

3. NOTES AND PROBLEM SET 3

Problem Set 3

If you need to consult, a good text for polymer dynamics is here <https://cbp.tnw.utwente.nl/PolymeerDictaat/polymerdynamics.pdf>.

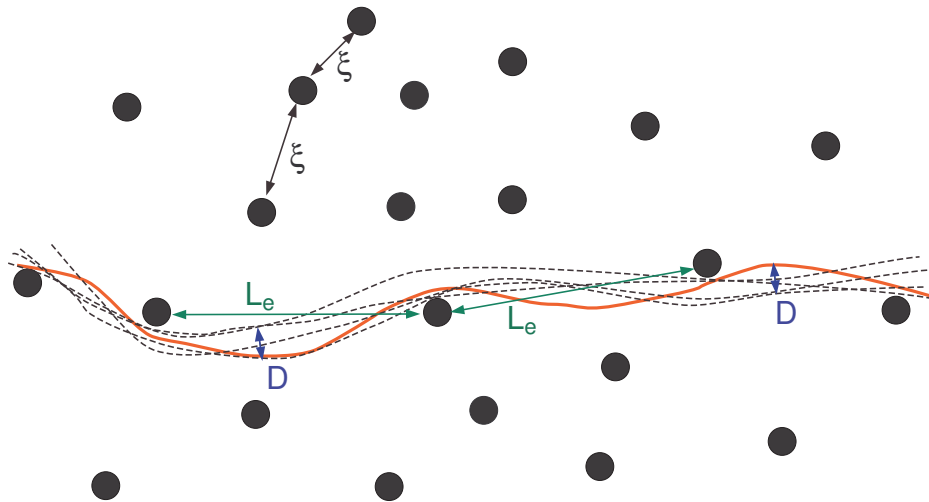


FIG. 5: Schematics of cross-section of semidilute solutions of semiflexible polymers: red line is a test polymer, solid circles - cross-sections of other polymers, dashed line - different conformations of the test polymer consistent with topological constraints. These conformations define the effective tube diameter D . Distance between two collisions along the polymer contour defines the topological constraints and the *entanglement* length L_e .

1. Consider a semidilute solution of semiflexible polymers of lengths $L \ll l_p$. The dynamics of a semiflexible polymer in a semidilute solution is restricted by an effective tube very much like that of the flexible polymers. However, the properties of the tube in solutions of semiflexible polymers are different from those of solutions of flexible polymers. In particular, one has to distinguish three characteristic sizes - the mesh size ξ , the effective tube diameter D and the entanglement length L_e (i.e. the distance along the contour of a given polymer between consecutive collisions with other polymers,

see Fig.) For the semidilute solutions of *flexible* polymers, all these three values are about the same. However, in solutions of *semiflexible* polymers they can differ a lot.

- Show that one of the relations between the entanglement length, the mesh size and tube diameter is: $L_e = \xi^2/D$. Hint: the treatment is very similar to that of mean-free path in gases.
 - Use the results of previous set on semiflexible polymers to derive the dependence of L_e and D on monomer concentration.
 - Estimate the dependence of osmotic pressure of semidilute semiflexible solutions on concentration. Compare this dependence to the corresponding dependence for flexible polymers.
2. Consider the diffusional motion of a bead in a potential trap (e.g. attached to the origin with a very flexible spring), such that the force acting on a bead depends on the bead position \vec{r} as $\vec{f} = -K\vec{r}$. The bead and a trap are immersed in the viscous liquid. Write Langevin equation for the bead's motion. Neglect acceleration term. Find the time dependence of the mean-square displacement of a bead in two situations:
- Bead initially is placed in the origin $\vec{r}(t=0) = 0$.
 - Initial position of the bead is random (but of course distributed with Boltzmann probabilities).

Explore the limiting cases and explain the differences in the results for two initial conditions

3. Consider the random motion of two beads attached by a very flexible spring (the length of the spring at rest is much smaller than the fluctuations caused by random forces) immersed in viscous liquid. Disregard the hydrodynamic interactions between the beads and the direct collisions of the beads.
- Write down Langevin equations describing beads' motion. Neglect accelerations.
 - Find the time dependence of the mean-square displacement of the center of mass of the beads:

$$\langle \Delta r_{cm}^2(t) \rangle = \left\langle \left(\frac{\Delta \vec{r}_1(t) + \Delta \vec{r}_2(t)}{2} \right)^2 \right\rangle$$

- Find the time dependence of the relative position of the beads:

$$\langle \Delta r_{rel}^2(t) \rangle = \left\langle \left(\frac{\Delta \vec{r}_1(t) - \Delta \vec{r}_2(t)}{2} \right)^2 \right\rangle$$

- Find the time dependence of the mean-square displacement of one of the beads $\langle \Delta r_1^2(t) \rangle$. Explain the different regimes in this dependence.

Everywhere above the notation is $\Delta \vec{r}_i(t) = \vec{r}_i(t) - \vec{r}_i(0)$. Beads friction coefficient is γ , spring constant is K .

4. Consider a worm-like chain with length $L \ll l_p$ aligned along X-axis (same conditions and notation as in Problem 5 of Set 2). The internal dynamics of such a chain can be described by the following Langevin equation:

$$\gamma_{\perp} \frac{\partial}{\partial t} \vec{r}_{\perp}(x, t) = -\kappa \frac{\partial^4}{\partial x^4} \vec{r}_{\perp}(x, t) + \vec{f}_{\perp}(x, t), \quad (3.1)$$

where $\gamma_{\perp} = 4\pi\eta$ is a friction coefficient to transverse motion of a unit length of polymer, the first term on the right hands side is the local force due to polymer contour curvature. It can be obtained (as any other potential force) by differentiating the potential energy of a semiflexible chain (approximate expression from Problem 5 of Set 2):

$$H = \frac{1}{2} \kappa \int_0^L dx \left(\frac{\partial^2 \vec{r}_{\perp}(x)}{\partial x^2} \right)^2 \quad (3.2)$$

with respect to $\vec{r}_{\perp}(x)$, just that in this case as $\vec{r}_{\perp}(x)$, is a function, one has to take functional derivative $-\delta H / \delta \vec{r}_{\perp}$. The second term on the right hand side represents transverse random forces: $\langle \vec{f}_{\perp}(x, t) \vec{f}_{\perp}(x', t') \rangle = 4k_B T \gamma_{\perp} \delta(x - x') \delta(t - t')$, like in Rouse model, the coefficient 4 entering instead of 6, since we consider transverse motion and forces only.

- Check that you understand how to get the above equation for dynamics. Make the problem discrete and take usual derivative instead of functional and then convert the result back to continuous. Check also that you understand why in the first approximation the friction coefficient per unit length of a rod does not depend on rod radius: for that estimate the friction a rod of diameter d by dividing it into spheres of diameter d each.

- Take convenient boundary conditions (like those in the corresponding problem in Problem Set 2) and separate the dynamics of polymer contour into the normal modes consistent with your boundary conditions. Write and solve the equation for the normal modes, find relaxation times of the modes.
- Find mean-square amplitudes of the modes from the dynamic equations using the properties of the random forces. Check that the result is consistent with previous calculation based on equipartition (Problem Set 2).
- Find the *temporal dependence* of the mean-square displacement of the monomer in the middle of the chain $\langle \vec{r}_\perp^2(t) \rangle$ for short time scales. What is the relevant criterion here for the time scale to be short? What happens at long time scales?