Solutions to Problem Set 5

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1 Restoring force for highly stretched polymers

1.1 A globally valid asymptotic approximation

Using the substitution $t = ua$ the expression can be rewritten as

$$\begin{aligned} P_N(r) &= \frac{1}{2\pi^2 r}\int_0^\infty \frac{t}{a}\sin(rt/a)\left[\frac{\sin t}{t}\right]^N \frac{dt}{a} \\ &= \frac{1}{2\pi^2 a^2 r}\int_0^\infty t\sin(rt/a)\left[\frac{\sin t}{t}\right]^N dt \end{aligned}$$

The integrand is even, and can be rewritten as

$$\begin{aligned} P_N(r) &= \frac{1}{4\pi^2 a^2 r}\int_{-\infty}^\infty t\sin(rt/a)\left[\frac{\sin(t)}{t}\right]^N dt \\ &= \frac{1}{8i\pi^2 a^2 r}\int_{-\infty}^\infty u\left(e^{irt/a} - e^{-irt/a}\right)\left[\frac{\sin(t)}{t}\right]^N dt \\ &= \frac{1}{4i\pi^2 a^2 r}\int_{-\infty}^\infty te^{irt/a}\left[\frac{\sin(t)}{t}\right]^N dt \\ &= \frac{1}{4i\pi^2 a^2 r}\int_{-\infty}^\infty t\exp\left[-Nf(t)\right] dt \end{aligned}$$

where

$$f(t) = -\frac{irt}{Na} - \log\left(\frac{\sin t}{t}\right).$$

We define $\xi = r/Na$ and keep it fixed. The first and second derivatives are

$$\begin{aligned} f'(t) &= -i\xi - \cot t + \frac{1}{t} \\ f''(t) &= 1 + \cot^2 t - \frac{1}{t^2}. \end{aligned}$$

*Solution to problem 1 based on sections of *Random Walks and Random Environments* by Barry Hughes. Solutions 2 and 3 based on previous years.

By putting $f'(t) = 0$, we find that there is a saddle point at $t_0 = iL^{-1}(\xi)$ where L is the Langevin function $L(\xi) = \coth\xi - 1/\xi$. Over the range $0 < \xi < 1$ the Langevin function is monotonic and thus has a well-defined inverse. We see that the second derivative of f can be written as

$$\begin{aligned} f''(t) &= 1 - \coth^2(-it) + \frac{1}{(-it)^2} \\ &= 1 - \left(\coth(-it) - \frac{1}{(-it)}\right)^2 - \frac{2\coth(-it)}{(-it)} + \frac{2}{(-it)^2} \\ &= 1 - \xi^2 - \frac{2\xi}{L^{-1}(\xi)}. \end{aligned}$$

This function is positive, so we deform the contour of integration to the line $\mathrm{Im}(t) = L^{-1}(\xi)$. Our main contribution comes from the above saddle point and we obtain

$$\begin{aligned} P_N(r) &\sim \frac{L^{-1}(\xi)}{4\pi^2 r a^2}\sqrt{\frac{2\pi}{N(1-\xi^2-2\xi/L^{-1}(\xi))}}e^{-N\xi L^{-1}(\xi)}\left[\frac{\sinh(L^{-1}(\xi))}{L^{-1}(\xi)}\right]^N. \\ &\sim \frac{L^{-1}(\xi)}{\xi\sqrt{8\pi^3N^3a^6(1-\xi^2-2\xi/L^{-1}(\xi))}}e^{-N\xi L^{-1}(\xi)}\left[\frac{\sinh(L^{-1}(\xi))}{L^{-1}(\xi)}\right]^N. \\ &\sim \frac{L^{-1}(r/aN)}{r\sqrt{8\pi^3Na^4(1-(r/aN)^2-2r/aNL^{-1}(r/aN))}}e^{-rL^{-1}(r/aN)/a}\left[\frac{\sinh(L^{-1}(r/aN))}{L^{-1}(r/aN)}\right]^N. \end{aligned}$$

1.2 Free energy

The free energy is given by

$$\begin{aligned} F &= TS \\ &= -T\log P_N(r) \\ &\sim \frac{T}{2}\log\left[8\pi^3Na^4(1-(r/aN)^2-2r/aNL^{-1}(r/aN))\right] + \frac{rTL^{-1}(r/Na)}{a} \\ &\quad -T\log L^{-1}(r/aN) + T\log r - TN\log\left[\frac{\sinh(L^{-1}(r/Na))}{L^{-1}(r/Na)}\right]. \end{aligned}$$

The restoring force is given by

$$\begin{aligned} f &= -\frac{dF}{dr} \\ &= -\frac{T(-2r/a^2N^2 - 2/aNL^{-1}(r/Na) + 2rM(r/Na)/(aNL^{-1}(r/Na))^2)}{2(1-(r/aN)^2-2r/aNL^{-1}(r/aN))} \\ &\quad -\frac{TL^{-1}(r/Na)}{a} - \frac{TrM(r/Na)}{Na^2} + T\frac{M(r/aN)}{aNL^{-1}(r/aN)} - T/r \\ &\quad +\frac{TN\coth(L^{-1}(r/Na)M(r/Na)}{Na} - \frac{TNM(r/Na)}{NaL^{-1}(r/Na)} \\ &= \frac{T(-2r/a^2N^2 - 2/aNL^{-1}(r/NA) + 2rM(r/Na)/(aNL^{-1}(r/Na))^2)}{2(1-(r/aN)^2-2r/aNL^{-1}(r/aN))} \\ &\quad -\frac{TL^{-1}(r/Na)}{a} + T\frac{M(r/aN)}{aNL^{-1}(r/aN)} - T/r \end{aligned}$$

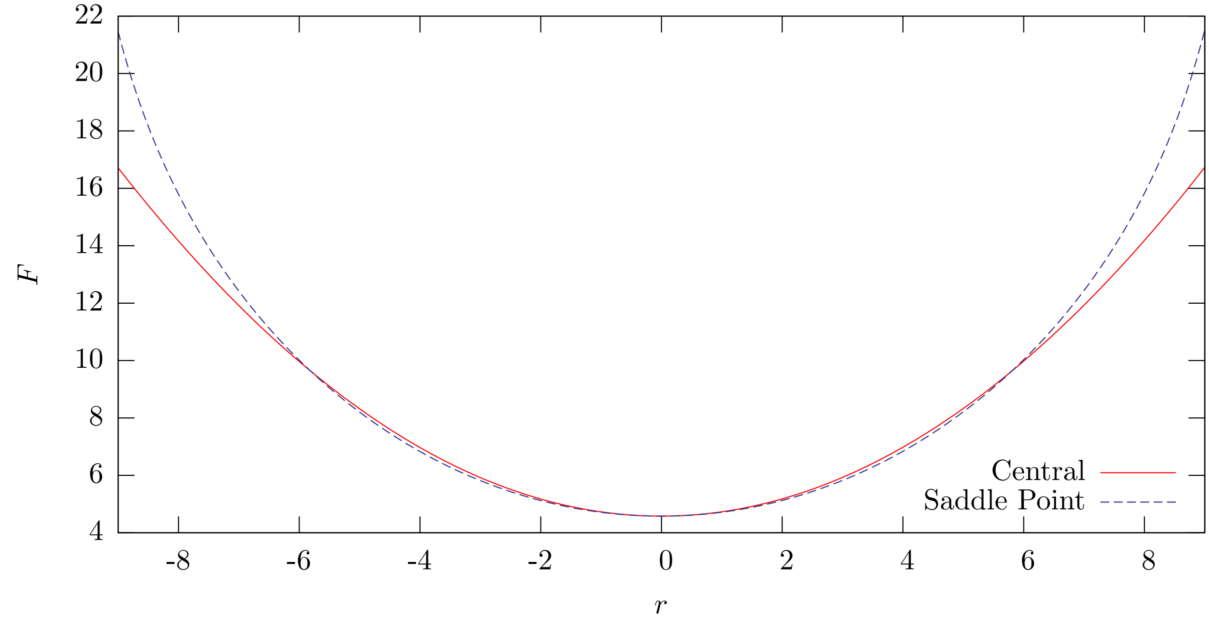

Figure 1: Comparison between the two approximations for free energy for the case when $a = T = 1$ and $N = 10$.

where $M(z)$ is the first derivative of $L^{-1}(z)$. By the inverse function theorem, we know that

$$M(z) = \frac{1}{L'(L^{-1}(z))}.$$

We compare this to the central region approximation, shown on problem set 1 to be

$$P_N^c(r) \sim \left(\frac{3}{2\pi a^2 N}\right)^{3/2} \exp\left(-\frac{3r^2}{2a^2 N}\right).$$

The free energy for this expression is

$$F^c = -\frac{3}{2}\log\left(\frac{3}{2\pi a^2 N}\right) + \frac{3r^2}{2a^2 N}.$$

and the restoring force is

$$f^c \sim -\frac{3r}{a^2 N}.$$

A comparison between the two expressions for free energy and restoring force are shown in figures 1 and 2 respectively. We see a good match in the central region between the two approximations. As $r \to a$, we see that the restoring force begins to get very large, as would be expected for a highly stretched polymer.

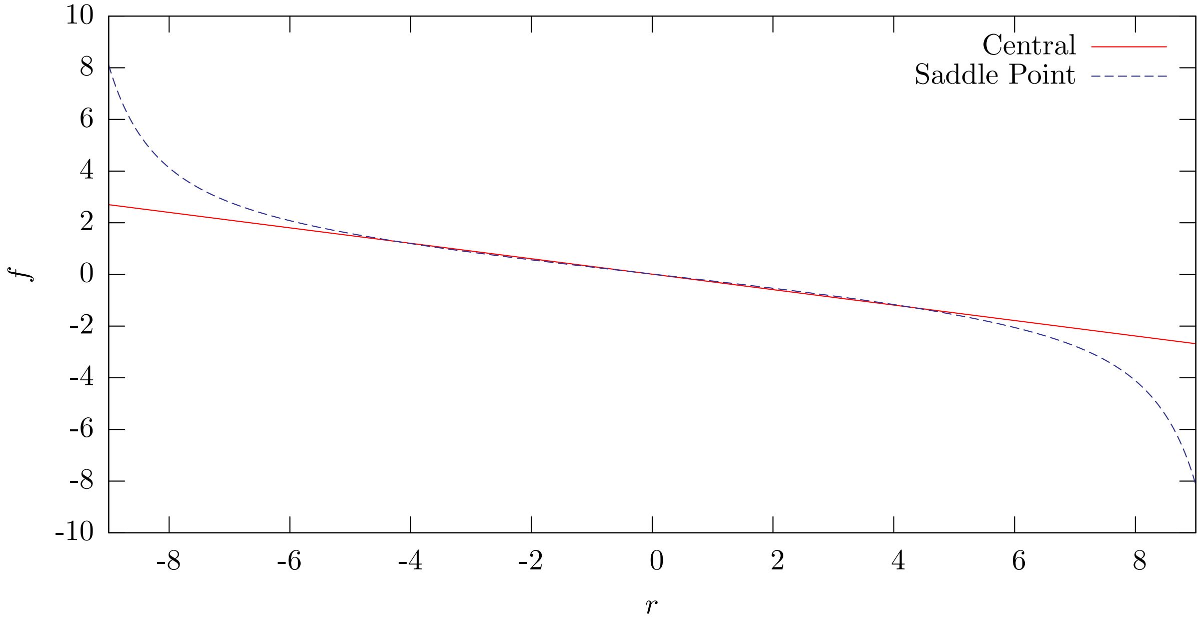

Figure 2: Comparison between the two approximations for the restoring force for the case when $a = T = 1$ and $N = 10$.

2 Linear Polymer Structure

2.1 Mean Total Energy

We define $\eta = \alpha\sigma^2/kT$ so that $p(\theta) \propto e^{\eta\cos\theta}$. The normalizing constant can be found as

$$\begin{aligned} A(\eta) &= \int_0^{2\pi}\int_0^{\pi} e^{\eta\cos\theta}\sin\theta d\theta d\phi \\ &= 2\pi\frac{e^{\eta}-e^{-\eta}}{\eta} = 4\pi\frac{\sinh\eta}{\eta}. \end{aligned}$$

Thus we have the normalized $p(\theta)$ as

$$p(\theta) = \frac{1}{A(\eta)}e^{\eta\cos\theta} = \frac{\eta}{4\pi\sinh\eta}e^{\eta\cos\theta}.$$

To get $\langle E_N\rangle$ we first calculate the correlation coefficient $\rho(T)$, which is

$$\rho(T) = \frac{\langle \Delta\vec{x}_n \cdot \Delta\vec{x}_{n+1}\rangle}{a^2} = \langle\cos\theta\rangle.$$

We can get this easily using the derivative of $A(\eta)$:

$$\begin{aligned} \langle\cos\theta\rangle &= \frac{1}{A(\eta)}\int_0^{2\pi}\int_0^{\pi}\cos\theta e^{\eta\cos\theta}\sin\theta d\theta d\phi \\ &= \frac{1}{A(\eta)}\frac{dA(\eta)}{d\eta} = \coth\eta - \frac{1}{\eta}. \end{aligned}$$

Therefore

$$\langle E_N \rangle = -(N-1)\alpha a^2 \rho(T) = -(N-1)\alpha a^2 \left(\coth\eta - \frac{1}{\eta}\right).$$

2.2 Asymptotic scaling

Since two adjacent steps have correlation $\rho(T)$, the correlation between n-th and $n+m$-th steps is generally given by

$$\frac{\langle \vec{\Delta x}_n \cdot \vec{\Delta x}_{n+m} \rangle}{a^2} = \rho(T)^m.$$

From the lecture we know

$$\langle R_N^2 \rangle \sim \frac{1+\rho(T)}{1-\rho(T)}\, a^2 \quad \text{and} \quad a_{\text{eff}}(T) \sim \sqrt{\frac{1+\rho(T)}{1-\rho(T)}}\, a \quad \text{as } N \to \infty.$$

Thus the asymptotic behaviors of $\rho(T)$ and $a_{\text{eff}}(T)$ are

$$\rho(T) = \frac{e^\eta + e^{-\eta}}{e^\eta - e^{-\eta}} - \frac{1}{\eta} = \begin{cases} \dfrac{\eta}{3} = \dfrac{3\alpha\sigma^2}{k_B T} & (\eta \to 0 \text{ or } T \to \infty) \\ 1 - \dfrac{1}{\eta} = 1 - \dfrac{k_B T}{\alpha\sigma^2} & (\eta \to \infty \text{ or } T \to 0), \end{cases}$$

$$\frac{a_{\text{eff}}(T)}{a} \sim \begin{cases} 1 + \dfrac{3\alpha\sigma^2}{k_B T} & (T \to \infty) \\ \sqrt{\frac{2\alpha\sigma^2}{k_B T}} & (T \to 0). \end{cases}$$

3 A persistent Lévy flight

First we take the sum of our non-independent steps, each expressed in terms of the independent steps, denoted with primes.

$$X_N = \sum_{n=1}^{N} \Delta x_n = (1+\rho)\Delta x_1' + \sum_{n=2}^{N-1} \Delta x_n' + (1-\rho)\Delta x_N'.$$

The structure function, $\hat{P}(k)$, of the PDF of $\sum \Delta x_n$ is given by the product of the structure functions associated with each step. The length scales of the first and last steps are renormalized by $1+\rho$ and $1-\rho$ respectively. Thus the structure function for the entire walk is given by

$$\hat{P_N}(k) = \exp\{-a(1+\rho)|k| - a(N-2)|k| - a(1-\rho)|k|\} = e^{-aN|k|}$$

and the corresponding PDF as found in Homework 1 is given by

$$P_N(x) = \frac{aN}{\pi(x^2 + a^2N^2)}.$$

Thus the half-width scales as $\Delta x_{1/2} \sim aN$ and it doesn't depend on ρ at all.

4 A continuous-time random walk

As shown in the lecture notes (2005, lecture 23), if the waiting time distribution is $\psi(t) = e^{-t}$, then the number of steps N that have taken place by time t follows a Poisson distribution

$$\mathcal{P}(N,t) = \frac{t^N}{e^{-t}} N!.$$

We also know that the probability of a Bernoulli walker being at a location x after N steps is

$$P(x,N) = \begin{cases} 2^{-N}\binom{N}{\frac{N+x}{2}} & \text{for } x+N \text{ even} \\ 0 & \text{for } x+N \text{ odd.} \end{cases}$$

By summing over all possible numbers of steps taken, we find that the probability disribution of the walker being at a location x after time t is

$$P(x,t) = \sum_{N=0}^{\infty} P(N,t)\mathcal{P}(N,t)$$

Only the terms in this sum of the form $N = x + 2m$ where $m = 0, 1, 2, \ldots$ will have a non-zero contribution, so

$$\begin{aligned} P(x,t) &= \sum_{m=0}^{\infty} P(x+2m,t)\mathcal{P}(x+2m,t) \\ &= \sum_{m=0}^{\infty} \frac{2^{-x-2m}\binom{x+2m}{m} t^{x+2m} e^{-t}}{(x+2m)!} \\ &= \sum_{m=0}^{\infty} \frac{(t/2)^{x+2m} e^{-t}}{(x+m)!m!} \\ &= I_x(t)e^{-t} \end{aligned}$$

where $I_x(t)$ is the modified Bessel function.