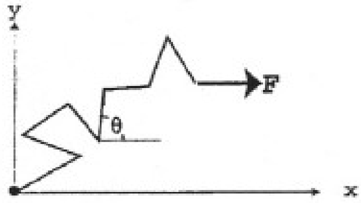
7. *Statistical Mechanics and Thermodynamics* (Fall 2002)

A chain consists of N links that can freely rotate in two dimensions. The links are joined end-to-end, as shown below.



The chain is subjected to a tension, F, in the x-direction, as indicated. The tension is applied at the end of the chain, so that the total energy of the chain is given by

$$E = -Fl\sum_{i=1}^{N}\cos\theta_i$$

where θ_i is the angle that the i^{th} link makes with the x-axis, and l is the length of each link in the chain.

(a) Calculate the partition function of this chain.

(b) From the partition function, find the relationship between the extension of the chain in the x-direction and the tension, F, assuming that the temperature is T.

(c) When the tension, F, is small, the extension-versus-tension expression implies a spring constant for the freely jointed chain. What is this effective spring constant?

If the integrals do not evaluate to elementary functions in parts a and b, it is not necessary to attempt to reduce them. Leave them as integrals. However, in part c, it is necessary to come up with something explicit.

a. Classically we just integrate over all parameters.

$$Z = \int_0^{2\pi}\cdots\int_0^{2\pi} e^{-\beta E}\,d\theta_1\cdots d\theta_N = \int_0^{2\pi}\cdots\int_0^{2\pi} e^{\beta F\ell\sum_{i=1}^{N}\cos(\theta_i)}\,d\theta_1\cdots d\theta_N$$

$$= \left[\int_0^{2\pi} e^{\beta F\ell\cos(\theta)}\,d\theta\right]^N \quad \text{and} \quad \ln(Z) = N\ln\left(\int_0^{2\pi} e^{\beta F\ell\cos(\theta)}\,d\theta\right)$$

b. $$X = \ell\sum_{i=1}^{N}\cos(\theta_i) = -\frac{E}{F} \Rightarrow \bar{X} = -\frac{\bar{E}}{F} = \frac{1}{F}\frac{\partial\ln(Z)}{\partial\beta}$$

$$\Rightarrow \bar{X} = \frac{1}{\cancel{F}}N\frac{\int_0^{2\pi}\cancel{F}\ell\cos(\theta)\,e^{\beta F\ell\cos(\theta)}\,d\theta}{\int_0^{2\pi}e^{\beta F\ell\cos(\theta)}\,d\theta} = N\ell\frac{\int_0^{2\pi}\cos(\theta)e^{\beta F\ell\cos(\theta)}\,d\theta}{\int_0^{2\pi}e^{\beta F\ell\cos(\theta)}\,d\theta}$$

c. $F_{spring} = -F$ since the spring tension is counter-balancing F

$F_{spring} = -K\bar{X} \Rightarrow K = \frac{F}{\bar{X}}$ and F is small so Taylor expand.

$$\bar{X} \cong N\ell\frac{\int_0^{2\pi}\cos(\theta)\left[1+\beta F\ell\cos(\theta)\right]d\theta}{\int_0^{2\pi}\left[1+\beta F\ell\cos(\theta)\right]d\theta} = N\ell\frac{\int_0^{2\pi}\beta F\ell\cos^2(\theta)\,d\theta}{2\pi}$$

$$= N\ell\beta F\ell\pi/2\pi = \frac{1}{2}N\beta F\ell^2$$

$$\Rightarrow K = \frac{F}{\bar{X}} = \frac{2}{N\beta\ell^2} = \frac{2kT}{N\ell^2}$$