Solutions to Problem Set 4

Edited by Chris H. Rycroft*

February 17, 2005

1 Linear Polymer Structure

1.1 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

$$\rho(T) = \frac{\langle \mathbf{\Delta x_n}\cdot\mathbf{\Delta x_{n+1}}\rangle}{a^2} = \langle\cos\theta\rangle.$$

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

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

*Based on solutions for problem 3 by Ryan Larsen and David Vener (2003), and problem 4 by Ahmed Ismail (2003).

1.2 Asymptotic scaling

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

$$\frac{\langle \mathbf{\Delta x_n} \cdot \mathbf{\Delta x_{n+m}} \rangle}{a^2} = \rho(T)^m.$$

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

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

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

2 Polymer Surface Adsorption

2.1 PDF of displacement between adsorption sites

To find the probability density function of the displacement between successive adsorption sites, we make use of the electrostatic analogy described in the lectures and in *A Guide To First Passage Processes* by S. Redner. To find the hitting probability of the walker on the plane we solve the problem of finding the electric potential ϕ due to a charge of size $q = 1/4\pi D$ at $\mathbf{r_0} = (0, 0, a)$, subject to the condition that $\phi = 0$ on the plane. By introducing an image charge at $-\mathbf{r_0}$ we see that

$$\phi(\mathbf{r}) = -\frac{q}{|\mathbf{r} - \mathbf{r_0}|} + \frac{q}{|\mathbf{r} + \mathbf{r_0}|}.$$

The hitting probability on the plane is given by

$$\begin{aligned} P(x,y) &= -D \left.\frac{\partial \phi}{\partial z}\right|_{z=0} \\ &= -Dq \left[\frac{z-a}{(x^2+y^2+(z-a)^2)^{3/2}} - \frac{z+a}{(x^2+y^2+(z+a)^2)^{3/2}} \right]_{z=0} \\ &= \frac{a}{2\pi(x^2+y^2+a^2)^{3/2}}. \end{aligned}$$

3 Position after N steps

To calculate the probability density function of the position $P_N(x,y)$ after N steps, we find the characteristic function of $p(x,y)$ found above:

$$\hat{p}(k,l) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy \frac{a e^{-ikx-ily}}{2\pi(x^2+y^2+a^2)^{3/2}}.$$

By symmetry, we know that $\hat{p}(\mathbf{k})$ must be a function of $|\mathbf{k}|$, and we therefore assume without loss of generality that $\mathbf{k} = (k, 0)$. By changing to polar coordinates $x = r\cos\theta$, $y = r\sin\theta$, we obtain

$$\hat{p}(\mathbf{k}) = \int_0^\infty dr \int_0^{2\pi} d\theta \frac{re^{-ikr\cos\theta}}{2\pi(r^2+a^2)^{3/2}}.$$

Carrying out the angular integration gives

$$\hat{p}(\mathbf{k}) = a\int_0^\infty \frac{rdr}{(r^2+a^2)^{3/2}} J_0(kr).$$

To solve this, we write the above integral as $I(k, a)$. We know that

$$\begin{aligned} I(0,a) &= a\int_0^\infty \frac{rdr}{(r^2+a^2)^{3/2}} \\ &= \left[-\frac{a}{\sqrt{r^2+a^2}}\right]_0^\infty \\ &= 1. \end{aligned}$$

By integrating by parts, we also know that

$$I(k,a) = a\int_0^\infty \frac{dr}{\sqrt{r^2+a^2}} kJ_0'(kr).$$

Differentiating this expression gives

$$I_k(k,a) = a\int_0^\infty \frac{dr}{\sqrt{r^2+a^2}} (krJ_0''(kr) + J_0'(kr)).$$

By definition, we know that the zeroth order Bessel function satisfies the differential equation $x^2 J_0''(x) + xJ_0'(x) + x^2 J_0(x) = 0$ and therefore we find that

$$I_k(k,a) = a\int_0^\infty \frac{dr}{\sqrt{r^2+a^2}} (-krJ_0(kr)).$$

Differentiating with respect to a gives

$$I_{ka}(k,a) = \frac{I_k(k,a)}{a} + a\int_0^\infty \frac{akrJ_0(kr)dr}{(r^2+a^2)^{3/2}}$$

and hence we have a partial differential equation

$$I_{ka}(k,a) = \frac{I_k(k,a)}{a} + akI(k,a).$$

By inspection, we see that a solution to this equation that satisfies the condition $I(0, a) = 1$ is $I(k, a) = e^{-ka}$ and hence

$$\hat{p}(\mathbf{k}) = e^{-a|\mathbf{k}|}.$$

From this expression, it is easy to see that $\hat{P}_N(\mathbf{k}) = e^{-aN|\mathbf{k}|}$ and hence

$$P_N(x,y) = \frac{Na}{2\pi(x^2+y^2+N^2a^2)^{3/2}}.$$

4 Solution to the Telegrapher's Equation

4.1 Fourier-Laplace Transform

First we apply the Laplace Transform to obtain

$$s\left(s+r\right)\tilde{c}\left(x,s\right)-\left(s+r\right)\delta\left(x\right)=v^{2}\tilde{c}\left(x,s\right)_{xx}.$$

Applying the Fourier Transform gives

$$s\left(s+r\right)\hat{\tilde{c}}\left(k,s\right)-\left(s+r\right)=-k^{2}v^{2}\hat{\tilde{c}}(k,s)$$

from which we obtain

$$\hat{\tilde{c}}(s,k)=\frac{s+r}{k^{2}v^{2}+s(s+r)}.$$

4.2 Variance of the position

We use the relationship

$$\left\langle x^{2}\left(t\right)\right\rangle=-\left.\frac{\partial^{2}\hat{c}}{\partial k^{2}}\right|_{k=0}.$$

Accordingly,

$$\mathcal{L}\left[\left\langle x^{2}(t)\right\rangle\right]=\frac{2v^{2}}{s^{2}\left(s+r\right)}=\frac{2v^{2}}{r^{2}}\left(\frac{r}{s^{2}}-\frac{1}{s}+\frac{1}{s+r}\right)$$

which we transform to obtain

$$\left\langle x^{2}(t)\right\rangle=\frac{2v^{2}}{r^{2}}(rt+e^{-rt}-1).$$

When $rt\ll 1$ we have $\langle x^{2}(t)\rangle\sim t^{2}$ (superdiffusion) and when $rt\gg 1$ we have $\langle x^{2}(t)\rangle\sim t/r$ (normal diffusion).

4.3 CLT for a persistent random walk

Beginning with the diffusion equation, $c_{t}=Dc_{xx}$, we first apply the Laplace transform to obtain

$$s\tilde{c}\left(x,s\right)-\delta\left(x\right)=D\tilde{c}\left(x,s\right)_{xx}.$$

Applying the Fourier transform gives

$$s\hat{\tilde{c}}\left(k,s\right)-1=-k^{2}D\hat{\tilde{c}}\left(k,s\right) \tag{1}$$

$$\hat{\tilde{c}}=\frac{1}{s+k^{2}D}=\frac{1}{s+v^{2}k^{2}/r} \tag{2}$$

where we used $D=v^{2}/r$. In long time limit ($s\ll r$), the solution from part (a) can be approximated as

$$\hat{\tilde{c}}=\frac{s+r}{s(s+r)+v^{2}k^{2}}=\frac{s/r+1}{s(s/r+1)+v^{2}k^{2}/r}\sim\frac{1}{s+v^{2}k^{2}/r}$$

which is the Fourier-Laplace transform of the diffusion equation.

4.4 Inverting the transforms

We carry out the Fourier inversion first; we obtain

$$\tilde{c}(x,s) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-ikx} \frac{s+r}{k^2v^2 + s(s+r)}.$$

The poles are located at $\pm i\sqrt{\frac{s(s+r)}{v^2}}$. In the usual fashion of performing Fourier integrals of this type, we arrive at

$$\tilde{c}\,(x,s) = \frac{1}{2v} \frac{s+r}{\sqrt{s\,(s+r)}} e^{-\sqrt{s(s+r)}\frac{|x|}{v}}.$$

By noting that $s\,(s+r) = (s+r/2)^2 - r^2/4$ and the property $\mathcal{L}^{-1}\,\{F\,(s+a)\} = e^{-at}\mathcal{L}^{-1}\,\{F\,(s)\}$ we obtain

$$c\,(x,t) = \frac{e^{-rt/2}}{2}\mathcal{L}^{-1}\left\{\frac{1}{v}\frac{s+r/2}{\sqrt{(s+r/2)\,(s-r/2)}}\;e^{-\sqrt{(s+r/2)(s-r/2)}\frac{|x|}{v}}\right\}.$$

We introduce the variables $\bar{s} = \frac{s|x|}{v}$ and $\alpha = \frac{r|x|}{2v}$ and $\bar{t} = \frac{vt}{|x|}$. We can then write the Laplace transform above as

$$\frac{1}{|x|}\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} d\bar{s}e^{\bar{s}\bar{t}}\frac{\bar{s}+\alpha}{\sqrt{(\bar{s}+\alpha)\,(\bar{s}-\alpha)}}\;e^{-\sqrt{(\bar{s}+\alpha)(\bar{s}-\alpha)}}.$$

Notice how in the complex $\bar{s}$-plane we have a branch cut on the real axis between $-\alpha$ and $+\alpha$. We must choose whether to close the the integration path on the right side (no singularities) or of the left side (branch cut). If we consider the original differential equation as a wave equation, we know from a physical argument that the signal cannot propagate faster than v. Therefore, when $|x| > vt$ (or $\bar{t} < 1$) then solution should be 0 and we will close the contour in the right-hand plane. However, when when $|x| < vt$ (or $\bar{t} > 1$) we close on the left-hand plane where we will pick up a non-zero contribution from the branch cut. Hence the integral reduces to

$$\frac{1}{|x|}\frac{1}{2\pi i}\left\{\int_{-\alpha}^{\alpha} d\bar{s}e^{\bar{s}\bar{t}}\frac{\bar{s}+\alpha}{-i\sqrt{\alpha^2-\bar{s}^2}}\;e^{i\sqrt{\alpha^2-\bar{s}^2}} + \int_{\alpha}^{-\alpha} d\bar{s}\;e^{\bar{s}\bar{t}}\frac{\bar{s}+\alpha}{i\sqrt{\alpha^2-\bar{s}^2}}\;e^{-i\sqrt{\alpha^2-\bar{s}^2}}\right\}.$$

If we change $\hat{s} \to -\hat{s}$ in the second integral, combine integrals, and perform a variable change $\bar{s} = \alpha\cos(\theta)$, we reduce the integral to

$$\frac{1}{|x|}\frac{\alpha}{2\pi i}\int_0^{\pi} d\theta\left\{(1+\cos\theta)\;e^{\alpha(\bar{t}\cos\theta+i\sin\theta)} + (1-\cos\theta)\;e^{-\alpha(\bar{t}\cos\theta+i\sin\theta)}\right\}.$$

We can then write $t\,\cos\theta + i\sin\theta = \sqrt{t^2-1}(\frac{t}{\sqrt{t^2-1}}\cos\theta + \frac{i}{\sqrt{t^2-1}}\sin\theta) = \cos(\theta - i\beta)$ where $\beta = \sinh^-1(\frac{1}{\sqrt{t^2-1}})$. We simplify the equations to

$$\frac{1}{|x|}\frac{\alpha}{\pi}\{\int_0^{\pi} d\theta\cosh((\alpha\sqrt{\bar{t}^2-1})\cos(\theta-\beta i)) + \int_0^{\pi} d\theta\cos(\theta)\sinh((\alpha\sqrt{\bar{t}^2-1})\cos(\theta-\beta i)\}.$$

Through a box contour integration we recognize that the above integral is equivalent to the integral $\int_{0+i\beta}^{\pi+i\beta}$. (The integrals along the lines of constant real θ cancel each other). Then through a change of variable $\theta \to \theta + i\beta$ we obtain

$$\frac{1}{|x|}\frac{\alpha}{\pi}\{\int_0^{\pi} d\theta\cosh((\alpha\sqrt{t^2-1})\cos\theta) + \int_0^{\pi} d\theta\cos(\theta+i\beta)\sinh((\alpha\sqrt{t^2-1})\cos(\theta))\}$$

or

$$\frac{1}{|x|}\frac{\alpha}{\pi}\{\int_0^\pi d\theta \cosh((\alpha\sqrt{t^2-1})\cos\theta) + \int_0^\pi d\theta(\cos(i\beta)\cos\theta - \sin(i\beta)\sin(\theta))\sinh((\alpha\sqrt{t^2-1})\cos\theta)\}.$$

The second term in the second integral reduces to 0 and we obtain

$$\frac{1}{|x|}\frac{\alpha}{\pi}\{I_0(\alpha\sqrt{\bar{t}^2-1}) + \cos(i\beta)I_1(\alpha\sqrt{\bar{t}^2-1})\}$$

or

$$\frac{1}{|x|}\frac{\alpha}{\pi}\{I_0(\alpha\sqrt{\bar{t}^2-1}) + \frac{\bar{t}}{\sqrt{\bar{t}^2-1}}I_1(\alpha\sqrt{\bar{t}^2-1})\}.$$

We define $z = \frac{r\sqrt{v^2t^2-x^2}}{2v}$ and obtain

$$c(x,t) = \frac{e^{-rt/2}}{2}\frac{r}{2v}\{I_0(z) + \frac{rt}{2z}I_1(z)\}$$

when $\bar{t} > 1$. Notice that at $\bar{t} = 1$ the Laplace integrand reduces to 1 as $\gamma \to \infty$. So the integral is $\delta(\bar{t}-1)$ or $\delta(vt - |x|)$. To summarize, we have

$$c(x,t) = \frac{e^{-rt/2}}{2}\{\delta(x-vt) + \delta(x+vt) + \frac{r}{2v}\{I_0(z) + \frac{rt}{2z}I_1(z)\}H(vt-|x|)\}.$$

5 Inelastic diffusion

5.1 Finding the PDF of X_N

In terms of $p(x)$ for the ΔX_n, the joint PDF of the sum will be given by an $(N-1)$-dimensional integral:

$$P_N(x_N) = \int\cdots\int p\left(\frac{x_N}{a^N} - \sum_{j=1}^{N-1} a^{j-N}\Delta x_j\right)\prod_{j=1}^{N-1}\left(p(\Delta x_j)\, d(\Delta x_j)\right).$$

Alternatively, since the steps are independent, we can write this as the inverse Fourier transform of the convolution. Define the characteristic function of the ΔX_n as

$$\hat{p}(k) = \int_{-\infty}^{\infty} e^{-ikx} p(x)\, dx.$$

Then the probability of the sum is given by

$$P_N(x_N) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}\hat{P}_N(k)\, dx = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}\prod_{n=1}^{N}\hat{p}(a^n k)\, dk. \tag{3}$$

5.2 Finding the cumulants of X_N

Since the steps are independent, we can write the cumulant expansion of $P_N(x)$ in terms of the cumulant expansion of $p_i(x)$:

$$\ln\hat{P}_N(k) = \sum_{m=1}^{N}\ln\hat{p}_m(k) = \sum_{m=1}^{N}\sum_{l=2}^{\infty}\frac{(-ik)^l}{l!}c_{m,l}, \tag{4}$$

where the sum over l in (4) is from 2 to infinity since we have assumed zero mean. However, we know that for the mth step in the random walk, we are computing the distribution of $a^m \Delta X_m$, which leads to the result that

$$c_{m,l} = a^{ml} c_l, \tag{5}$$

where c_l is the lth cumulant of $p(x)$. Therefore, inserting (5) into (4), we have

$$\ln \hat{P}_N(k) = \sum_{m=1}^{N} \sum_{l=2}^{\infty} \frac{(-ik)^l}{l!} a^m c_l = \sum_{l=2}^{\infty} \frac{(-ik)^l}{l!} \left(\sum_{m=1}^{N} a^m \right) c_l. \tag{6}$$

Of course, we know that the bracketed summation in (6) is just

$$\sum_{m=1}^{N} a^m = \frac{a^{N+1} - a}{a - 1}$$

for $0 < a < 1$, and therefore (6) becomes

$$\ln \hat{P}_N(k) = \sum_{m=1}^{N} \sum_{l=2}^{\infty} \frac{(-ik)^l}{l!} a^m c_l = \sum_{l=2}^{\infty} \frac{(-ik)^l}{l!} \left(\frac{a^{N+1} - a}{a - 1} \right) c_l,$$

which allows us to conclude that

$$C_{N,l} = \frac{a - a^{N+1}}{1 - a} c_l.$$

5.3 Limit of Cumulants

In the given limit, we have

$$\frac{C_{2m}}{C_2^m} = \frac{\lim_{N\to\infty} \left(\frac{a - a^{N+1}}{1-a} c_{2m} \right)}{\left[\lim_{N\to\infty} \left(\frac{a - a^{N+1}}{1-a} \right) c_2 \right]^m}. \tag{7}$$

When $a = 1 - \varepsilon$, where $\varepsilon > 0$, (7) becomes

$$\begin{aligned}
\frac{C_{2m}}{C_2^m} &= \frac{\lim_{N\to\infty} \left(\frac{(1-\varepsilon) - (1-\varepsilon)^{N+1}}{1-(1-\varepsilon)} c_{2m} \right)}{\left[\lim_{N\to\infty} \left(\frac{(1-\varepsilon) - (1-\varepsilon)^{N+1}}{1-(1-\varepsilon)} \right) c_2 \right]^m} \\
&= \frac{\frac{c_{2m}}{\varepsilon} \lim_{N\to\infty} \left((1-\varepsilon) - (1-\varepsilon)^{N+1} \right)}{\left[\frac{c_2}{\varepsilon} \lim_{N\to\infty} \left((1-\varepsilon) - (1-\varepsilon)^{N+1} \right) \right]^m}.
\end{aligned} \tag{8}$$

But we have

$$\lim_{N\to\infty} \left((1-\varepsilon) - (1-\varepsilon)^{N+1} \right) = 1 - \varepsilon - \lim_{N\to\infty} (1-\varepsilon)^{N+1} = 1 - \varepsilon,$$

and thus evaluating (8) we have

$$\frac{C_{2m}}{C_2^m} = \frac{\frac{c_{2m}}{\varepsilon} \left((1-\varepsilon) \right)}{\left[\frac{c_2}{\varepsilon} (1-\varepsilon) \right]^m} = \frac{\varepsilon^{m-1} c_{2m}}{c_2^m (1-\varepsilon)^{m-1}}.$$

Consequently, as $\varepsilon \to 0$, we have $(1-\varepsilon)^{m-1} \approx 1 - (m-1)\varepsilon$, and therefore

$$\frac{C_{2m}}{C_2^m} \approx \frac{\varepsilon^{m-1} c_{2m}}{c_2^m (1 - (m-1)\varepsilon)} = \frac{c_{2m}}{c_2^m} \varepsilon^{m-1} + \left(\frac{c_{2m}}{c_2^m} (m-1) \right) \varepsilon^m \approx O\left(\varepsilon^{m-1}\right),$$

which is the result we wanted to establish.

5.4 Effective Central Limit Theorem

From (3), we can write the function $P_\infty\left(\zeta C_2^{1/2}\right)$ as

$$P_N\left(\zeta C_2^{1/2}\right) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ik\zeta C_2^{1/2}} \exp\left(\ln \hat{P}_N(k)\right) d\left(\zeta C_2^{1/2}\right).$$

However, since $\ln \hat{P}_N(k)$ defines the cumulant expansion, we have

$$P_N\left(\zeta C_2^{1/2}\right) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ik\zeta C_2^{1/2}} \exp\left(\sum_{l=2}^{\infty} \frac{(-ik)^l}{l!} C_{N,l}\right) d\left(\zeta C_2^{1/2}\right). \tag{9}$$

But, from part (c), we have

$$C_{2m} \approx O\left(\varepsilon^{m-1} C_2^m\right),$$

and therefore as $\varepsilon \to 0$, (9) reduces to

$$P_N\left(\zeta C_2^{1/2}\right) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ik\zeta C_2^{1/2}} \exp\left(-\frac{1}{2}k^2 C_2\right) d\left(\zeta C_2^{1/2}\right),$$

from which we obtain

$$P_N\left(\zeta C_2^{1/2}\right) = \frac{1}{\sqrt{2\pi C_2}} e^{-\zeta^2/2},$$

and therefore we have the desired limit,

$$\phi(\zeta, \varepsilon) \to \phi_a(\zeta) = \frac{1}{\sqrt{2\pi}} e^{-\zeta^2/2}.$$