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Scaling theory of polymer solutions trapped in small pores : the θ -solvent case

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Abstract. — We study theoretically the behavior of a single macromolecular chain dissolved in a θ -solvent and confined in a tube with a diameter D comparable to the natural size ($R_0 = N^{1/2}a$) of the chain (N being the number of monomers of the chain). We find that for $D \ll R_0$ the longitudinal dimension R_{\parallel} of the chain increases as $R_{\parallel} \cong Na (a/D)$, in contrast with the longitudinal behavior of an ideal chain which is unaffected by the confinement. We show that this extension of the chain is a consequence of the three-body interactions which are still present at the Flory temperature. We then generalize these results to semi-dilute solutions where the overlap between different chains is significant.

1. Introduction.

The properties of flexible polymer chains moving inside porous structures are relevant to many practical problems such as filtration, gel permeation chromatography, oil recovery etc. [1]. Recently a large number of studies have been devoted to the properties of polymers in confined geometry [1-5]. In particular, Daoud and de Gennes [1] have analyzed in detail the theoretical behavior of macromolecular chains dissolved in a *good solvent* and confined into tubes of diameter D comparable to the coil radius. The case of macromolecular chains dissolved in a θ -solvent and squeezed in a tube has (to the best of our knowledge) not yet been addressed in the literature [6]. The problem is interesting because we know that : (1) the behavior of a single, unconfined chain at the Flory temperature is similar to the behavior of an ideal chain (i.e. a random walk), and (2) the longitudinal dimension of an ideal chain trapped in a tube is unperturbed by the confinement [7]. Since for very small tubes the real chain (dissolved in the θ -solvent) must be fully extended, its behavior must at some point depart from that of an ideal chain.

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In section 2, we discuss the single chain problem. In section 3, we consider the semi-dilute case where the overlap between different chains is significant. Our analysis is restricted to scaling laws; the exact prefactors in all our formulas remain unknown.

2. The single chain problem.

Let us start from a single chain immersed in a θ -solvent. The coil behaves like an ideal chain with a radius of the form :

$$R, \cong N^{1/2} a \quad (1)$$

where N is the polymerization index and a the monomer size [8].

We now confine the chain in a cylindrical pore of diameter D (the precise shape of the cross-section is not important for our scaling arguments). We assume that polymer adsorption on the solid wall is negligible. If $D \gg R_0 = N^{1/2} a$ no change in the behavior of the chain is expected : the chain remains ideal. But if $D < R$, the chain is squeezed into a « cigar » of length R_{\parallel} . The Flory free energy of the confined chain is then given by

$$\frac{F}{kT} \cong \frac{R_{\parallel}^2}{a^2 N} + \frac{w^2 N^3}{(R_{\parallel} D^2)^2} \quad (2)$$

where $w^2 (\approx a^6)$ is the third virial coefficient. The first term of equation (2) is an elastic deformation energy. The second term is a repulsive term due to three-body interactions. (The usual repulsive term $vN^2/(R_{\parallel} D^2)$ is absent since the two-body interactions vanish at the Flory temperature).

From equation (2) one can define a perturbation parameter as $\zeta = w^2 N^3 / (R_0 D^2)^2 \cong N^2 (a/D)^4$. For $D < R_0$ the perturbation parameter ζ is large and the chain is swollen ($R_{\parallel} > R_0$). The length R_{\parallel} of the chain can be derived directly by minimizing the free energy (2). This leads to :

$$R_{\parallel} \cong N a \left(\frac{a}{D} \right) \quad (D < R_0) \quad (3)$$

The result (3) can also be derived from scaling arguments by writing

$$R_{\parallel} \cong R_0 h \left(\frac{R_0}{D} \right) \quad (4)$$

where the dimensionless function $h(x)$ has the following features : $h(x) \rightarrow 1$ for $x \rightarrow 0$ and $h(x) \rightarrow x^m$ when $x \rightarrow +\infty$. The value of m is obtained from the requirement that R_{\parallel} is a linear function of N for a thin tube ($x \rightarrow +\infty$) :

$$\begin{aligned} R_0 (R_0/D)^m &\cong N^{(m+1)/2} (a/D)^m \\ (m+1)/2 &= 1 \\ R_{\parallel} &\cong aN (a/D) \end{aligned} \quad (5)$$

in agreement with equation (3).

Another derivation of equation (3) is based on a « blob » picture. The chain can be pictured as a sequence of blob of diameter D (see Fig. 1). At scales smaller than D the effects of the boundaries are weak and the chain behaves as an unconstrained chain. At scales greater than D the chain can be described as a sequence of blobs of size D , each containing

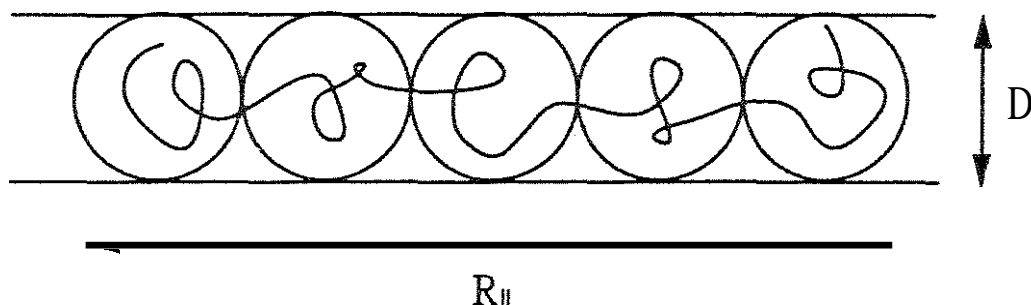


Fig. 1. — Conformation of a single chain immersed in a θ -solvent and trapped in a capillary of diameter $D (\ll R_0)$. The chain can be described as a linear sequence of blob of size D each containing N/g monomers. Within one blob the behavior is ideal ($g \cong (D/a)^2$). At larger scales the N/g blobs repel each other leading to an overall size $R_{||} = (N/g)D$.

$g \cong (D/a)^2$ monomers. The N/g blobs repel each other, leading to an overall length :

$$R_{||} \cong (N/g)D. \quad (6)$$

One can check that equations (6) and (3) do coincide.

Let us now consider the confinement energy F . It must be of the form :

$$\frac{F}{kT} \cong s \left(\frac{R_0}{D} \right) \quad (7)$$

where $s(x) \rightarrow 1$ for $x \rightarrow 0$ and $s(x) \rightarrow x^n$ when $x \rightarrow +\infty$. The value of n is obtained from the requirement that F be an extensive function of N :

$$(R_0/D)^n \cong N^{n/2} (a/D)^n$$

$$\frac{F}{kT} \cong N \left(\frac{a}{D} \right)^2 \quad (8)$$

equation (8) can be rewritten as $F \cong kT (N/g)$: the energy F corresponds to the loss of entropy due to the confinement of N/g blobs. Note that equation (8) is identical (up to numerical prefactors) to the confinement energy of an ideal chain [7], despite the fact that their respective behaviors are very different.

The free energy F can be obtained by measuring the partition coefficient (i.e. the ratio of concentration inside the *pore* to the concentration outside) for a pore exchanging chains with a bulk solution :

$$\frac{C_{\text{pore}}}{C_{\text{bulk}}} \cong \exp - (F/kT) \quad (9)$$

It is also of some interest to consider the internal filling fraction $f = Na^3/R_{||} D^2$. It scales according to :

$$f \cong a/D \quad (10)$$

and is independent of N . Note that f is smaller than the ideal value $f_0 \cong N^{1/2}(a/D)^2$ and reaches a value of order unity only when $D \cong a$.

3. The semi-dilute solution.

We now increase the number of chains inside the tube (we assume $D < R_0$). Above the critical concentration :

$$\Phi^* = Na^3/R_{\parallel} D^2 \cong a/D \quad (11)$$

the different chains overlap. **As** in the case of a good solvent [7], the transition from $\Phi < \Phi^*$ to $\Phi > \Phi^*$ is very different from what happens in three dimensions. If one tries to define a correlation length of the form

$$\xi' = R_{\parallel} (\Phi/\Phi^*)^p \quad (12)$$

one finds that no value of the exponent p would lead to ξ' which is independent of N (since Φ^* is independent of N). The physical answer is the following [7] : as soon as $\Phi > \Phi^*$ the three dimensional correlation length $\xi = a\Phi^{-1}$ becomes smaller than the tube diameter D and all local correlation properties return to their three dimensional value. In particular, the osmotic pressure is given by :

$$\Pi \cong \frac{kT}{a^3} \Phi^3 \quad (\Phi^* \ll \Phi \ll 1). \quad (13)$$

4. Conclusion.

We have extended the analysis of Daoud and de Gennes [1] to the case of macromolecular chains dissolved in a θ -solvent and confined in tubes of diameter D . For $D \gg R_0$ the longitudinal dimension R_{\parallel} of the chain is unperturbed ($R_{\parallel} \cong R_0$). For $D \ll R_0$, the size R_{\parallel} increases as $R_{\parallel} \cong Na(a/D)$. We have shown that this extension of the chain is a consequence of the three-body interactions.

It is of some interest to compare these results with the conformations of individual chains for a monodisperse melt (N monomers per chain) confined in a tube of diameter D [2], since in both cases the unconfined chain is ideal. In the melt case the two-body interactions are screened out. **As** shown by Brochard and de Gennes [2], this phenomena leads to the following results : as long as $D \gg aN^{1/4}$ the longitudinal dimension R_{\parallel} of the chain is unperturbed ($R_{\parallel} \cong R_0$). For $D \ll aN^{1/4}$, the size R_{\parallel} increases as $R_{\parallel} \cong Na^3/D^2$.

It is hoped that future experiments (e.g. in ternary solutions : lipid + water + polymer) and computer simulations will allow a test of the predictions presented in this work.

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