E2351:Tension on a chain molecule

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The problem:

N monomeric units are arranged along a straight line to form a chain molecule. Each unit can be either in a state α (with length a and energy E_a) or in a state β (with length b and energy E_b).

(1) Write down the function $Z_G(\beta, f)$.
(2) Derive the relation between the length L of the chain molecule and the tension f applied at the ends of the molecule.
(3) Find the compressibility $\chi_T = (\partial L/\partial f)_T$.
(4) Describe the dependence of L and χ_T on (fa/T). explain.
(5) Write down the partition function $Z(\beta, L)$. What is the probability function of L for $f = 0$?

The solution:

(1)

Let us use n for the number of monomers in the state α, and $(N-n)$ for the number of monomers in the state β. In order to derive the relation between f and L, we shall define the grand-hamiltonian

$H_G = H + fL = nE_a + (N-n)E_b + fL$

The physical interpertation of this definition is putting a piston at the end of the polymer applying tension f on it. Mathematically, the transition from H to H_G changes the identity of the parameter determining the behavior of the system from L to f (Legendre transform). Adding the term fL to H translates into multiplying Z by $e^{-\beta fL}$, and thus the Legendre transform on H corresponds to the Laplace transform on the partition function Z.

Putting $L = na + (N-n)b$ yields

$H_G = nE_a + (N-n)E_b + naf + (N-n)bf$

With this Hamiltonian, we shall calculate the function Z_G, from which we can derive the $L-f$ relation:

$Z_G(\beta, f) = \sum e^{-\beta H_G} = \sum \binom{N}{n} e^{-\beta(NE_b + Nbf + n(E_a - E_b) + n(af - bf))} = \sum \frac{N!}{(N-n)!n!} e^{-\beta(NE_b + Nbf + n(E_a - E_b) + n(af - bf))}$
$= e^{-\beta N(fb + E_b)} (e^{-\beta(E_a - E_b + fa - fb)} + 1)^N = (e^{-\beta(E_a + fa)} + e^{-\beta(E_b + fb)})^N$

(2)

Equipped with the f-dependent function Z_G, we shall use the free energy function to obtain the connection between L and f:

$F(\beta,f) = -\frac{\ln Z_G}{\beta} = -\frac{N}{\beta}\ln(e^{-\beta(E_a+fa)} + e^{-\beta(E_b+fb)})$

$L = -(\partial F/\partial f) = -(\frac{N}{\beta})(\frac{-\beta a e^{-\beta(E_a+fa)} - \beta b e^{-\beta(E_b+fb)}}{e^{-\beta(E_a+fa)}+e^{-\beta(E_b+fb)}})$

$L = N\frac{a+be^{-\beta f(b-a)}e^{-\beta(E_b-E_a)}}{1+e^{-\beta f(b-a)}e^{-\beta(E_b-E_a)}}$

(3)

We shall calculate the compressibility directly by differentiating. After some algebra, we get:

$\chi_T = (\partial L/\partial f)_T = -\frac{N(b-a)^2}{4T}\frac{1}{\cosh^2(\frac{1}{2}\beta(E_b-E_a)+\frac{1}{2}\beta fa(\frac{b}{a}-1))}$

(4)

Defining

$\alpha = \frac{b-a}{a}$; $\Delta = \beta(E_b - E_a)$; $y = \frac{fa}{T}$;

We get

$L(y) = N\frac{a+be^{-\Delta-\alpha y}}{1+e^{-\Delta-\alpha y}}$

$\chi_T(y) = -\frac{Na^2\alpha^2}{4T}\frac{1}{\cosh^2(\frac{1}{2}\alpha y+\frac{1}{2}\Delta)}$

Without the loss of generality, we shall assume that $b > a$, and thus $\alpha > 0$. $L(y)$ goes to Na as y goes to positive infinity, and goes to Nb as y goes to negative infinity.
The physical intuition - a large positive tension f will "shrink" the polymer to its minimum length (Na) while a large negative tension will "strech" the polymer to its maximum length (Nb). Those are the asymptotic lines of $L(y)$.

The derivative $\chi_T(y)$ is always negative, as L always decreases with y, and it has one global minimum - at $y = -\frac{\Delta}{\alpha} = -\beta a\frac{E_b-E_a}{b-a}$, which is determined by the energy gap between the two monomer states and by the lengths ratio $\frac{b}{a}$.

(5)

We will now return to the ordinary partition function Z, derived from the original hamiltonian $H = nE_a + (N-n)E_b$. Once the length L is determined, the energy is determined:

$H = \frac{Nb-L}{b-a}E_a + \frac{L-Na}{b-a}E_b$

(notice that both the fractions are non-negative, by our assumption $b > a$).

By taking into account the degeneration, we get

$$Z(\beta, L) = \frac{N!}{(N-n)!n!} e^{-\beta(\frac{Nb-L}{b-a}E_a + \frac{L-Na}{b-a}E_b)}$$

(Which is no other than one summand from the function Z_G calculated in section 1 without the fL term)

Where $n = \frac{Nb-L}{b-a}$

For $f = 0$, each monomer will be totally independent of the other monomers, and thus will have a probability of $\frac{1}{Z_1}e^{-\beta E_a}$ to be in the state α, and a probability of $\frac{1}{Z_1}e^{-\beta E_b}$ to be in the state β, when the one-monomer partition function is defined as

$$Z_1 = e^{-\beta E_a} + e^{-\beta E_b}.$$

In such a situation, where the N components of the system are independent, the partition function Z "factorizes" into an N-exponent of a one-component partition function: $Z_N = (Z_1)^N$.

For convenience, we shall define

$$q = \frac{1}{Z_1}e^{-\beta E_a}$$

$$1 - q = \frac{1}{Z_1}e^{-\beta E_b}$$

The expectation value and standard deviation of the length of one monomer are given by

$$< L_1 >= qa + (1-q)b$$

$$< L_1^2 >= qa^2 + (1-q)b^2$$

$$Var(L_1) =< L_1^2 > - < L_1 >^2= q(1-q)(b-a)^2$$

$$\sigma_1 = \sqrt{q(1-q)}(b-a)$$

By the central limit theorem, for $N >> 1$, summing on N independent variables with a common expectation value and a common standard deviation will sum up (in the limit of infinity) to give a normal distribution, characterized by the expectation value $N < L_1 >$ and by the standard deviation $\sqrt{N}\sigma_1$.

Thus, the probability function of L will be given by

$$P(L) = \frac{1}{\sqrt{2\pi N{\sigma_1}^2}} e^{-\frac{(L-N<L_1>)^2}{2N{\sigma_1}^2}}$$

We can see here, that up to a factor $Z(\beta, L)$ is the probability to find the polymer in the length L (as pointed in the lecture notes, 3.6). Using the Gaussian approximation (according to the central limit theorem) allowed us to avoid a calculation of the probability function using the Stirling formula.