Ex 2353: Tension of a stretched chain

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The problem:

A rubber band is modeled as a single chain of $N \gg 1$ massless non-interacting links, each of fixed length a. Consider a one-dimensional model where the links are restricted to point parallel or anti-parallel to a given axis, while the endpoints are constraint to have a distance $X = (2n - N)a$, where n is an integer. Later you are requested to use approximations that allow to regard X as a continuous variable. Note that the body of the chain may extend beyond the length X, only its endpoints are fixed. In items (c,d) a spring is pushed between the two endpoints, such that the additional potential energy $-KX^2$ favors large X, and the system is released (i.e. X is free to fluctuate).

(a) Calculate the partition function $Z(X)$. Write the exact combinatorial expression. Explain how and why it is related trivially to the entropy $S(X)$.

(b) Calculate the force $f(X)$ that the chain applies on the endpoints. Use the Stirling approximation for the derivatives of the factorials.

(c) Determine the temperature T_c below which the $X = 0$ equilibrium state becomes unstable.

(d) For $T < T_c$ write an equation for the stable equilibrium distance $X(T)$. Find an explicit solution by expanding $f(X)$ in leading order.

The solution:

(a) The partition function is defined:

$$Z = \sum e^{-\beta E_r}$$

If all $E_r = 0$:

$$Z = \#\text{states}$$

$$Z(X) = \frac{N!}{n!(N-n!)} = \frac{N!}{((Na+X)/2a)!((Na-X)/2a)!}$$

The entropy:

$$\begin{aligned} S(X) &= \ln(\#\text{states}) = \ln(Z(X)) \\ &= \ln(N!) - \ln\left(\left(\frac{Na+X}{2a}\right)!\right) - \ln\left(\left(\frac{Na-X}{2a}\right)!\right) \end{aligned}$$

(b) Realizing that the force is conjugate to X:

$$f(X) = T\frac{\partial \ln Z}{\partial X} = -\frac{T}{2a}\ln\left[\frac{Na+X}{Na-X}\right] = -\frac{T}{a}\tanh^{-1}\left(\frac{X}{Na}\right)$$

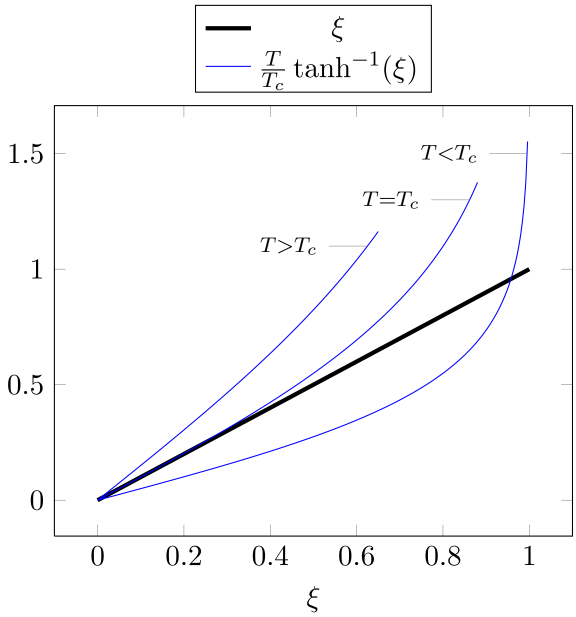
(c) The free energy of the system:

$$F = E - TS = -KX^2 - T\ln(Z(X))$$
$$\left.\frac{d^2F(T = T_c)}{dX^2}\right|_{X=0} = 0$$
$$0 = -2K + \frac{T_c}{2a}\left(\frac{1}{Na} + \frac{1}{Na}\right)$$
$$T_c = 2NKa^2$$

(d) While $T < T_c$ there is a stable solution were $X \neq 0$:

$$\frac{dF}{dX} = 0$$
$$0 = -2KX + \frac{T}{a}\tanh^{-1}\left(\frac{X}{Na}\right)$$
$$\frac{X}{Na} = \frac{T}{T_c}\tanh^{-1}\left(\frac{X}{Na}\right)$$

Setting a new variable $\xi = \frac{X}{Na}$ one can graphically analyse the solution.



Expanding while using $\tanh^{-1}(\varepsilon) \approx \varepsilon + \frac{\varepsilon^3}{3}$ (were $\frac{X}{Na} \ll 1$):

$$f(X) \approx \frac{T}{a}\left(\frac{X}{Na} + \frac{X^3}{3(Na)^3}\right)$$

Finding X that is non zero:

$$\frac{X}{Na} = \frac{T}{T_c}\left(\frac{X}{Na} + \frac{X^3}{3(Na)^3}\right)$$
$$X = \sqrt{3}Na\sqrt{\frac{T_c}{T} - 1}$$