ICFP M2 – SOFT MATTER PHYSICS
Tutorial 8. Polymer chain through a pore

Jean-Marc Di Meglio and Thomas Salez

Due to the Saffman-Taylor instability, oil extraction by water injection into porous-soil reservoirs has a limited efficiency. Increasing the viscosity of water using the addition of polymers was thus a natural idea. In a very different field, the translocation of DNA molecules through a membrane pore is central to some biological processes. Besides, we know that excluded-volume effects are more pronounced in lower dimensions. Therefore, the understanding of the conformation and dynamics of a real polymer chain of N monomers of size a, in a good solvant, inside a pore appears crucial. Before attacking this matter, we recall the "blob" concept for a semi-dilute solution, and we address the neighbouring problem of a real chain under external traction.

I The blob concept

Let us consider a semi-dilute polymer solution with a good (athermal) solvant. Therein, all the chains form an average transient network of mesh size ξ. We may thus see the solution as a closely packed succession of units – the blobs – of size ξ. A given chain is itself a succession of blobs inside which the chain does not interact with other chains. It can be shown that on larger distances than ξ the excluded-volume interactions are screened ("Flory theorem").

1 What is the minimal monomeric volume fraction ϕ^* for a polymer solution to be defined as "semi-dilute" ? And the melt volume fraction ?

2 How many monomers are present in one given blob ?

3 Express ξ in terms of the monomeric volume fraction ϕ, and depict the blobs for the range of interest : $\phi^* < \phi < 1$.

4 In the same concentration range, describe the average end-to-end radius of a chain as a function of ϕ (Daoud's result).

II Chain under traction

There is a geometrical similarity between a confined chain in a pore and a chain extended by pulling on its extremities through a force $\mathbf{f}$ (of norm f). We focus on the latter problem, as studied by Pincus. We consider a dilute solution, with a good (athermal) solvant at temperature T.

1 What are the typical sizes of the problem, and in particular the one, d, associated with the force ?

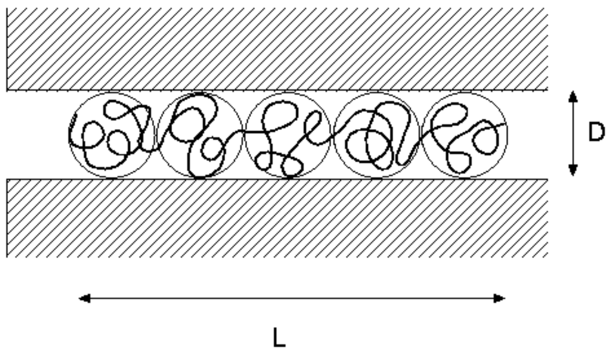
2 By dimensional analysis, provide the expected expression for the norm L of the average end-to-end vector. Show that $L \sim N^{6/5} a^2 f/(k_\mathrm{B}T)$ in the low-force limit, and interpret the N dependence by comparing to the ideal case.

3 At sufficiently large forces (keeping $fa \ll k_\mathrm{B}T$), we assume that the chain can be divided into consecutive blobs of size d. Inside those, the force has no influence, while it aligns the blobs into a straight assembly. Discuss the force-elongation relation.

4 Discuss why the expected form of the entropy reduction is $\Delta S \sim -k_\mathrm{B} \left[L/\left(N^{3/5}a\right)\right]^\alpha$ in the large-force limit. Specify the exponent α by free-energy minimization, and provide the resulting free energy.

III Confinement energy

We consider a chain in a good (athermal) solvant inside a cylindrical channel of diameter D much smaller than the end-to-end radius of the free chain, but still much larger than the monomer size. The diameter defines a length scale below which the chain is free – and thus blobs by definition.



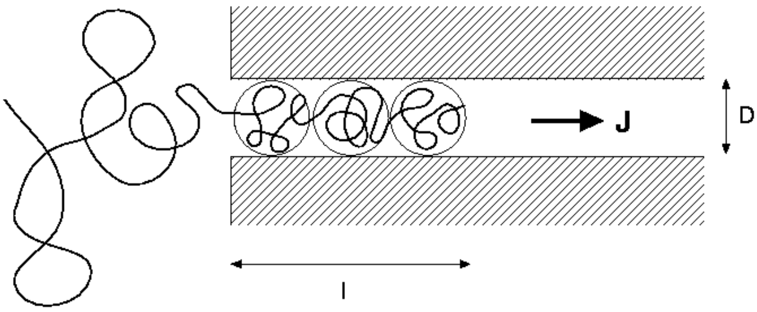
1 Estimate the extent L of the confined chain ?

2 By dimensional analysis, provide the form of the confinement free energy.

3 What must be the dependence of the latter with N ? Deduce the free energy per blob.

4 Compare the results to the ideal case, and to the previous traction problem.

IV Suction dynamics



Considering the previous pore, we now apply a flux J in the solvant of viscosity η, in order to push the chain inside the confined region.

1 Why is a nonzero flux important ?

2 What is the fluid velocity inside the pore ?

3 Express the confinement free energy for a penetration length l.

4 Assuming each blob is a rigid object, what is the viscous force exerted on the chain inside the pore ? Estimate the corresponding work.

5 Represent the total free energy of the chain as a function of l and deduce the critical flux for pore invasion. Why is the mechanism referred to as "suction" ?