[pex53] Freely jointed chain (FJC) model

Consider a chain of N freely jointed segments of length a subject to thermal fluctuations and to an external stretching force F. The FJC model approximates the stretching force as acting on each segment in the same way, namely as a force seeking to align each segment with the direction of the force in 3D space. The Hamiltonian splits into a sum of terms involving only individual segments,

$$\mathcal{H} = -\sum_{i=1}^{N} \vec{a}_i \cdot \vec{F} = -Fa \sum_{i=1}^{N} \cos\theta_i, \tag{1}$$

where θ_i is the polar angle of bond vector $\vec{a}_i$ relative to the direction $\vec{F}$. The canonical partition function factorizes and can be calculated as follows:

$$Z_N \doteq \mathrm{Tr}[e^{-\beta\mathcal{H}}] = Z_1^N, \quad Z_1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, e^{\beta F a \cos\theta}, \quad \beta \doteq 1/k_B T. \tag{2}$$

(a) Evaluate Z_N and infer an expression from it for the Gibbs free energy $G(T,F,N) = -k_B T \ln Z_N$.
(b) Calculate the average end-to-end distance, $\langle L\rangle \doteq -(\partial G/\partial F)_{T,N} = \beta^{-1}\partial(\ln Z_N)/\partial F$. Plot a universal curve for the force-extension characteristic: scaled average length $\langle L\rangle/Na$ versus scaled force βFa. Find the leading term in an expansion of this function at weak forces.
(c) Calculate the fluctuations of the end-to-end distance, $\langle\langle L\rangle\rangle \doteq \langle L^2\rangle - \langle L\rangle^2 = \beta^{-2}\partial^2(\ln Z_N)/\partial F^2$. Plot the scaled mean-square distance $\langle\langle L^2\rangle\rangle/Na^2$ versus the scaled force βFa. Find the value of the mean-square distance in the absence of a force. Comment on all noteworthy features.
(d) Show that the entropy $S \doteq -(\partial G/\partial T)_{F,N}$ and the heat capacity $C_F \doteq T(\partial S/\partial T)_{F,N}$ are given by the following expressions:

$$\frac{S}{Nk_B} = \ln\left(4\pi \frac{\sinh(\beta Fa)}{\beta Fa}\right) + 1 - \beta Fa \coth(\beta Fa), \quad \frac{C_F}{Nk_B} = 1 - \frac{(\beta Fa)^2}{\sinh^2(\beta Fa)}. \tag{3}$$

Plot both functions over the range $0 < \beta Fa < 20$ and interpret the results. Note that βFa can be interpreted as scaled force at constant temperature or as inverse scaled temperature at constant force. Identify any features that are unphysical and, therefore, in need of being fixed by a better model.

Solution: