Soft Matter and Polymer Physics

problem set November 29, 2016

Free energy of Gaussian chain – force-extension curve

Consider a Gaussian polymer, $\{\mathbf{r}_i\}$, that is comprised of N segments, $i = 0, \cdots, N-1$. The Hamiltonian is given by

$$\beta\mathcal{H}_0 = \frac{3(N-1)}{2R_{e0}^2}\sum_{i=0}^{N-2}(\mathbf{r}_{i+1}-\mathbf{r}_i)^2 \tag{1}$$

where $\beta = 1/k_{\mathrm{B}}T$ denote the inverse temperature. The partition function, $\mathcal{Z}_0$, of this Gaussian polymer is given by

$$\mathcal{Z}_0 = \frac{1}{\lambda_T^{3N}}\int\prod_{i=0}^{N-1}\mathrm{d}^3\mathbf{r}_i\; e^{-\beta\mathcal{H}_0} = \frac{V}{\lambda_T}\left(\frac{2\pi R_{e0}^2}{3(N-1)\lambda_T^2}\right)^{\frac{3(N-1)}{2}} \tag{2}$$

where V and λ_T denote the volume of the system and the thermal de-Broglie wavelength, respectively.

Consider two ensembles:

(a) *fixed end-to-end distance*, $\mathbf{R}$ – The end-to-end distance $\mathbf{r}_{N-1}-\mathbf{r}_0$ along is fixed to $\mathbf{R}$, and the partition function takes the form

$$\begin{aligned}\mathcal{Z}_a(\mathbf{R}) &= \frac{1}{\lambda_T^{3N}}\int\prod_{i=0}^{N-1}\mathrm{d}^3\mathbf{r}_i\; e^{-\beta\mathcal{H}_0}\delta(\mathbf{r}_{N-1}-\mathbf{r}_0-\mathbf{R}) \\ &= \mathcal{Z}_0\left\langle\delta(\mathbf{r}_{N-1}-\mathbf{r}_0-\mathbf{R})\right\rangle_0\end{aligned} \tag{3}$$

where the $\mathcal{Z}_0$ is the partition function of a Gaussian polymer, see Eq. (2), and the average $\langle\cdots\rangle_0$ refers to the canonical average of a free Gaussian polymer. Define the free-energy of a polymer with a fixed end-to-end distance vector $\mathbf{R}$ (thermodynamic macrostate) by

$$\beta F(\mathbf{R}) = -\ln\mathcal{Z}_a(\mathbf{R}) \tag{4}$$

(b) *force along the end-to-end distance*, $\mathbf{f}$ – In addition to the bonded Hamiltonian (i.e., harmonic springs between neighboring beads along the chain) there acts a force $\mathbf{f}$ between the first and last bead. Let , the partition function takes the form

$$\begin{aligned}\mathcal{Z}_b(\mathbf{f}) &= \frac{1}{\lambda_T^{3N}}\int\prod_{i=0}^{N-1}\mathrm{d}^3\mathbf{r}_i\; e^{-\beta\mathcal{H}_0-\beta\mathbf{f}\cdot(\mathbf{r}_{N-1}-\mathbf{r}_0)} \qquad (5)\\ &= \frac{1}{\lambda_T^{3N}}\int\prod_{i=0}^{N-1}\mathrm{d}^3\mathbf{r}_i\; e^{-\beta[\mathcal{H}_0+\mathcal{H}_b(\mathbf{f})]} \\ \text{with}\quad \beta\mathcal{H}_b(\mathbf{f}) &\equiv \beta\mathbf{f}\cdot(\mathbf{r}_{N-1}-\mathbf{r}_0)\end{aligned}$$

The concomitant free energy of this ensemble is given by

$$\beta G(\mathbf{f}) = -\ln \mathcal{Z}_b(\mathbf{f}) \tag{6}$$

Using analytical considerations or computer simulations, consider the following tasks:

- Use Eqs. (3) and (4) to calculate the free-energy difference $\beta\Delta F_{21}(R)$ between the states (1) $\mathbf{R} = 0$ and (2) $\mathbf{R} = R\mathbf{e}_x$ in a computer simulation.

- Calculate the force that acts between the end segments in state (2) according to

$$\beta\tilde{\mathbf{f}}(\mathbf{R}) \equiv -\frac{\partial\beta\Delta F_{21}(\mathbf{R})}{\partial\mathbf{R}} \tag{7}$$

  Use thermodynamic integration to compute the free energy change,

$$\beta\Delta F_{21}(R) = -\int_0^R \mathrm{d}R'\ \beta\tilde{\mathbf{f}}(R'\mathbf{e}_x) \tag{8}$$

- Calculate the force-extension curve in the ensemble (b), i.e., $\mathbf{R}(\mathbf{f}) \equiv \langle \mathbf{r}_{N-1} - \mathbf{r}_0 \rangle_b$.

- Use the force-extension curve to compute the free-energy change between the states (1) $\beta\mathbf{f} = 0$ and (2) $\beta\mathbf{f} = \frac{3R}{R_{e0}^2}\mathbf{e}_x$

$$\beta\Delta G_{21}(f) = \int_0^f \mathrm{d}f'\ \left\langle \frac{\partial\beta\mathcal{H}_b}{\partial f'} \right\rangle_b \tag{9}$$