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Statistical Mechanics
Problem Source: **CMU August 2006 Qualifying Exam**

Consider the following very simple model of a rubber band. Describe the rubber band as a one-dimensional polymer, with N monomers of length d that can point in either the $+z$ or $-z$ direction. One end of the polymer is attached to a point a couple of meters above the floor, and the other is attached to a mass M. The whole thing is in thermal equilibrium at temperature T.

(a) Calculate the partition function.

Taking the system in the Canonical ensemble, then, to be composed of N subsystems with energies $Mgd, -Mgd$:

$$Z = \prod_N \left(e^{-\beta Mgd} + e^{\beta Mgd}\right) = \left(e^{-\beta Mgd} + e^{\beta Mgd}\right)^N$$

(b) Calculate the free energy.

$$A = -kT\ln Z = -NkT\ln\left(e^{-\beta Mgd} + e^{\beta Mgd}\right)$$

(c) Calculate the energy.

$$U = -\frac{\partial}{\partial\beta}(\ln Z) = -\frac{1}{Z}\frac{\partial}{\partial\beta}Z = -\frac{N\left(e^{-\beta Mgd} + e^{\beta Mgd}\right)^{N-1}\left(-Mgde^{-\beta Mgd} + Mgde^{\beta Mgd}\right)}{Z}$$
$$= MgdN\frac{e^{-\beta Mgd} - e^{\beta Mgd}}{e^{-\beta Mgd} + e^{\beta Mgd}} = -MgdN\tanh(\beta Mgd)$$

(d) Calculate the average length $\langle L\rangle$ of the polymer.

This is linearly related to the energy:

$$\langle L\rangle = \left|\frac{U}{Mg}\right| = MgdN\tanh(\beta Mgd) \quad because \quad \beta > 0$$

(e) Based on the results you've obtained for this simple model of a rubber band, show whether the mass rises or falls when temperature is increased.

Consider the shape of $\tanh(\beta Mgd)$. This function is approximately 1 for large β corresponding to cold temperatures, and is approximately 0 for small β corresponding to hot temperatures. In this case, then, I expect $\langle L \rangle$ to be smaller for a hot ideal rubber band.

(f) If you could obtain a real rubber band, you would be able to confirm that it gets hotter when stretched and cooler when released. Therefore for real rubber bands, $\left(\frac{\partial T}{\partial L}\right)_S > 0$, where S is the entropy, as usual. From this result and your knowledge of how to derive thermodynamic identities, determine whether a mass hanging from the end of a real rubber band, as in part (e), should rise or fall when the rubber band is heated.

I need the sign of $\left(\frac{\partial L}{\partial T}\right)_F$, with F the force on the object.

Certainly, since the longer polymer becomes more ordered, then $\left(\frac{\partial S}{\partial L}\right)_T > 0$.

$$\left(\frac{\partial L}{\partial T}\right)_F = \left(\frac{\partial (L,F)}{\partial (L,S)}\right)\left(\frac{\partial (L,S)}{\partial (L,T)}\right)\left(\frac{\partial (L,T)}{\partial (T,F)}\right)$$

First, I see that the band will get longer when pulled, so that :
$\frac{\partial (L,T)}{\partial (F,T)} > 0$. However, since the entries are crossed here, $\frac{\partial (L,T)}{\partial (T,F)} < 0$

Next, I identify the heat capacity, which is always positive:
$$\frac{\partial (L,S)}{\partial (L,T)} = \frac{N}{T} c_L$$

Finally, I have:
$$U = TS + FL$$
$$dU = TdS + FdL$$
$$\frac{\partial^2 U}{\partial S \partial L} = \left(\frac{\partial T}{\partial L}\right)_S = \left(\frac{\partial F}{\partial S}\right)_L$$

Now I see that the first term, $\frac{\partial (L,F)}{\partial (L,S)}$, is positive.

Since I have two positive terms and one negative term, the product overall is negative and $\left(\frac{\partial L}{\partial T}\right)_F$ is negative, for a shrinking band.