ICFP M2 – SOFT MATTER PHYSICS
Tutorial 5. Ideal chain in confinement using Schrödinger equation

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The probability distribution $P(\mathbf{r}', \mathbf{r}, N)$ of the conformations of an ideal polymer chain of N identical monomers, each of size a, whose spatial extremities are located at $\mathbf{r}'$ and $\mathbf{r}$, obeys in a good approximation a diffusion-like equation (see Tutorial 1). The mathematical structure of the latter being analogous to the Schrödinger equation, we would like to invoke the results for a quantum particle freely evolving along time t in a parallelepipedic box of volume $V = L_x\, L_y\, L_z$, in order to understand the statistical properties of an ideal chain confined in box. We encourage the students to prepare this tutorial by revisiting the quantum problem of a particle in a box.

I Problem definition

1 Recall the governing equation, the normalization, and the "initial" ($N = 0$) condition satisfied by $P(\mathbf{r}', \mathbf{r}, N)$ in the $V \to \infty$ limit. What does the spatial integral of $P(\mathbf{r}', \mathbf{r}, N)$ over both its extremities represent ?

2 How are the results above modified in the box ? What about the spatial boundary conditions ?

3 Describe in details the mathematical analogy with the time-dependent Schrödinger equation for a free particle in a box. In particular, what does the "propagator" $P(\mathbf{r}', \mathbf{r}, N)$ represent in the quantum problem ?

II Probability distribution

1 For a given quantum eigenstate ν of energy E_ν, characterized by the wave function $\Psi_\nu(\mathbf{r}, t) = \Phi_\nu(\mathbf{r}) \exp(-iE_\nu t/\hbar)$, provide the expression of the propagator $G_\nu(\mathbf{r}', \mathbf{r}, t)$. What equation does the spatial amplitude $\Phi_\nu(\mathbf{r})$ satisfy ?

2 The three directions x, y, and z being equivalent and independent, the spatial amplitude of the eigenstate $\nu = (l, p, q)$ satisfies $\Phi_\nu(\mathbf{r}) = \phi_l(x)\phi_p(y)\phi_q(z)$, and the associated eigenvalue reads $E_\nu = E_l + E_p + E_q$. Using separability and the boundary conditions above, specify the expressions of the ϕ_n and E_n, and the values allowed for the quantum number n. We can fix for instance the origin of coordinates at one corner of the box.

3 Check the orthonormality of the ϕ_n.

4 Deduce the expression of the propagator $G_\nu(\mathbf{r}', \mathbf{r}, t)$ in the eigenstate $\nu = (l, p, q)$, and translate it into the polymer language.

5 Invoking a partition on all possible conformation modes ν, provide the total expression of $P(\mathbf{r}', \mathbf{r}, N)$ and check the "initial" ($N = 0$) condition therein.

6 Show the validity of the composition rule :

$$P(\mathbf{r}', \mathbf{r}, N) = \int_V \mathrm{d}\mathbf{s}\, P(\mathbf{r}', \mathbf{s}, M)\, P(\mathbf{s}, \mathbf{r}, N - M)\ , \tag{1}$$

for any integer M with $0 \leq M \leq N$, and discuss the contribution of the conformations with at least one monomer touching the walls.

7 Express formally the local monomeric concentration $c(\mathbf{r}_0)$ at a given point $\mathbf{r}_0$, and verify conservation of the total number of monomers.

III Effect of confinement

1 Define what is a non-confined situation. Calculate the partition function, the entropy, the free energy, and the pressure in such a case.

2 What is the local monomeric concentration in the non-confined situation ?

3 In confinement, the problem is said to be "ground-state dominated". Explain the meaning of this statement.

4 Estimate the entropy change for an ideal chain confined between two parallel walls. Compare the scaling of the free energy in confinement to the one associated with bulk entropic elasticity in Tutorial 1.

5 Deduce that the pressure becomes anisotropic and estimate the force exerted by one chain against the confining walls. One can use for instance : $N = 10^4$, $a = 0.2$ nm, and a 5 nm spacing between the walls. Comment the result.

6 Calculate the concentration profile and provide the asymptotic depletion law.

Useful formulas

$$\begin{aligned} \frac{2}{\pi} \sum_{n=0}^{\infty} \sin(nu) \sin(nv) &= \delta(u - v) \\ \frac{2}{\pi} \int_0^{\pi} \mathrm{d}u\ \sin(mu) \sin(nu) &= \delta_{m,n} \end{aligned}$$