M2 International Centre for Fundamental Physics **2016 – 2017**
Soft matter examination

Scaling theory of stretched polymers in nanoslits

(*Macromolecules* **46** (2013) 7989-8002)

Friday, January 6th, 2016

Duration 4h00. Documents allowed. Telephone and internet access not allowed.

NB: in all scaling results, numerical prefactors can be omitted.

1. Make a drawing to sketch the two different situations of confinement (*i.e.* de Gennes and Odijk) in a channel.

2. In the introduction, the authors explain that it is possible to use fluorescence microscopy to probe the configuration of a confined polymer single strand. Could you then describe a possible experiment for such a task?

3. What does *partial blobs draining* mean? (introduction)

4. Let us consider a single chain made of N monomers of size (width) w.
 a) What is the contour length L of the chain? What is its radius R_0? (the chain is considered as ideal).
 b) What is the radius R_F of this chain in presence of excluded volume ? (assuming a good solvent situation with an excluded volume parameter $v = w^3$). It is asked to derive R_F from the free energy of a single chain in solution (Flory's derivation).
 c) It is now assumed that the chain (N monomers of size w) is *semi-rigid*. It can be considered as made of connected rods (width w and (persistence) length P). What is the chain radius R_0 for a chain considered as Gaussian? (as a function of N, w and P).
 d) The semi-rigid chain is in a good solvent. Determine the excluded volume parameter v in this situation (as a function of w and P) (hint: think about the Onsager excluded volume in the theory of liquid crystals). What is the Flory radius R_F of the semi-rigid chain in a good solvent? (as a function of L, w and P).

5) Using the results of the previous question, derive equations (1) and (2) of the article for a chain confined in a cylindrical channel of radius h in the de Gennes regime ($h \gg P$).

6) Sketch schematically the situation described in the article for the definition of the *recoiling* force. If the chain is forced to enter the cylindrical channel by flushing the solvent, deduce from this force the critical hydrodynamic flow J_c needed to push the chain into the channel (the viscosity of the solvent is η).

7) Using equations (1) and (2), express the free energy of the confined chain as a function of the extension of the chain $R^{\mathrm{deG}}_{\mathrm{channel}}$. Deduce from this expression the spring stiffness of the confined chain (equation (5)). Compare, in the case of a flexible chain in a θ situation, this expression with the spring stiffness of an unconfined chain. Comment. Describe a possible experiment to determine the spring stiffness of a confined chain.

8) We would like to derive the expression of the characteristic Odijk length λ : $\lambda = h^{2/3}P^{1/3}$ where h is the confinement size and P the persistence length of the chain.

a) The free energy of curvature F_c of a rigid rod (per unit length) is given by:

$$F_c = \frac{1}{2}\frac{\kappa}{R^2}$$

where R is the radius of curvature of the rod (supposed to be straight in absence of any force) and κ an elastic constant. What is the dimension of κ? Give a reasonable expression of κ for a semi-rigid polymer as a function of the thermal energy k_BT and the persistence length P.

b) Sketch a string of *deflection rodlets* of length λ inside a channel of diameter h. Give an estimation of a typical radius of curvature for this string (as a function of h and λ).(hint: think about the curvature as a second derivative).

c) Using the equipartition of the energy, and defining the size of a statistical unit in the channel, deduce the expression of λ as a function of h and P.

9) What is the radius of an ideal flexible chain (N monomers of size w) in 2 dimensions? What is the Flory radius R_F of a chain with an excluded volume parameter $v = w^3$ in 2 dimensions? (use the Flory derivation).

10) Deduce from the behaviour of the 2D Flory radius with N the expressions of equations (14) and (15) (de Gennes regime).

11) Establish equation (19) (Odijk regime) to prove the result of equation (20).

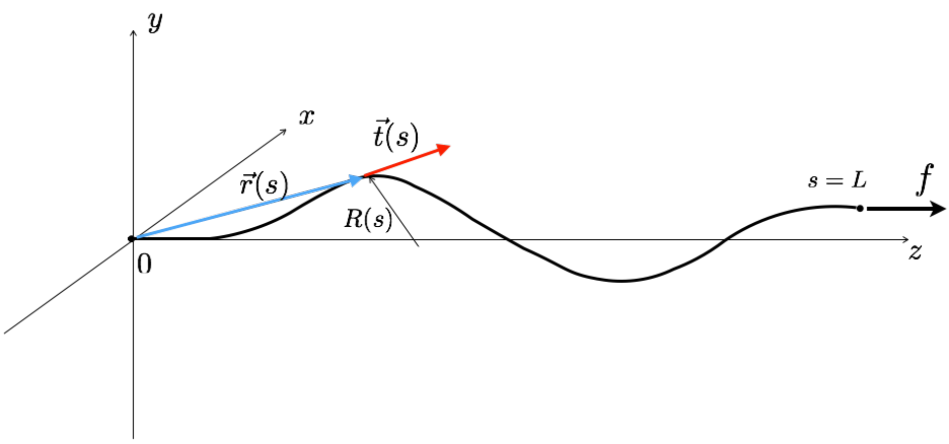
12) We aim to derive in this question the WLC (*worm like chain*) expression on which is based equation (32).

a) We have seen in the lecture that the FJC ((*freely joint chain*) expression for the force-extension of an ideal flexible chain made of N monomers of size w is given by:

$$z = Nw\,\mathcal{L}\left(\frac{fw}{k_BT}\right) = Nw\left(\coth\frac{fw}{k_BT} - \frac{k_BT}{fw}\right)$$

where z is the extension of the chain submitted to a stretching force f ($\mathcal{L}(x)$ is the so-called Langevin equation). Give a sketch of the graph of $z/(Nw)$ versus $fw/(k_BT)$ and determine the limiting behaviours for small forces and large forces.

We consider now a worm like chain (a continuous elastic rod) highly stretched along the z-direction (figure below):



The chain is defined by $\vec{r}(s)$ with s the curvilinear abscissa along the chain ($0 \leq s \leq L$, L is the contour length of the chain). $\vec{t}(s)$ is the tangent vector at point s:

$$\vec{t}(s) = \frac{\partial \vec{r}}{\partial s}$$

The radius of curvature of the chain at point s is defined by:

$$\left| \frac{1}{R(s)} \right| = \left\| \frac{\partial \vec{t}}{\partial s} \right\|$$

The energy of the chain E is given by:

$$E = \frac{1}{2}\kappa \int_0^L \frac{1}{R(s)^2}\, ds - f z(L)$$

where κ has been introduced in question 8, $z(L)$ is the extension of the chain and f the force applied to the chain extremities.

b) What is the reason of the presence of the last term $(-fz(L))$ in E ?

c) Show that E can be written, in the case of a stretched chain (*i.e.* when the chain is almost parallel to the z-axis) as:

$$E \simeq \int_0^L \left\{ \frac{\kappa}{2} \left[\left(\frac{\partial t_x}{\partial s} \right)^2 + \left(\frac{\partial t_y}{\partial s} \right)^2 \right] + \frac{f}{2} \left[t_x^2 + t_y^2 \right] \right\} ds - fL$$

where t_x and t_y are the projections of $\vec{t}(s)$ on the x-axis and the y-axis.

d) Introduce the Fourier transforms of t_x and t_y ($\tilde{t}_x(q) = \int t_x(s) \exp(iqs) ds$ and $\tilde{t}_y(q) = \int t_y(s) \exp(iqs) ds$) to write the energy E as an integral of normal modes.

e) Using equipartition, show that:

$$\langle t_x^2 \rangle = \langle t_y^2 \rangle = \frac{1}{2} \frac{k_B T}{\sqrt{f \kappa}}$$

(reminder: $\int \frac{1}{1+x^2}\, dx = \arctan x$)

f) Deduce from the last equation the extension of the chain z:

$$z = L \left(1 - \frac{k_B T}{\sqrt{4 f \kappa}} \right)$$

g) Assuming that the extension z in the WLC model in the limit of small forces is identical to the expression given by the FJC model, show that, for small forces:

$$z = L \frac{2Pf}{3k_B T}$$

while for large forces, the extension is given by (using a result of question 8):

$$z = L \left(1 - \sqrt{\frac{k_B T}{4 f P}} \right)$$

where P is the persistence length of the chain.

h) Finally, explain how to derive the following interpolation formula (WLC formula) for the whole range of z/L which is asymptotically exact in the limits of small and large forces:

$$\frac{fP}{k_B T} = \frac{z}{L} + \frac{1}{4\left(1 - \frac{z}{L}\right)^2} - \frac{1}{4}$$

i) Describe a typical experiment that can be used to test the WLC formula. What is the typical force needed to stretch a DNA chain?

13) Explain why the WLC formula (preceding question) had to be modified to give the so-called mWLC equation (32) of the article.

14) An *extended de Gennes regime* is introduced in the article (page 7999, last paragraph of the second column). How are obtained the limits of this regime?

15) Give the different force-extension relations used in Figure 3. Establish their expressions (for the scaling expressions). Comment on their domain of validity (in terms of R/L). Why is it legitimate to use the mWLC (equation (32)) equation as a benchmark?

16) Explain what is the channel-like regime for a chain confined in a slit.

17) Justify the term *tug-of-war* used to describe the situation when the extension R of the stretched chain is equal to the length of the confining channel. Make a realistic sketch (*i.e.* respecting the scales) of the section of the nanoslit with the confined polymer in the tug-of-war situation (the photograph of Figure 1 would be very helpful for that); your sketch should take into account the differences of the fluorescence intensity observed experimentally.

18) Make an abstract of the article in 10 lines highlighting the main results *for a non-specialist* public (but with a scientific background) in the style of a *News in brief* in the science section of a newspaper.

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