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T VI: Soft Matter and Biological Physics

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Problem set 3

Problem 3.1 *freely jointed chain*

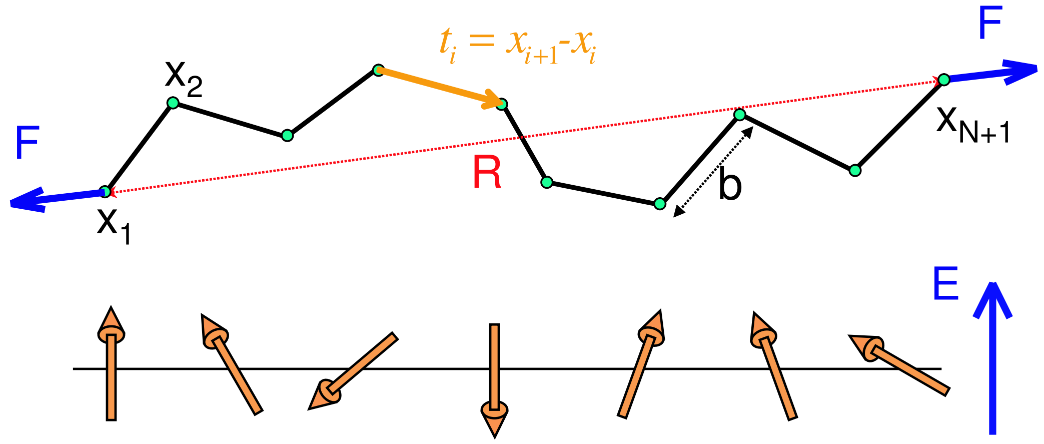
A simple polymer model is the *freely jointed chain* where segments $\{\vec{r}_i\}_{i=1,\ldots N}$ of fixed length $b = |\vec{r}_i|$ are concatenated by joints. The orientation of the segments are taken as independent and initially random. Applying an external force $\vec{F}$ at both ends favors configurations where the end-to-end distance $\vec{R} = \sum_{i=1}^{N} \vec{r}_i$ is aligned with $\vec{F}$.

1. Argue that the partition sum should read

$$Z_N = \int \left[\prod_{i=1}^{N} d\vec{r}_i \frac{1}{4\pi b^2} \delta(|\vec{r}_i| - b) \right] \exp\left[\frac{1}{k_B T} \vec{F} \cdot \sum_{i=1}^{N} \vec{r}_i \right] .$$

2. Calculate the partition sum and determine the free energy.

3. Using probabilistic arguments, show that $Z_N(\vec{F})$ is essentially the moment generating function for the end-to-end distance of the force-free chain. What rôle plays the free energy? Calculate the average alignment $\langle \vec{R} \rangle$ of the chain and discuss in particular the limiting cases of small and large forces.



Freely jointed chain under tension

Problem 3.2 *structure factor*

For a particular conformation of a single polymer $\vec{r}(s)$, $0 \le s \le L$, a quantity of interest is the fluctuating mass density in real space, $\rho(\vec{r})$, or reciprocal space, $\rho(\vec{q})$, which read up to irrelevant factors

$$\rho(\vec{r}) = \frac{1}{L}\int_0^L \mathrm{d}s\, \delta(\vec{r} - \vec{r}(s))\,, \qquad \rho(\vec{q}) = \int \mathrm{d}^3\vec{r}\, \mathrm{e}^{-\mathrm{i}\vec{q}\cdot\vec{r}} \rho(\vec{r}) = \frac{1}{L}\int_0^L \mathrm{d}s\, \mathrm{e}^{-\mathrm{i}\vec{q}\cdot\vec{r}(s)}\,.$$

In a scattering experiment the scattering cross section is proportional to the *structure factor*

$$S(\vec{q}) = \langle |\rho(\vec{q})|^2 \rangle = \frac{1}{L^2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \langle \exp\left(\mathrm{i}\vec{q}\cdot[\vec{r}(s) - \vec{r}(s')]\right)\rangle\,.$$

1. Check for yourself that the given relations hold.
2. Evaluate the correlation function

$$\langle \exp(\mathrm{i}\vec{q}\cdot[\vec{r}(s) - \vec{r}(s')])\rangle = \int \mathrm{d}^3\vec{R}\, \exp\left(\mathrm{i}\vec{q}\cdot[\vec{R} - \vec{R}']\right) G(\vec{R}, s|\vec{R}', s')$$

   for a *gaussian chain* characterized by a mean-square end-to-end distance $\langle R^2 \rangle$. Here $G(\cdot)$ denotes the propagator (conditional probability) of the chain which is the solution of the diffusion equation

$$\frac{\partial}{\partial s} G(\vec{R}, s|\vec{R}', s') = \frac{\langle R^2 \rangle}{6L} \nabla^2 G(\vec{R}, s|\vec{R}', s')\,, \qquad G(\vec{R}, s'|\vec{R}', s') = \delta(\vec{R} - \vec{R}')\,.$$

3. Determine the corresponding structure factor $S(\vec{q})$ and discuss the regime of small and large wavenumbers q.

Problem 3.3 *Worm-like chain*

In the worm-like chain model for semi-flexible polymers a large number N of segments of fixed length b is concatenated by joints. The resistance to bending is modeled by attributing an energy

$$\mathcal{H}_{\mathrm{WLC}} = -J \sum_{i=1}^{N-1} \vec{t}_i \cdot \vec{t}_{i+1}\,, \qquad |\vec{t}_i| = 1\,, \qquad J > 0\,,$$

to a configuration given by the tangent vectors $\{\vec{t}_i\}_{i=1,\dots,N}$ of the chain.

1. Show that the joint probability in the canonical ensemble factorizes

$$P(\{\vec{t}_i\}_{i=1,\dots,N}) = \left[\prod_{k=1}^{N-1} P(\vec{t}_{k+1}|\vec{t}_k)\right] p_1(\vec{t}_1)\,,$$

   where $P(\vec{t}_{k+1}|\vec{t}_k)$ denotes a conditional probability and $p_1(\vec{t}_1) = 1/4\pi$ is the probability distribution for the orientation of the first segment.

2. Show that

$$\int \mathrm{d}\vec{t}_{k+1} P(\vec{t}_{k+1}|\vec{t}_k)\vec{t}_{k+1} = C\vec{t}_k$$

   and determine the constant C.

3. Demonstrate that the tangent-tangent correlation function fulfills

$$\langle \vec{t}_1 \cdot \vec{t}_N \rangle = C^{N-1} \quad \text{or more generally } \langle \vec{t}_k \cdot \vec{t}_{k+n} \rangle = C^n\,.$$

   Calculate the persistence length $l_p = b/\ln C$ of the worm-like chain.