Ex2351: Tension of a rubber band

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The problem:

The Elasticity of a rubber band can be described by a one dimensional model of a polymer. The polymer consists of N monomers that are arranged along a straight line, hence forming a chain. Each unit can be either in a state of length a with energy E_a, or in a state of length b with energy E_b. We define f as the tension, i.e. the force that is applied while holding the polymer in equilibrium.

(1) Write expressions for the partition function $Z_G(\beta, f)$.

(2) For very high temperatures $F_G(T, f) \approx F_G^{(\infty)}(T, f)$, where $F_G^{(\infty)}(T, f)$ is a linear function of T. Write the expression for $F_G^{(\infty)}(T, f)$.

(3) Write the expression for $F_G(T, f) - F_G^{(\infty)}(T, f)$. Hint: this expression is quite simple - within this expression f should appear only once in a linear combination with other parameters.

(4) Derive an expression for the length L of the polymer at thermal equilibrium, given the tension f. Write two separate expressions: one for the infinite temperature result $L(\infty, f)$ and one for the difference $L(T, f) - L(\infty, f)$.

(5) Assuming $E_a = E_b$, write a linear approximation for the function $L(T, f)$ in the limit of weak tension.

(6) Treating L as a continuous variable, find the probability distribution $P(L)$. Write also the result that you get from this expression. Assume that $E_a = E_b$ and $f = 0$.

(7) Write an expression that relates the function $f(L)$ to the probability distribution $P(L)$. Write also the result that you get from this expression.

(8) Find what would be the results for $Z_G(\beta, f)$ if the monomer could have any length $\in [a, b]$. Assume that the energy of the monomer is independent of its length.

(9) Find what would be the results for $L(T, f)$ in the latter case.

Note: Above a "linear function" means $y = Ax + B$.
Please express all results using $(N, a, b, E_a, E_b, f, t, L)$

The solution:

(1) The Hamiltonian for a single monomer in a polymer chain is:

$$\mathcal{H}(x_i) = E_{x_i} - f x_i \tag{1}$$

Therefore, the partition function for a single monomer with 2 possible configurations (a and b) will be:

$$Z^1 = e^{-\beta \mathcal{H}(a)} + e^{-\beta \mathcal{H}(b)} = e^{-\beta(E_a - fa)} + e^{-\beta(E_b - fb)} \tag{2}$$

and for N monomers:

$$Z_G = (Z^1)^N \tag{3}$$

(2) Using the identity:

$$e^x + e^y = \exp\left(\frac{x+y}{2}\right)\cosh\left(\frac{x-y}{2}\right) \tag{4}$$

We can factorize out of Z^1 the term

$$\exp\left[\beta\left(f\frac{a+b}{2} - \frac{E_a+E_b}{2}\right)\right] \tag{5}$$

and get:

$$Z^1 = \exp\left[\beta\frac{fa+fb}{2} - \beta\frac{E_a+E_b}{2}\right] \cdot 2\cosh\left[\beta\left(\frac{E_b-E_a}{2} - \frac{b-a}{2}f\right)\right] \tag{6}$$

And the Gibbs Free energy is:

$$\frac{F}{N} = -T\ln Z^1 = \left(\frac{E_a+E_b}{2} - \frac{a+b}{2}f\right) - T\ln\left(2\cosh\left[\beta\left(\frac{E_b-E_a}{2} - \frac{b-a}{2}f\right)\right]\right) \tag{7}$$

For high temperature, we'll use $\cosh(x) \approx 1$ and therefore

$$\frac{F^\infty}{N} = \left(\frac{E_a+E_b}{2} - \frac{a+b}{2}f\right) - T\ln 2 \tag{8}$$

(3) Using previous results:

$$\frac{1}{N}\left(F - F^\infty\right) = -T\ln\left(\cosh\left[\beta\left(\frac{E_b-E_a}{2} - \frac{b-a}{2}f\right)\right]\right) \tag{9}$$

(4) We can derive L, using the conjugated general force f:

$$\frac{L}{N} = T\frac{\partial}{\partial f}\ln Z^1 = \frac{a+b}{2} - \frac{b-a}{2}\cdot\tanh\left(\frac{(E_b-E_a)-(b-a)f}{2T}\right) \tag{10}$$

Using $\tanh(x) \approx x$ we get:

$$\frac{L^\infty}{N} = \frac{a+b}{2} + \frac{(b-a)^2}{4T}f - \frac{(b-a)(E_b-E_a)}{4T} = Af + B \tag{11}$$

And then:

$$\frac{1}{N}\left(L - L^\infty\right) = \frac{(b-a)(E_b-E_a)}{4T} - \frac{(b-a)^2}{4T}f - \frac{b-a}{2}\tanh\left(\frac{(b-a)f-(E_b-E_a)}{2T}\right) \tag{12}$$

(5) For $E_a = E_b$ and a weak tension ($f \to 0$):

$$\frac{L}{N} = \frac{a+b}{2} + \frac{(b-a)^2}{4T}f \tag{13}$$

So we can see hook's law as expected.

(6) Now, since $E_a = E_b$, each possible configuration of a single monomer has the same probability $P_a = P_b = \frac{1}{2}$, so the mean value $\langle L\rangle$ and variance σ^2 are (x_i representing a single monomer):

$$\langle L\rangle = \sum_{i=1}^{N}\langle x_i\rangle = N\langle x_i\rangle = N\left(\frac{a+b}{2}\right) \tag{14}$$

$$\sigma^2 = \langle L^2\rangle - \langle L\rangle^2 = N\left(\langle x_i^2\rangle - \langle x_i\rangle^2\right) = N\left(\frac{a-b}{2}\right)^2 \tag{15}$$

Assuming a long monomer chain L where $N \gg 1$, we can now use the central limit theorem, and the probability distribution $P(L)$ takes the form:

$$P(L) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{L-\langle L\rangle}{\sigma}\right)^2} \tag{16}$$

(7) The probability $P(L)$ for the chain to assume a specific finite length L is:

$$P(L) = \frac{1}{Z} Z(L) \tag{17}$$

With Z being the summation on all possible length states of the polymer (a normalization constant). So we can derive the tension $f(L)$ same as before:

$$f(L) = \frac{1}{\beta} \frac{\partial \ln P(L)}{\partial L} = -T \frac{L - \langle L\rangle}{\sigma^2} \tag{18}$$

(8) The size of a single monomer is now a continuous variable $x_i \in [a, b]$ with E independent of x_i, so that the Hamiltonian of a monomer takes the form of

$$\mathcal{H}(x_i) = E - f x_i \tag{19}$$

And the partition function becomes:

$$Z^1 = e^{-\beta E} \int_a^b e^{\beta f x_i} dx_i = \frac{e^{-\beta E}}{f\beta} e^{\beta f x_i}\Big|_a^b = \frac{e^{-\beta E}}{f\beta} \left(e^{\beta f b} - e^{\beta f a}\right) \tag{20}$$

Setting $E = 0$ we get:

$$Z^1 = \frac{1}{f\beta} \left(e^{\beta f b} - e^{\beta f a}\right) \tag{21}$$

And for N monomers:

$$Z_G = \left(Z^1\right)^N = \left[\frac{1}{f\beta} \left(e^{\beta f b} - e^{\beta f a}\right)\right]^N \tag{22}$$

(9) Repeating the algebra in (2) and (5), we get for the new partition function:

$$Z_G = \left[\frac{1}{f\beta} \exp\left(\beta f \frac{a+b}{2}\right) \cdot 2\sinh\left(\beta f \frac{b-a}{2}\right)\right]^N \tag{23}$$

$$\frac{F}{N} = -f\frac{a+b}{2} - T\ln\left[2\sinh\left(\beta f \frac{b-a}{2}\right)\right] + T\ln(f\beta) \tag{24}$$

$$\frac{L}{N} = T\frac{\partial}{\partial f}\left(\ln Z^1\right) = \frac{a+b}{2} - \frac{T}{f} + \frac{b-a}{2}\coth\left(\beta f \frac{b-a}{2}\right) \tag{25}$$

$$\tag{26}$$

And for high temperature approximation ($\coth x \approx x^{-1} + \frac{1}{3}x$):

$$\frac{L^\infty}{N} = \frac{a+b}{2} + \frac{(b-a)^2}{12}\beta f \tag{27}$$