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ADSORPTION OF CHAIN MOLECULES WITH A POLAR HEAD A SCALING DESCRIPTION

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Résumé. — L'adsorption de molécules en chaînes à une interface est étudiée en supposant que chaque molécule présente un point d'interaction localisé sur la chaîne (du type tête polaire) et une interaction uniforme de ses monomères avec la surface. Une description en terme de lois d'échelles des configurations de chaînes et des interactions est discutée. L'existence d'une attraction de surface uniforme affecte profondément le diagramme de phase. Un régime bidimensionnel de faible densité et une phase haute densité avec les chaînes confinées dans des cylindres étroits peuvent être rencontrés. La transition entre les deux phases est du premier ordre. Les lois de puissance pour la densité à l'interface, l'épaisseur de la couche et la pression de surface sont dérivées. Le comportement des lipides et agents de surface à chaînes courtes est qualitativement semblable et il est suggéré qu'une interaction de surface uniforme peut aussi jouer un rôle important dans ce cas.

Abstract. — The adsorption of chain molecules at an interface is investigated assuming that the molecule has both a polar head type of attraction localized on the chain and a uniform interaction of the chain monomers with the surface.

A scaling description of the chain configurations and interactions is used. It is shown that the presence of a uniform surface attraction changes the phase diagram drastically. Both a low density two-dimensional regime and a high density phase with the chains confined in narrow cylinders can occur. The transition between the two phases is first order. Power laws for the surface density, layer thickness and surface pressure are derived. The qualitative similarity with the behaviour observed for short chain lipids and surfactants is also noted and it is suggested that a uniform surface interaction may also play an important role there.

1. Introduction. — Adsorption of chain molecules at an interface can occur for two qualitatively different reasons. One can have a situation where the monomers of the chain are preferred to the solvent molecules at the interface. This is the adsorption usually discussed for long chain polymers. We shall refer to it as uniform adsorption (UA). On the other hand the dominant surface attraction may be due to a specific segment of the chain e.g. a polar head. This is the typical situation for soaps and other surfactants. For long chains it could occur e.g. for suitable bloc copolymers. We shall refer to this type of adsorption as polar head adsorption (PHA). Scaling concepts have recently been applied to both problems and qualitatively different predictions for the two types of regimes have been

obtained. Uniform adsorption was discussed by de Gennes in reference [1]. It was found that the only equilibrium surface states have a relatively low surface density, the chains are spread out and can be described as a semidilute 2-dimensional solution. The radius of a chain is always much larger than the layer thickness. The PHA predictions are quite different. The surface density can become quite large, the layer thickness is, in equilibrium, always larger than the dimensions of the free chain, and the chains are found to be confined to a narrow cylinder whose cross-section is the free area per polar head. The chain configurations are thus found to be very similar to those found for short chain molecules (3). There is certainly no reason to assume that the two types of surface interaction are mutually exclusive. Our purpose here is to investigate the effect of introducing a uniform interaction into the discussion of PHA. The most interesting situation is found to occur when the PH interaction is dominant

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but a significant uniform surface attraction exists. One then predicts two types of regime, a high density PHA type of surface state passing, by a first-order transition, into a dilute UA phase as the parameters of the system are changed. This transition should be observable in suitable systems.

The asymptotic scaling description is certainly only valid for long chains. The behaviour predicted in both limits is nevertheless similar to that found for short chains. One would therefore hope that the present discussion might also be relevant to situations where relatively short chains are absorbed at an interface and in particular to situations where surface instabilities occur. We therefore believe that this possibility should be investigated in detail. This is however not attempted here.

In section 2 we discuss the conformation of adsorbed chains on an interface assuming that the density is given. Equilibrium conditions are then discussed in section 3. The results and some implications are discussed in section 4.

2. Chain conformations at fixed density. — We consider polymers of length N adsorbed at the interface of two solvents (W and O) so that the chains are in O but the polar head is attracted to W and therefore attached to the surface. We first assume that the density and therefore the area per polar head (σ) is given. The Helmholtz free energy per chain can then be written :

$$f = f_1 + f_2 \quad (2.1)$$

where f_1 includes the interaction of the polar head ($-C$) with the surface, the translational contribution to the free energy (f_{tr}) and any explicit interactions between the polar heads (f_{int}) :

$$f_1 = -C + f_{tr} + f_{int} \quad (2.2)$$

All the contributions of the chains to the free energy are included in f_2 . Following the discussion of adsorption by de Gennes in reference [1] we write :

$$f_2 = -\delta N/D + k_1 N(N/\sigma D)^{5/4} + f_s \quad (2.3)$$

where for convenience, all energies are in units of $k_B T$ and all lengths in units of the monomer dimension of the chain (a). We also follow reference [1] in using exponents derived by scaling arguments from the Flory value of ν . This applies to all exponents used later in this paper.

Since we are only attempting to derive qualitative results and power laws, we shall also omit all numerical coefficients except when they are essential for the arguments.

The first term on the r.h.s. of eq. (2.3) is the (uniform) interaction of the chain monomers with the surface where D is the thickness of the adsorbed layer.

The chain is, in the situation we are discussing, tied to the surface by the polar head. It is however clear that the interface can still prefer monomers of the chain (or molecules of O). The difference in free energy (in units $k_B T$), per monomer, is the interaction (δ) which is defined in the same way as for the uniform adsorption case [1]. The only difference is that in the present case the chains are already attached to the surface so that δ can be very small or repulsive and the chains will still be adsorbed. The form we use, following reference [1], assumes weak adsorption and should be valid, for attractive interactions, when, for a single chain on the surface :

$$D_{s,c} = (D/a) \gg 1 \quad (2.4)$$

We shall comment briefly on the strong adsorption limit, which is non-trivial in the present case, in section 4 below. For repulsive (i.e. negative) δ we shall show that the interaction is always renormalized and, as a result, unimportant.

The explicit uniform surface interaction of a chain, which is usually neglected in this context, can have a very profound effect on the adsorption process.

The second term on the r.h.s. of (2.3) is the scaling form of the repulsive energy of the polymer layer, valid as long as this layer can be regarded as a 3-dimensional semidilute solution in the sense of Daoud and de Gennes [4]. This form is thus valid as long as the 3-dimensional coherence length (ξ) obeys

$$\xi < D \quad (2.5)$$

where ξ is given by

$$\xi = \left(\frac{4\pi}{3} c \right)^{-3/4} = \left(\frac{4\pi N}{3\sigma D} \right)^{-3/4} \quad (2.6)$$

and c is the monomer density in the adsorbed layer.

The third term on the r.h.s. of eq. (2.3) (f_s) is the stretching energy of the chain. Since we will be interested in discussing situations where the surface attraction (i.e. δ) is not dominant, it is important to include this term. At a given density the semi-dilute solution can be regarded as a dense (and therefore ideal) solution of chains of blobs of dimension ξ . We express f_s as the stretching energy of these ideal chains of blobs :

$$f_s = k_2 D^2/N\xi^{1/3} = k_2 \left(\frac{4\pi}{3} \right)^{1/4} D^{7/4}/N^{3/4} \sigma^{1/4} \quad (2.7)$$

We first consider layers of given density (i.e. fixed σ), and determine D by minimizing f_2 . Depending on the relative magnitude of the three terms in f_2 (eq. (2.3)) there are 3 regimes :

a) The surface interaction is weak :

$$|\delta| \ll N\sigma^{-7/6} \quad (2.8)$$

where it should be remembered that $\sigma (= \sigma/a^2)$ can be a large number. The layer thickness is then given by the equilibrium between the repulsive energy and the stretching energy (f_s). One finds :

$$D \approx N\sigma^{-1/3} \quad (2.9)$$

$$\xi \approx \sigma^{1/2} . \quad (2.10)$$

The free energy is :

$$f_2 \approx + N\sigma^{-5/6} - \delta\sigma^{1/3} \quad (2.11)$$

where we have omitted all numerical coefficients.

When the inequality (2.8) holds the second term on the r.h.s. of (2.11) is always small compared to the first.

Two things are interesting in this result. Eq. (2.9) and (2.10) imply that the chain of blobs is fully stretched. This is essentially equivalent to the confinement of the chain in a cylinder of cross-section σ [5].

This type of confinement is essentially a geometrical effect resulting from the constraints imposed by the boundary conditions. It has been observed and studied in detail for short chain lipids [3] and de Gennes [6] has shown that it can be explained by the boundary conditions on the chains together with the requirement that the density be constant. It appears here, for long chains, for the same reasons.

One also notes that a mean-field calculation [7] gives the layer thickness (i.e. eq. (2.9)) correctly. For the free energy such a calculation predicts :

$$f_{MF} \approx N\sigma^{-2/3} \quad (2.12)$$

i.e. a slightly different power law. The difference (a factor $\sigma^{1/6}$) reflects the fact that a mean-field ansatz over-estimates both repulsive and attractive terms in the same way, as discussed by de Gennes in reference [8]. As a result it gives correct predictions for the dimensions as long as no other energies enter the problem (as in the present case). The energy is of course still overestimated.

The limits of the free PHA regime envisaged here are given by the stricter of the two inequalities (2.5) and (2.8).

The condition (2.5) is essentially a low density limit i.e. :

$$\xi \approx \sigma^{1/2} < R_F = N^{3/5} < D . \quad (2.13)$$

We note however that (2.8) only holds at the limit ($\xi \approx D$) if

$$K = N |\delta|^{5/2} \ll 1 \quad (2.14)$$

which implies that there should usually be a crossover to a regime dominated by the surface interaction when δ is positive.

One notes that the reverse is true at high densities ($\sigma \ll N^{6/7}$) where (2.8) should hold for all δ .

b) The interface is attractive and dominates the stretching energy (f_s). The results are then identical to those found in reference [1] for adsorbed polymers ; one has :

$$\delta \gg N\sigma^{-7/6}$$

$$D \approx (N/\sigma)^5 \delta^{-4} < N\sigma^{-1/3} \quad (2.15)$$

$$\xi \approx (N/\sigma\delta)^3 < \sigma^{1/2} \quad (2.16)$$

$$f_2 = - N(\delta\sigma/N)^5 < - N\sigma^{-5/6} \quad (2.17)$$

which is equivalent to eq. (2.9) and (2.10) of reference [1].

In this case (2.5) implies a cross-over to a 2-dimensional regime. Substituting (2.15) and (2.16) in (2.5) the condition becomes :

$$\delta < (N/\sigma)^2 ; \quad D > \delta^{-3/2} . \quad (2.18)$$

c) We only give the results for the 2-dimensional regime derived in detail in references [1] and [9]

$$D_{2d} \approx [\delta - k_3(N/\sigma)^2]^{-3/2} \quad (2.19)$$

$$f_2 \approx - N[\delta - k_3(N/\sigma)^2]^{5/2} . \quad (2.20)$$

The two-dimensional coherence length is :

$$\xi_2 \approx D^{1/2}(N/\sigma)^{-3/2} \quad (2.21)$$

and one requires :

$$D < \xi_2 < R_{F2} = D^{-1/4} N^{3/4} ; \quad \sigma^{1/2} < R_{F2} . \quad (2.22)$$

We note that these inequalities do in fact follow automatically if a stretching term analogous to f_s is included for the 2-dimensional stretching on the surface.

d) For completeness we also give the results when a surface repulsion of the chains is dominant. We emphasize however that the results are in fact not consistent, in the physical situation we are considering.

The layer thickness is determined by the balance between the surface repulsion and the stretching energy.

One has :

$$- \delta > N\sigma^{-7/6} \quad (2.23)$$

$$D \approx N^{7/11} \delta^{4/11} \sigma^{1/11} \quad (2.24)$$

$$\xi \approx \sigma^{9/11} (\delta/N)^{4/11} > \sigma^{1/2} \quad (2.25)$$

$$f_2 \approx \delta^{7/11} N^{4/11} / \sigma^{1/11} > N\sigma^{-5/6} . \quad (2.26)$$

It is however evident that the form we have used for the surface interaction cannot be adequate in the present case. The repulsive energy is short range and localized near the surface. It certainly cannot balance the stretching energy throughout the layer as is implied. Thus the assumption that the surface density is proportional to the average density in the layer is not adequate. There must be a depletion layer near the

surface and the functional dependence of case *a*) should still hold. A repulsive localized δ is renormalized so that the inequality (2.8) is not violated. A localized surface repulsion is thus expected to have a relatively minor effect.

3. Equilibrium conditions. — In general surface properties are studied at constant chemical potential (μ). A macroscopic bulk should provide an inexhaustible reservoir of molecules which determines μ . When the surface area becomes very large the equilibrium condition is of course still the same but the bulk concentration has to be determined from the actual constraints. In both cases equilibrium with the bulk implies that the chemical potential has to be negative. This strongly restricts the maximum surface density one can obtain in equilibrium. It is therefore important to note that the times for establishing equilibrium with the bulk may be very long so that experiments may very well correspond to situations where the chemical potential becomes positive.

In equilibrium one must have :

$$\mu = \log c_B = \mu_1 + \mu_2 \quad (3.1)$$

where c_B is the bulk concentrations of polymers and μ_1 and μ_2 are the contributions of f_1 and f_2 respectively.

For simplicity, we only discuss situations where the chain interactions are dominant, i.e. :

$$\mu_2 \gg \mu_{\text{int}} \quad (3.2)$$

so that interactions between the polar heads can be neglected. We can then write :

$$\mu_1 = -C + \log \gamma/N \quad (3.3)$$

where γ is the surface density of monomers

$$\gamma = N/\sigma \quad (3.4)$$

The chain contributions are (for $\delta > 0$)

$$\mu_2 \approx (N\gamma^5)^{1/6}; \quad \gamma > (N\delta^6)^{1/7} \quad (3.5a)$$

$$\mu_2 \approx N(\delta/\gamma)^5; \quad (N\delta^6)^{1/7} > \gamma > \delta^{1/2} \quad (3.5b)$$

$$\mu_2 \approx -N(\delta - k_3 \gamma^2)^{3/2} (\delta - 6k_3 \gamma^2); \quad (3.5c)$$

From eq. (2.11), (2.17) and (2.20) respectively.

Consider first situations when δ is repulsive or very weak (eq. (2.8)) so that it can be neglected. The crossover from the dilute to the semidilute regime occurs at a density

$$\gamma^* \approx N^{-1/5} \quad (3.6)$$

For $\gamma < \gamma^*$ the chemical potential depends on γ only through the term $\log(\gamma/N)$ in μ_1 , thus :

$$\log c_B + C < 0 \quad (3.7)$$

$$\gamma/N \approx e^C c_B \quad (3.8)$$

At high densities ($\gamma \gg \gamma^*$) μ_2 is dominant and

$$\log c_B + C > 0 \quad (3.9)$$

$$\gamma/N \approx (C/N)^{6/5} [1 + (\log c_B)/C]^{6/5} \quad (3.10)$$

Thus the layer thickness is (from (2.9)) :

$$D \approx N^{2/3} \gamma^{1/3} \approx C^{2/5} N^{3/5}$$

essentially independent of c_B in this regime. The surface pressure becomes

$$\pi = -\Sigma_0 + \gamma/N; \quad \gamma < \gamma^* \quad (3.11a)$$

$$\pi = -\Sigma_0 + N(\gamma/N)^{11/6}; \quad \gamma > \gamma^* \quad (3.11b)$$

where $-\Sigma_0$ is the surface pressure of the free WO interface.

The situation becomes considerably more complex when the surface attraction becomes significant :

$$K = N\delta^{5/2} > 1 \quad (3.12)$$

At very low densities the chains do not overlap (4)

$$\gamma < \gamma_1 = (N\delta^{3/2})^{-1/2} = (\delta/K)^{1/2} \quad (3.13)$$

so that :

$$\gamma/N \approx e^{C+\Lambda} c_B \quad (3.14)$$

$$D \approx \delta^{-3/2} \quad (3.15)$$

$$\pi = -\Sigma_0 + \gamma/N \quad (3.16)$$

At higher densities one predicts a two-dimensional semidilute regime :

$$\gamma \approx \delta^{1/2} f\left(\frac{\log c_B + C}{K}\right) \approx \delta^{1/2} \left(1 + \frac{C + \log c_B}{K}\right)^{1/2} \quad (3.17)$$

$$\bar{D} \approx [\delta - k_3 \gamma^2]^{-3/2} \quad (3.18)$$

$$\pi = -\Sigma_0 + 3k_3 \gamma^3 [\delta - k_3 \gamma^2]^{3/2} \quad (3.19)$$

To study the behaviour at higher densities it is important to notice that μ_2 is not a monotonic function of γ . It has a maximum in the 2-dimensional regime :

$$\mu_2^{\text{max}} \approx K/\sqrt{2}; \quad \gamma_{\text{max}} \approx (\delta/2k_3)^{1/2} \quad (3.20)$$

and a minimum at the crossover between (3.5a) and (3.5b) :

$$\mu_2^{\text{min}} \approx K^{2/7}; \quad \gamma_{\text{min}} \approx K^{1/7} \delta^{1/2} > \gamma_{\text{max}} \quad (3.21)$$

Thus there are no stable solutions in the intermediate regime and a first-order transition is predicted.

The position of the transition is determined by :

$$\mu(\gamma_l) = \mu(\gamma_h) = \mu \quad (3.22a)$$

$$\pi(\gamma_l) = \pi(\gamma_h) \quad (3.22b)$$

This type of behaviour where the adsorbed layer displays two qualitatively different regimes is expected as long as K is not too large

$$1 < K \lesssim C. \quad (3.23)$$

When K is very large only the 2-dimensional uniform adsorption regime is stable in equilibrium because μ becomes positive. One notes however that the reduction of the surface density involves removal of polymers to the bulk which may be a very slow process for long chains.

4. Discussion. — The main conclusion of our analysis is the prediction of a very dramatic effect of a small surface attraction ($K < C$).

One predicts a transition from a high density ($\sim N^{-1/5} C^{6/5}$) with a layer thickness larger than R_F to a low density regime ($\gamma \sim \delta^{1/2}$; $D \sim \delta^{-3/2}$) in equilibrium. This should be observable even for fairly short chains where the scaling exponents would of course no longer be applicable.

A number of points should be noted :

a) We have assumed weak adsorption ($\delta < 1$). If δ becomes large the expressions for the two-dimensional regime are modified because the layer thickness cannot decrease below $D = 1$. A transition is nevertheless predicted. Near $\gamma = 1$ the repulsive energy of the monolayer becomes large and one expects a transition to a PHA type state.

b) An explicit polar head repulsion (e.g. a screened coulomb interaction) will add a contribution $\mu_{\text{int}} \sim \gamma$ to the chemical potential and $\Delta\pi \approx \gamma^2$ to the pressure. In any case this is not drastically different from the chain repulsion terms we have obtained. Such a repulsion would tend to stabilize the low density UA phase.

Finally, as mentioned earlier, it is not at all obvious that the high density phase will not be observed experimentally even in the absence of a polar head interaction. The chemical potential of such a state is of course always positive (for $C = 0$). Nevertheless the times involved in removing the adsorbed molecules to the bulk may be so long that one is in practice working with a fixed number of molecules in the surface. Under these conditions a first-order transition to the PHA phase is to be expected.

Taking e.g. the experimental results of Ober and Vilanove [10] and of reference [11] one finds, omitting the term $-\Sigma_0$ in eq. (3.19) and fitting the result to their data :

$$\delta \approx 2^{1/2} (3 k_3/5)^{1/6} \approx 1 \quad (4.1)$$

and a transition is predicted for ($\gamma \approx \delta^{1/2}$)

$$c_s = \left(\frac{3 k_3}{10} \right)^{1/2} \text{ mg/m}^2 \quad (4.2)$$

not far above the densities they investigated.

We note that we have fitted both δ and the numerical constant (a^2/M) [12] relating γ and ($c_s = \gamma a^2/M$) from the two leading terms they measure in the expansion of the pressure.

Using molecular values for M and a^2 does not change the result significantly. The results in the semidilute regime thus seem in good agreement with our predictions. We note however that the N-dependence of the cross-over to the dilute regime seems too weak to agree with eq. (3.12).

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