ICFP M2 – SOFT MATTER PHYSICS
Tutorial 13. Polymer dynamics

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We aim at understanding the dynamics of polymers under thermal noise and friction forces. Based on Langevin dynamics, we address in particular the Zimm and Rouse models, as well as the elastic-dumbbell and hydrodynamic-blob descriptions for the relaxation of inner degrees of freedom. Finally, we sketch the reptation idea for entangled melts.

0. Brief reminder [1] : Langevin dynamics

First, we ignore the internal structure of the macromolecule of total mass M, and we focus on the trajectory $\boldsymbol{r}(t)$ of its center of mass. We assume that the forces exerted by the solvant are decomposed into two main contributions : an average friction force $\boldsymbol{F} = -\xi\dot{\boldsymbol{r}}$, and a random force $\boldsymbol{f}(t)$ of thermal origin. We assume the components $\{f_i\}$ of the latter to be independent random noises, delta-correlated in time, and with a null average. We note $A\,\delta(0)$ their mean-square value (where δ is the Dirac delta distribution), in an isotropic medium, and T the solvant temperature.

1 Express the correlator $g_{ij}(\tau) = \langle f_i(t)f_j(t+\tau)\rangle$.

2 Write the equation of motion.

3 Estimate the relaxation time of inertial effects.

4 What is the formal solution of the equation of motion ? One can for instance assume a start from the origin with zero velocity.

5 Express the mean-square velocity at time t.

6 At equilibrium, how are A and ξ related ?

I The Zimm and Rouse models

1 In a liquid, at long times, friction dominates over inertia. How is the equation of motion modified ?

2 Show that the mean-square displacement follows a diffusive law.

3 What is the diffusion coefficient D in one dimension ?

4 In the Zimm description, a polymer coil can be viewed as a rigid sphere with a radius equal to the radius of the entire chain. Estimate D for a Stokes drag.

5 In the Rouse view, each rigid monomer contributes individually to the friction. Estimate D.

1. See details in the courses by S. Hénon and M. Lenz.

II Internal degrees of freedom

In order to describe the internal degrees of freedom of the chain, we invoke a simplified description : the so-called “elastic dumbbell”. Let us consider two particles, without inertia, experiencing solvant friction and linked together through a spring of extension $\boldsymbol{R}$ and stiffness K. We further assume the two particles to feel random and independent forces, $\boldsymbol{f_1}(t)$ and $\boldsymbol{f_2}(t)$, with similar properties as $\boldsymbol{f}(t)$ above.

1 What is the required expression of K in order to recover the ideal-chain properties at equilibrium ?

2 Provide the two equations of motion, and explain how to study their statistical properties.

3 Estimate the internal relaxation times for both the Zimm and Rouse models.

4 What is the relaxation time τ_p of a portion of chain containing p monomers ?

5 The hydrodynamic interactions are screened similarly to the static ones. By invoking hydrodynamic blobs for a real chain in a semi-dilute solution, within a good (athermal) solvant, propose a refined picture for internal relaxation and describe the crossover between the dilute and melt regimes.

III Entangled melt : reptation

We consider a polymer melt made of long and thus entangled chains. We assume that a chain diffuses inside an effective rigid tube created by its neighbours.

1 Why do we refer to this picture as a mean-field description ?

2 What is the length of the tube ?

3 How does the diffusion coefficient depend on the number N of monomers ?

4 Deduce a scaling law for the reptation time $\tau_{\text{rep}} \sim N^{\nu}$. Estimate its value.

5 Experimentally, on finds $\tau_{\text{rep}} \sim N^{3.4}$. Comment.