# Suspensions and polymer solutions

## Solution of Exercise 5

1. Since the chain is assumed to consist of $N$ segments of fixed length $2l_{\rm p}$ each, we can define a certain chain configuration by specifying the $N$ solid angles, $\{\theta_n, \varphi_n\}_{n=1,\ldots,N}$, of segment orientations, where $\theta_n$ are measured with respect to the $x$ axis. The extension of the chain along the $x$ axis in the given configuration is $X = 2l_{\rm p}\sum_{n=1}^N \cos\theta_n$, and its energy is $U = -\vec{f}\cdot\vec{R} = -fX = -2fl_{\rm p}\sum_{n=1}^N \cos\theta_n$. This energy is analogous to that of $N$ independent dipoles, of dipole moment $2l_{\rm p}$ each, interacting with an external field $\vec{f} = f\hat{\mathbf{x}}$. Since there is no coupling between the "dipoles", the partition function can be decomposed into a product of independent partition functions for each "dipole" separately,

$$\begin{aligned} Z(T,f,N) &= \int_0^{2\pi} d\varphi_1 \cdots \int_0^{2\pi} d\varphi_N \int_{-1}^1 d(\cos\theta_1)\cdots\int_{-1}^1 d(\cos\theta_N) e^{2\beta f l_{\rm p}\sum_{n=0}^N \cos\theta_n} \\ &= \left[\int_0^{2\pi} d\varphi \int_{-1}^1 d(\cos\theta) e^{2\beta f l_{\rm p}\cos\theta}\right]^N = \left[4\pi\frac{\sinh(2\beta f l_{\rm p})}{2\beta f l_{\rm p}}\right]^N. \end{aligned} \tag{1}$$

2. The free energy is

$$G(T,f,N) = -k_{\rm B}T\ln Z = -Nk_{\rm B}T\left[\ln\left(\frac{\sinh(2\beta f l_{\rm p})}{2\beta f l_{\rm p}}\right) + \text{const}\right]. \tag{2}$$

3. The mean extension is

$$\langle X\rangle = -\left(\frac{\partial G}{\partial f}\right)_{T,N} = 2Nl_{\rm p}\left[\coth(2\beta f l_{\rm p}) - \frac{1}{2\beta f l_{\rm p}}\right] \equiv 2Nl_{\rm p}\mathcal{L}(2\beta f l_{\rm p}), \tag{3}$$

where $\mathcal{L}(u) = \coth(u) - 1/u$ is called the Langevin Function. For small arguments $\mathcal{L}(u \ll 1) \simeq u/3$. Hence, for $f \ll k_{\rm B}T/l_{\rm p}$ we get $\langle X\rangle \simeq [4Nl_{\rm p}^2/(3k_{\rm B}T)]f$, i.e., an "entropic spring", as expected. For large arguments $\mathcal{L}(u \gg 1) \simeq 1 - 1/u$. Hence, for $f \gg k_{\rm B}T/l_{\rm p}$ we get $\langle X\rangle \simeq 2Nl_{\rm p}[1 - k_{\rm B}T/(2l_{\rm p}f)]$, i.e., the extension approaches its maximum possible value, $L = 2Nl_{\rm p}$, as $f^{-1}$.

4. From Eq. (3) we see that to get $\langle X\rangle = L/2$ we need $u$ that satisfies $\mathcal{L}(u) = 1/2$. Numerical solution of this equation gives $u \simeq 1.8$. The required force is, therefore, $f \simeq 1.8k_{\rm B}T/(2l_{\rm p}) \simeq 7.5\times 10^{-14}$ N, or 0.075 pN.

*Remark*: As shown in the class, the actual approach to maximum extension goes as $f^{-1/2}$ and not as $f^{-1}$. This is because when the chain is highly stretched the assumption of dividing it into many freely jointed segments breaks down.