Exercise 5: Ultrafiltration of Macromolecules

Introduction

We focus on macromolecules passing through nanopores. These phenomena can be generated in order to perform ultra-filtration of molecules of various sizes and shapes: this is the topic of today´s exercise. The first part will be dedicated to linear flexible chains forced through nanopores. In a second part, we will extend the Flory model of linear chains to star shapes macromolecules. Finally this result will be used to deduce the behavior of star shaped macromolecules in a flow facing a nanopore.

More generally, this topic is of interest for the life science where proteins or DNA, RNA molecules have to migrate for various locations within a cell and also outside of their original cell. It also appears in the field of microfluidics when used with biological material for diagnostics for example or in analytical chemistry especially for electrophoresis or size exclusion chromatography.

1) Linear Chain

We consider a linear chain of polymer made of *N* monomers of typical size *a*. We will assume that the polymer is flexible having a persistence length of *a*.

1) Can you give the expression of the polymer coil size *R* considering the isolated chain is in the solvent theta? How is this expression modified in a good solvent? What is the origin of this modification?

We now consider the polymer in a good solvent facing a nano-pore. In this problem, the polymer does not adsorb on the tube surface; the tube diameter *D* is smaller than the polymer size R and the tube cross section is constant (no rugosity). We depict the chain which has partially entered into the pore over a length *l* larger than *D* as a sequence of blobs, each of size *D*, see figure 1 [1].

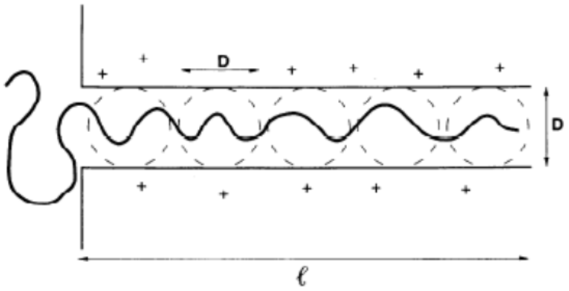

Figure 1: a polymer chain which has partially entered into a nanopore of diameter *D*.

2) Using Flory´s law, give the expression of g_D the number of monomer per blob? Assuming the confinement energy per blob is of the order of *kT*, give the expression of the confinement energy for a chain which has entered of a distance l. What is the energy required to insert a full chain into the tube which then exhibits a length *L*? Replacing g_D by its expression, give the corresponding energy as a function of *kT*, *R* and *D*.

3) What can you deduce from the previous calculation regarding the selectivity of such membranes for linear chain in absence of flows? Note that the permeation coefficient of such a membrane is proportional to exp(-E/kT) where *E* is the confinement energy. How can this be used for gel permeation chromatography?

We now want to force the chains in the pore by using a strong flow. We introduce *J* the solvent volume flowing through the pore per unit of time, see figure 2 [1]. The solvent viscosity is noted η.

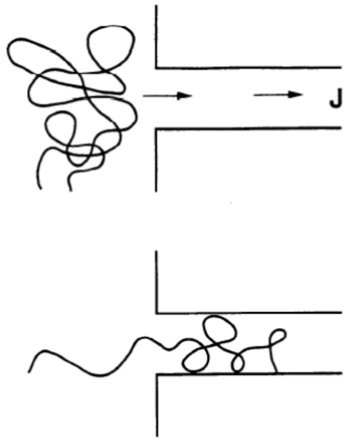

Figure 2: a polymer chain facing a nanopore (top) and forced to pass through (bottom), from [1].

4) What is the typical drag force to which each blob is subjected to? Deduce the overall hydrodynamic force for a chain which entered in the pore of a distance l? What is the smallest hydrodynamic force available? What can you deduce regarding the movement of a chain which just entered the pore? Deduce the velocity/flow rate threshold leading to the permeation of a chain.

2) Star shaped polymers

Let us think of a star with f arms, each of N monomers, the total number of monomers is thus given by X=fN. We assume long arms i.e $N \gg f^{1/2}$

5) With the help of the figure 3, explain why in a dilute solution of good solvent, these stars exhibit a radius $\mathbf{R=a\, N^{3/5} f^{1/5}}$.

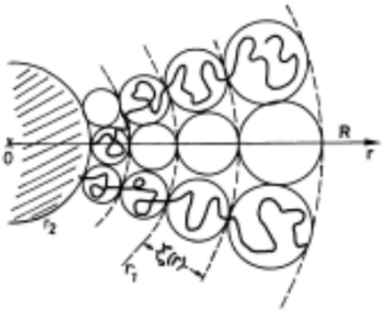

Figure 3: Star polymer, from [2]. Excluded volume is screened till a certain radius. From this radius on, each branch can be seen as a succession of blobs of size ξ(r).

3) Star polymers facing nano pores

Consider now the star inserted in a tube of diameter $D<R$ and assume that the arms extend over lengths much larger than D. Then each arm is essentially uniformly stretched. As we are going to see later, the conformation corresponding to the lowest energy is symmetric meaning that $f^*=f/2$ arms are forward and f^* arms backward. This configuration is depicted in figure 4 [1]. No flow is applied.

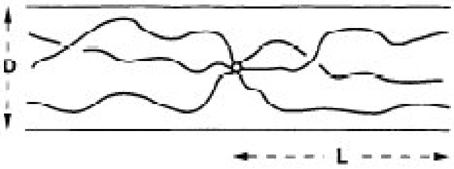

Figure 4: Star polymer in a pore of diameter D showing “symmetric” configuration, from [1].

6) What is the expression of ξ the cross section available for each arm? Deduce the stretched length of one arm.

7) Write the expression of the minimal diameter allowing the passage of the polymer. We will consider that the minimal diameter is reached when $\xi=a$ i.e. when no solvent is left.

We keep considering that the energy of confinement is in the order of kT for each blob.

8) What is the energy F of confinement of the star?

Using the result of question 6, show that this energy can be rewritten as $F=kTN(a/D)^{5/3}f^{11/6}$ Comment on the variation of F with f.

Let´s now consider the same polymer and the same pore in the presence of a flow, slightly above the threshold found in the first part of this exercise. It has been observed that under such a flow, the symmetric mode described above is not necessarily the most observed mode. Instead, the star enters the pore due to the aspiration of one branch, see figure 5.

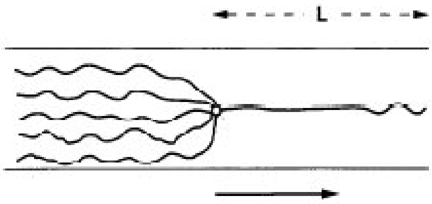

Figure 5: Star polymer in a pore of diameter D with a strong flow, from [1].

9) Can you give a qualitative explanation to this observation?

References :

[1] Flexible Polymers in Nanopores, Pierre Gilles de Gennes (1999)

[2] Brochard lectures « soft matter and polymers » (2005)