ICFP M2 – SOFT MATTER PHYSICS
Tutorial 1. Elasticity of an ideal polymer chain

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We would like to build up a first intuition on rubber elasticity. Therefore, we consider a single macromolecule and describe it by a linear chain made of a large number N of freely-joint monomers. We assume that the latter are identical rigid molecules with length a, oriented along the vectors [1] $\{\boldsymbol{r_i}\}$ (where $1 \leq i \leq N$). Due to thermal fluctuations, the orientation $\boldsymbol{r} = \boldsymbol{r_i}$ of any monomer is random and described through a probability density per unit volume $p(\boldsymbol{r})$, that we assume to be isotropic and independent of the other monomers. Finally, fixing one extremity ($i = 0$) as the origin, we define $\boldsymbol{R}$ as the end-to-end vector. The latter random variable is described by the probability density per unit volume $P(\boldsymbol{R}, N)$.

I Scaling and orders of magnitude

1 Provide the expression of $p(\boldsymbol{r})$.

2 What is the average value $\langle \boldsymbol{R} \rangle$ of $\boldsymbol{R}$ on all possible conformations ?

3 Calculate the associated root-mean-square (RMS) value $\sqrt{\langle \boldsymbol{R}^2 \rangle}$, and estimate it in the case of polystyrene ($a \sim 0.2$ nm) with a polymerization index $N \sim 10^4$.

4 Estimate the volume fraction actually occupied by the monomers inside the typical volume pervaded by the chain.

5 In a solution, schematize the typical spatial arrangement of the macromolecules as a function of the monomeric concentration. What concentration scale does naturally appear ?

II Scale invariance

1 What is the RMS distance between two given monomers of the same chain ?

2 Estimate the number of monomers of the chain present within one sphere of radius b centred on a given monomer. What is the associated volume fraction ?

3 Calculate the minimum number of such spheres required to cover the entire chain. Comment.

4 What is the domain of validity for the above scale invariance ?

[*]All tutorials benefitted from critical feedback by previous students. We thank them for that.

1. In all tutorials, bold quantities indicate vectors.

III Conformational statistics

1 Express $P(\boldsymbol{R}, N)$ as a function of $P(\boldsymbol{R'}, n)$ and $P(\boldsymbol{R} - \boldsymbol{R'}, N - n)$ for a fixed integer n such that $0 \leq n \leq N$. How does this result depend on the choice of n ?

2 Evaluate $P(\boldsymbol{R}, 0)$ and $P(\boldsymbol{R}, 1)$.

3 Expand $P(\boldsymbol{R} - \boldsymbol{r}, N)$ at second order in the monomeric orientation $\boldsymbol{r}$.

4 We consider the limit where $a \to 0$ and $N \to \infty$, with $a\sqrt{N}$ kept constant. Deduce from above a partial differential equation satisfied by P.

5 Obtain its solution.

6 Propose another method to get P directly from p.

IV Entropic elasticity

1 What is the entropic cost of elongating a chain from $\boldsymbol{R} = \boldsymbol{0}$ to $\boldsymbol{R}$?

2 Justify why the energetic cost is null.

3 Deduce the free-energy variation at fixed temperature. Comment.

4 What happens when one heats up a rubber thread taut with a hanging mass ?

5 At the microscopic scale, what is the typical force needed to significantly elongate a given macromolecule ? Compare to the rupture force of the latter.

6 What are the limits of the developed model ?