (4.5c) only exist when δ is sufficiently large so that the inequality (2.14) holds. Otherwise only the uninteresting weak adsorption regime occurs.

It can be seen that F_n^a can only become convex in $n\left(\frac{\partial^2 F}{\partial n^2} > 0\right)$ in the two-dimensional regime of eq. (4.5c). This implies that the chemical potential for the spheres $(- \partial F/\partial n)$ has a maximum and stable solutions (of eq. (2.4)) will always have a most probable $n(= \bar{n})$ in the two-dimensional regime. Specifically (from (4.5c)) the condition $\partial^2 F/\partial n^2 > 0$ implies :

$$\bar{n} > (2 k_2/\lambda\delta)^{1/2}, \quad (N/4 \, R_s^2) \qquad (4.6)$$

with a larger thickness :

$$D_n \gtrsim (5 k_1/3 \, \lambda\delta)^{3/2} . \qquad (4.7)$$

We emphasize that we have assumed that any direct interaction between the spheres can be neglected. When such an interaction exist it has to be included in F_n for $n > 1$. A repulsive interaction will tend to reduce n and can stabilize the 3-dimensional regime. In particular it can lead to situations where the cluster with a single adsorbed sphere is stable in equilibrium.

5. **Clustering and phase separation.** — The above discussion has a serious defect resulting from the geometry of the problem. The clusters we have envisaged have spheres embedded inside a deformed polymer. The resulting cluster however also has an outer surface which, at the given density, is strongly attractive to spheres and will tend to attach additional spheres on the outside. The outer free surface of these spheres is in turn attractive to polymers. There is therefore an effective attractive interaction which can produce phase separation. The condensed phase would be concentrated in polymers and spheres. The effect is expected to be largest when the equilibrium n (eq. (4.6)) is ~ 1 and the outer surface therefore relatively large.

Since a discussion of the condensed phase in the analog of the two-dimensional regime is complicated by geometrical considerations we restrict ourselves to 3-dimensional regimes where the polymers can be regarded as semidilute solutions.

For a dense polymer solution of concentration c_p in which a concentration c_s of spheres is immersed one finds, in complete analogy to eq. (2.4)-(2.6) :

$$\bar{V}/V.c_p = (4 \pi/3) N(c_p/c_s)^4 A^4 \qquad (5.1)$$

$$\xi = (c_p/c_s)^3 A^3 \qquad (5.2)$$

$$F_{3d}/V = - (kNc_p/n) (c_s/c_p)^5 A^{-5} \qquad (5.3)$$

where $\bar{V}$ is the free volume available to the polymers :

$$\bar{V} = V(1 - c_s(4 \pi/3) R_s^3) . \qquad (5.4)$$

The expressions (5.2) and (5.3) remain valid when the adsorption layer gets thin so that the free volume is not fully occupied, as long as ξ remains small compared to the separation of the spheres, but the expression for the layer thickness which replaces eq. (5.1) then depends on the geometry.

The expression for the energy (eq. (5.3)) cannot represent a stable solution. It is in fact unstable with respect to both c_s and c_p. For the spheres one has

$$\mu_s = \frac{\partial F}{\partial N_s} \propto - (N_s/N_p)^4; \qquad \frac{\partial\mu_s}{\partial N_s} < 0 \qquad (5.5)$$

in analogy to our discussion of eq. (4.6). For the polymers one has

$$\mu_p = \frac{\partial F}{\partial N_p} \propto + (N_s/N_p)^5 > 0 \qquad (5.6)$$

i.e. F can be decreased by decreasing N_p. (Note that the *average* energy (F/N_p) is still negative.) This is clearly not a stable regime. In general this implies that the stable solutions are in the 2-dimensional adsorption regime which essentially represents the adsorption of the polymers on the free surfaces of an aggregate of spheres. The geometrical considerations do however become fairly delicate and we shall not attempt detailed estimates.

An interesting alternative can occur when the spheres are small i.e.

$$R_s < D_f \sim \delta^{-3/2} \tag{5.7}$$

where D_f is the adsorbed thickness of the polymer on a flat surface with the same δ. One notes that the volume $\overline{V}$ cannot shrink indefinitely (as implied by eq. (5.1)). The geometry sets a lower limit

$$\overline{V}/V > \alpha^3 \, c_s \, \frac{4 \, \pi R_s^3}{3} = \hat{V}; \qquad \alpha^3 \gtrsim 1 - \frac{\pi\sqrt{2}}{6} \sim 0.28 \tag{5.8}$$

where the r.h.s. is the free volume in the closed packed limit. Assuming this limit for the volume and minimizing the free energy one finds

$$(Nc_p/c)_{\hat{V}} = (3(4 \, \delta/k)^4 \, \alpha^3 \, R_s^{11})^{1/5} \tag{5.9}$$

where

$$c_s = [(1 + \alpha^3).4 \pi R_s^3/3]^{-1} \tag{5.10}$$

$$F/V \approx - (\delta/R_s)^{9/5}/\alpha^{12/5}(1+\alpha^3) \tag{5.11}$$

where we have omitted the less obvious constants in the last expression and retain only the power laws.

We note however that the inequality (5.7) implies :

$$\xi > R_s, \qquad \alpha R_s \tag{5.12}$$

and corrections to the free expression for the polymer repulsive energy are certainly required. It is also not obvious that completely different arrangements could not be more favourable under these circumstances. Thus eq. (5.9) and (5.11) should only be regarded as qualitative. It is however clear that as long as the

adsorption energy per polymer and per sphere is large compared to $k_B T$ one does indeed expect condensation to occur. The gain in free energy of the condensed phase should be comparable to the single sphere adsorption energy and will dominate at fairly low concentrations, when no other interactions are important.

In practice there may be difficulties in observing this transition which depend on the method of preparation because the times involved could become extremely long. A state with small clusters as the dominant species is locally stable. Thus even in the presence of a nucleus of the condensed phase its growth might very well be dominated by the very low concentrations of free chains and spheres.

6. **Relevance to micelles.** — As noted in the introduction the most obvious application of our results is to the adsorption of polymers on micelles. Stoichiometric adsorption of polymers on single micelles has been observed and studied in detail by Cabane [2]. Our results seem to imply that such behaviour must be stabilized by an effective micelle-micelle repulsion, presumably the same interaction responsible for stabilizing spherical micelles in the first place. Thus the results of section 2 should apply and the parameters of the system can be determined from the experimental results. One notes however that these results imply a surface tension which depends strongly on the chain length. One would expect this to affect the micelle size (and shape), which would compete with the fixed micelle clustering we have discussed. Other experimental situations can of course also be envisaged.

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