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Charged copolymers at an interface : a model

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Résumé. — Dans cette lettre on étudie la conformation et l'énergie libre de copolymères bi-séquencés formés d'une séquence hydrophobe neutre et d'une séquence polyelectrolyte soluble dans l'eau, à une interface eau-huile ou eau-air. On restreint l'étude à la séquence chargée. On montre qu'à toutes les concentrations le polyelectrolyte reste étiré. Dans le régime semi-dilué, il y a une seule longueur caractéristique égale à la distance entre chaînes; la pression de surface a le même ordre de grandeur que la pression osmotique des contre-ions.

Abstract. — In this letter we investigate the conformation and free energy of diblock copolymers containing a neutral hydrophobic and a water-soluble polyelectrolyte sequence, at an oil-water or air-water interface. We restrict ourselves to the study of the charged sequence. We show that at all concentrations the polyelectrolyte remains fully stretched. In the semi-dilute regime there is one characteristic length scale, the inter-chain distance; the surface pressure has the same order of magnitude as the counterion osmotic pressure.

1. The system.

We consider a diblock copolymer film, at an oil-water or air-water interface; the first sequence is neutral and water-insoluble, whereas the second one is a water-soluble polyelectrolyte. We assume that the configuration of the copolymer at the interface is that shown on the figure (hydrophobic part (not shown) in oil or air, hydrophilic part in water). In such a film the surface pressure is expected to be the sum of two contributions [1]: one from the neutral layer, the other from the charged layer. The first contribution has been already studied [1-3]. The present note deals only with the second contribution.

2. The method.

In a first part we examine the electrostatics and geometry of the layer (i.e. electrical potential, counterion concentration profile, layer thickness), following closely the Gouy-Chapman treatment of the ionic double-layer [4, 5]. Then we study the different contributions to the free energy, and derive the surface pressure.

Fig. 1. — Representation of the ionized layer.

3. Geometry of the charged layer.

The polyelectrolytes considered here carry N ionizable monomers of charge e ($N \gg 1$, $e > 0$), separated by the Bjerrum length $l = \frac{e^2}{\epsilon kT}$ (where T is the temperature, k the Boltzmann constant and ϵ the dielectric constant of water). In other words we are at the condensation threshold [6]. Let us call c the monomer concentration (number of charged monomer per unit surface of the film) and L the layer thickness (Fig. 1). In the mean-field approximation the electrical potential ϕ , the ionic densities ρ_+ and ρ_- only depend on x , the distance from the surface. In this approximation the charge distribution $\rho_+(x)$ of the polyions is given by

$$\begin{cases} \rho_+(x) = \frac{c}{L} & \text{if } 0 < x < L \\ \rho_+(x) = 0 & \text{if } x > L, \end{cases}$$

while the counterion distribution is :

$$\rho_-(x) = \rho_- \exp\left[\frac{e\phi(x)}{kT}\right],$$

where ρ_- remains to be determined.

On the other hand, $\phi(x)$ obeys Poisson's equation :

$$\frac{d^2\phi}{dx^2} + 4\pi \frac{e}{\epsilon} (\rho_+(x) - \rho_-(x)) = 0.$$

Letting $\kappa^2 = 4\pi l \frac{c}{L}$, we obtain the Poisson-Boltzmann equation

$$\begin{cases} 0 = \frac{d^2}{dx^2} \left(\frac{e\phi(x)}{kT} \right) + \kappa^2 \left(1 - \frac{\rho_- L}{c} \exp\left(\frac{e\phi}{kT}\right) \right) & \text{if } 0 < x < L \\ 0 = \frac{d^2}{dx^2} \left(\frac{e\phi(x)}{kT} \right) + 4\pi l \rho_- \exp\left(\frac{e\phi}{kT}\right) & \text{if } x > L, \end{cases}$$

to which we must add boundary conditions

- $\phi(x)$ and $E(x) = -\frac{d\phi}{dx}$ are continuous for $x = L$;
- the surface electric field $E(0)$ vanishes.

An exactly identical problem was examined by L. Auvray, J. F. Joanny and P. Pincus [7], and we simply reproduce here their main conclusions in the special case $\kappa L \ll 1$ (thick layer) which will be of interest here :

- the counterions are trapped in the region $0 < x < L$;
- in this region the potentials are weak ($e(\phi(0) - \phi(x)) < kT$), so that the Debye-Hückel approximation is valid;
- outside ($x > L$), the electric field decreases with a characteristic length κ^{-1} , the Debye screening length ($\kappa^{-1} \ll L$).

The thickness L has not been determined yet. If the chains are stretched, L is of order Nl . This is certainly the case when they are not overlapping, i.e. when :

$$c \ll c^* = \frac{N}{(Nl)^2} = \frac{1}{Nl^2} \quad (\text{dilute regime}).$$

In this regime the parameter $kL = (cNl^2)^{1/2} \ll 1$. For $c \approx c^*$, kL is of order unity.

In the semi-dilute regime ($c^* < c < Nl^{-2}$) which will be studied here, we find L following Cantor's line of reasoning in the problem of neutral copolymer monolayers [1]. Assuming $\kappa L \gg 1$, we compute the mean-field free energy $F(L)$ as a function of L .

a) The energy per chain is the sum of the self-energy of a chain and of the energy of interaction with the neighbouring chains. The polyion being stretched on scale κ^{-1} , the calculation of reference [8] is valid and gives a self-energy per monomer :

$$- kT \ln(\kappa l). \quad (1)$$

To compute the interaction energy, we have to know the mean distance d between monomers of two different chains. Considering that each chain is located inside a tube of diameter d , in which other polyions do not penetrate, and that these tubes densely fill space, we can get the monomer concentration, c/L , using a cylindrical volume of base d and length κ^{-1} , centred around a given polyion. The volume $d^2 \kappa^{-1}$ contains κ^{-1}/l monomers, so that (apart from a numerical factor of order unity) :

$$\frac{c}{L} \sim \frac{\kappa^{-1}}{l} \cdot \frac{1}{d^2 \kappa^{-1}}$$

i.e. $d \sim \kappa^{-1}$, the range of the potential. Thus each monomer interacts with (about) κ^{-1}/l monomers of the neighbouring chains, giving an interaction energy :

$$\frac{e^2}{\epsilon d} \cdot \frac{\kappa^{-1}}{l} \sim kT. \quad (2)$$

The total electrostatic energy is the sum of (1) and (2) :

$$F_{\text{el/monomer}} = - kT \ln(\kappa l) + \alpha kT \quad (3)$$

α being a pure number.

b) The entropy per chain comes from the stretching of the chain and from the counterion atmosphere. The first term is, in the Flory theory (1) :

$$- \frac{3}{2} \frac{L^2}{Nl^2} \quad (4)$$

while the second is an ideal gas term [7, 11] :

$$- \text{Ln} \left(\frac{c}{L} T^{3/2} \right) \quad (\text{per monomer}). \quad (5)$$

We get thus the entropic contribution to the free energy (4) + (5) :

$$\frac{F_{\text{ent/monomer}}}{kT} = \frac{3}{2} \frac{L^2}{N^2 l^2} + \text{Ln} \left(\frac{c}{L} T^{3/2} \right). \quad (6)$$

Consequently the total free energy $F(L)$ is (3) + (6) :

$$\frac{F(L)}{kT} / \text{monomer} = - \text{Ln}(\kappa l) + \alpha + \frac{3}{2} \frac{L^2}{N^2 l^2} + \text{Ln} \left(\frac{c}{L} T^{3/2} \right). \quad (7)$$

The minimization with respect to L gives :

$$0 = - \frac{1}{2L} + 3 \frac{L}{N^2 l^2} \quad L \sim Nl.$$

The chains are essentially stretched in the semi-dilute regime, whatever the value of N , in striking contrast with the case of neutral chains [1-3]. A change in N only modifies the concentration of first contact c^* .

Finally, we obtain the screening length : $\kappa^{-1} \sim \left(\frac{c}{N} \right)^{-1/2} \sim d$, the mean inter-chain distance. Indeed, $d \ll L$ if $c \gg c^*$.

4. Surface pressure.

In this part we compute the Langmuir surface pressure $\pi = - \frac{\partial F}{\partial A}$ (A being the film area).

The free energy takes the form :

$$\frac{F}{kT} / \text{monomer} = - \text{Ln} \left(\frac{c}{N} \right)^{1/2} l + \text{Ln} \left(\frac{c}{Nl} T^{3/2} \right) + \alpha + \frac{1}{4}.$$

π , as well as F , can be viewed as the sum of an electrostatic and of an entropic contribution. The first one :

$$\pi_{\text{el}} = - \frac{1}{2} kTc$$

is negative and contains no contribution from the repulsive energy between polyions, as generally expected in the description of charged monolayers [9, 10]. In our case, this comes from the fact that the range κ^{-1} scales like the inter-chain distance d . The second contribution :

$$\pi_{\text{ent.}} = kTc$$

corresponds to that of the ideal gas of counterions confined in the layer, as in three-dimensional polyelectrolyte solutions [8, 11].

Finally the total pressure is :

$$\pi = \frac{1}{2} kTc.$$

The three features — π linear in c , independent of N , and order of magnitude kTc — have been checked in recent experiments on diblock copolymers in which the contribution of the neutral layer could be experimentally measured [12].

5. Conclusion.

In this letter, we have described in detail a simple model for charged block-copolymer monolayers on salt-free water. We have proved that the polyelectrolyte sequence is always stretched. In the semi-dilute regime, the Langmuir pressure is half the counterion osmotic pressure. So the conformation, but not the pressure, deviates from the case of three-dimensional polyelectrolyte solutions.

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