

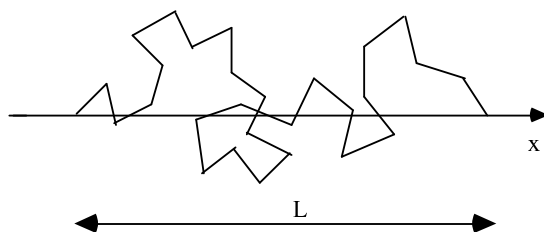
Ex2340: Tension of a chain molecule

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The problem:

A chain molecule consists of N units, each having a length a , see figure. The units are joined so as to permit free rotation about the joints. At a given temperature T :

- Derive the relation between the tension f acting between both ends of the three-dimensional chain molecule of length L .
- Derive the distance L between the two ends of the three-dimensional chain for a given force, and compare the results.



The solution:

Constrained length solution:

We can calculate the average (directional) projection on an arbitrary direction (3D) of each monomer as:

$$\langle \hat{x}_i \rangle = \langle a \cos \theta \rangle = 0 \quad (1)$$

This of course makes sense, since the probability of directions is spread equally. consequently we can find the variance as:

$$\text{Var}(\hat{x}_i) = \langle a^2 \cos^2 \theta \rangle = a^2/3 \quad (2)$$

We define the length of the polymer as:

$$\hat{L} = \sum_{i=1}^N \hat{x}_i \quad (3)$$

Now since $N \gg 1$ we can use the central limit theorem, and claim that \hat{L} has a normal distribution with $\hat{L} \sim N(0, Na^2/3)$. hence:

$$P(\hat{L} = \vec{R}) = \left(\frac{3}{2\pi Na^2} \right)^{3/2} e^{-\frac{3\vec{R}^2}{2Na^2}} \quad (4)$$

The vector notion in the last equation emphasizes the fact that we summed over projections along an arbitrary direction.

For more details see "Polymer Solutions" (Wiley & Sons, 2002, ISBN: 0-471-38929-3).

However the probability isn't enough, we need the partition function. We can relate the probability to the partition function by thinking about the probability as the fraction of "good" states, compared to the whole set. Therefore dividing the constrained partition function, by the unconstrained:

$$P(\hat{L} = \vec{R}) = \frac{Z(\beta, \vec{R})}{Z(\beta)} \quad (5)$$

The last result is very meaningful, because it implies that the constrained partition function deviates from the probability by an expression which doesn't involve the length ($Z(\beta)$ doesn't depend on the length), and therefore after we take a logarithm, and the derivative by R this expression will vanish.

We can write the Helmholtz free energy as follows:

$$F = -T \ln(Z(\beta, \vec{R})) = -T \left(\frac{3}{2} \ln \left(\frac{3}{2\pi N a^2} \right) - \frac{3\vec{R}^2}{2N a^2} + \ln(Z(\beta)) \right) \quad (6)$$

Eventually, we can derive the force exerting on the polymer as:

$$f = -\frac{\partial F}{\partial R} = -\frac{3T\vec{R}}{N a^2} = -k\vec{R} \Rightarrow k = \frac{3T}{N a^2} \quad (7)$$

Unconstrained length solution:

In this solution we exert a force f on the polymer and measure its length.

the force contributes to each monomer's energy by interacting with the orientation according to:

$$\epsilon_i = -\vec{r}_i \cdot \vec{f} \quad (8)$$

The one monomer partition function will be:

$$Z_{G,1} = \int e^{\beta \vec{r} \cdot \vec{f}} \frac{d\Omega}{4\pi} = \frac{1}{2} \int e^{\beta a f \cos \theta} d(\cos \theta) = \frac{\sinh(\beta a f)}{\beta a f} \quad (9)$$

Since the monomers aren't interacting the partition function can be factorized. However since the monomers are clearly distinguishable as they are aligned we won't divide by permutations, hence:

$$Z_{G,N} = Z_{G,1}^N = \left(\frac{\sinh(\beta a f)}{\beta a f} \right)^N \quad (10)$$

We can now find the mean length:

$$\langle R \rangle = T \frac{\partial \ln(Z)}{\partial f} = N a \left(\coth(\beta f a) - \frac{1}{\beta f a} \right) = N a \mathcal{L}(\beta f a) \quad (11)$$

As we can see the grand hamiltonian approach gave us a slightly different answer, in terms of Langevin function. However, by approximating the result for a small force $\frac{f a}{T} \ll 1$:

$$\mathcal{L}(x) \approx \frac{x}{3} + \mathcal{O}(x^3) \quad (12)$$

we'll get:

$$\langle R \rangle \approx \frac{N a^2 f}{T} \quad (13)$$

as we did before.