18.366 Random Walks and Diffusion, Spring 2005, M. Z. Bazant.

Solutions to Exam 2

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1. **Electrochemical Equilibrium.**

   (a) The Fokker-Planck (or Nernst-Planck) equations for diffusion and drift of ions in the "mean-field" electrostatic potential, ϕ, are:

$$\frac{\partial c_\pm}{\partial t} = \frac{\partial}{\partial x}\left(\pm\mu_\pm e\frac{d\phi}{dx}c_\pm\right) + \frac{\partial^2}{\partial x^2}\left(D_\pm c_\pm\right) \tag{1}$$

where $\mu_\pm = D_\pm/kT$ are the ionic mobilities, given by the Einstein relation. Assuming steady state and constant $D_\pm$, we obtain ODEs for equilibrium:

$$\pm\frac{d}{dx}\left(c_\pm\frac{d\psi}{dx}\right) = \frac{d^2c_\pm}{dx^2} \tag{2}$$

where $\psi = -e\phi/kT$. Integrating twice, using the boundary conditions, $\psi(\infty) = 0$ and $c_\pm(\infty) = c_0$, we obtain the expected concentration profiles of Boltzmann equilibrium:

$$c_\pm(x) = c_0e^{\pm\psi(x)} = c_0e^{\mp e\phi(x)/kT} \tag{3}$$

The diffuse charge density of ions is then

$$\rho(x) = e(c_+(x) - c_-(x)) = 2c_0\sinh\psi(x) \tag{4}$$

which combines with Poisson's equation of electrostatics :

$$-\varepsilon\frac{d^2\phi}{dx^2} = \rho \tag{5}$$

to produce the Poisson-Boltzmann equation. Changing variables, we obtain the required dimensionless form:

$$\frac{d^2\psi}{dy^2} = \sinh\psi \tag{6}$$

where $y = x/\lambda$ with a characteristic length scale,

$$\lambda = \sqrt{\frac{\varepsilon kT}{2e^2c_0}}. \tag{7}$$

   (b) Putting the units back, the linearized problem is

$$\lambda^2\frac{d^2\phi}{dx^2} = \phi, \quad \phi(\infty) = 0, \phi(0) = -\zeta \tag{8}$$

which is easily solved:

$$\phi(x) = -\zeta e^{-x/\lambda} \tag{9}$$

It is clear that the influence of the surface potential ζ decays exponentially with a characteristic length scale, λ. Equivalently, the (linearized) charge density

$$\rho(x) = \frac{\varepsilon\zeta}{\lambda^2}e^{-x/\lambda} \tag{10}$$

is "screened" in the bulk solution beyond a distance, λ, usually called the "Debye screening length" (even though it was derived earlier by Gouy).

(c) The region near the charged surface is commonly called a "double layer" since it looks like a capacitor, with the charge q on the surface, equal and opposite to the diffuse charge in solution which screens it:

$$q = -\int_0^\infty \rho(x)dx = \varepsilon \frac{d\phi}{dx}|_0^\infty = -\varepsilon \frac{d\phi}{dx}(0) \tag{11}$$

To obtain the charge-voltage relation $q(\zeta)$, and thus the differential capacitance, $dq/d\zeta$, we integrate the dimensionless PBE, using the trick of multiplying by ψ':

$$\psi'\psi'' = \psi' \sinh\psi \tag{12}$$

Integrating and requiring $\psi(\infty) = \psi'(\infty) = 0$, we obtain

$$\frac{1}{2}(\psi')^2 = \cosh\psi - 1 = 2\sinh^2(\psi/2) \tag{13}$$

We choose the "-" square root

$$\psi' = -2\sinh(\psi/2) \tag{14}$$

because the surface charge q in Eq. (11) has the opposite sign of the diffuse charge density, $\rho(0) \propto \psi(0) \propto zeta$. Putting units back and using Eq. (11), we obtain the desired result:

$$q(\zeta) = \frac{2\varepsilon kT}{\lambda e} \sinh\left(\frac{e\zeta}{2kT}\right) \tag{15}$$

(Note that in the limit of small voltage, $\zeta \ll kT/e$, the interface behaves like a parallel-plate capacitor of dielectric constant ε and width λ, since the capacitance is $dq/d\zeta \sim \varepsilon/\lambda$.)

(d) Since Eq. (14) is separable,

$$\frac{d\psi}{2\sinh(\psi/2)} = -dy \tag{16}$$

it is easily integrated (provided that you are comfortable with hyperbolic functions!):

$$\log\tanh(\psi/4) = -y + C \tag{17}$$

The constant C is typically replaced by γ:

$$\tanh(\psi/4) = \gamma e^{-y} \tag{18}$$

where

$$\gamma = \tanh(e\zeta/4kT) \tag{19}$$

Thus, we arrive at the Gouy-Chapman solution to the full, nonlinear Poisson-Boltzmann equation:

$$\psi(y) = 4\tanh^{-1}(\gamma e^{-y}) \tag{20}$$

or

$$\phi(x) = -\frac{4kT}{e}\tanh^{-1}(\gamma e^{-x/\lambda}), \tag{21}$$

which exhibits nonlinear screening at the same length scale λ.

2. **First passage of a set of random walkers.**

(a) For each (independent) walker, we make a continuum approximat and solve

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}, \quad P(x,t=0) = \delta(x-x_0) \tag{22}$$

subject to an absorbing boundary condition $P = 0$ at the origin, the "target". By linearity, we can satisfy the boundary condition by introducing an image source of negative sign at $-x_0$, which respresents "anti-walkers" which annihilate with the true walkers whenever they meet, at the origin (e.g. see Redner's book):

$$P(x,t) = \frac{e^{-(x-x_0)^2/4Dt} - e^{-(x+x_0)^2/4Dt}}{\sqrt{4\pi Dt}} \tag{23}$$

In terms of this solution, the survival probability is

$$S_i(t) = \mathrm{Prob}(T_i > t) = \int_0^\infty P(x,t)dt = \mathrm{erf}(x_0/\sqrt{4Dt}) \tag{24}$$

in terms of the error function

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-x^2}dx \tag{25}$$

The PDF of the first passage time is then

$$f_i(t) = -S_i'(t) = \frac{x_0}{\sqrt{4\pi Dt}}\, e^{-x_0^2/4Dt} \tag{26}$$

which is the Lévy-Smirnov density, derived by different means in lecture.

(b) On exam 1, we studied the largest step of a random walk, and here we need the smallest return time. By the same basic argument, the indepedence of the walkers implies:

$$S(t) = \mathrm{Prob}(T > t) = \mathrm{Prob}(T_i > t)^N = S_i(t)^N \tag{27}$$

Therefore, the PDF for the minumum first passage time is

$$f(t) = -S'(t) = Nf_i(t)S_i(t)^{N-1} \tag{28}$$

(c) Since $\mathrm{erf}(z) \sim 2z/\sqrt{\pi}$ as $z \to 0$, we have

$$S(t) \sim \left(\frac{x_0}{\sqrt{\pi Dt}}\right)^N \propto t^{-N/2} \tag{29}$$

and $f(t) \propto t^{-1-N/2}$ as $t \to \infty$. Therefore, the mth moment of the minimum first passage time

$$\langle T^m \rangle = \int_0^\infty t^m f(t)dt \tag{30}$$

is finite if and only if $m - 1 - N/2 > -1$, or $N > 2m$. In particular, the mean first passage time ($m = 1$) is finite if and only if $N \geq 3$.

3. **Escape from a symmetric trap.**[1].

(a) Mean escape time. We have:

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2} + \frac{D}{kT}\frac{\partial}{\partial x}\big(\phi'(x)P(x,t)\big)$$

where $P(x,t) = p(x,t|0,0)$ within initial condition at the bottom of the well, $P(x,0) = \delta(x)$, and absorbing boundary conditions at the exit points, $P(\pm x_1, t) = 0$. We can write:

$$\frac{\partial P}{\partial t} = \mathcal{L}_x P \tag{31}$$

with:

$$\mathcal{L}_x = D\frac{\partial}{\partial x}\left[e^{-\phi(x)/kT}\frac{\partial}{\partial x}\left(e^{\phi(x)/kT}\quad\right)\right] \tag{32}$$

The probability $S(t)$ of realization which have started at $x = 0$ and which have not yet reached $x = \pm x_1$ up to time t is given by:

$$S(t) = \int_{-x_1}^{x_1} p(x,t|0,0)\mathrm{d}x = \int_{-x_1}^{x_1} P(x,t)\mathrm{d}x$$

The distribution function $f(t)$ for the first passage time is then given by:

$$f(t) = \frac{\partial}{\partial t}\big(1 - S(t)\big) = -\frac{\partial S}{\partial t} = -\int_{-x_1}^{x_1}\frac{\partial P}{\partial t}\mathrm{d}x$$

The mean escape time is then given by[2]:

$$\tau = \int_0^\infty t f(t)\mathrm{d}t = \int_{-x_1}^{x_1} U_1(x)\mathrm{d}x \quad \text{with} \quad U_1(x) = -\int_0^\infty t\frac{\partial P}{\partial t}\mathrm{d}t$$

Performing an integration by part gives:

$$U_1(x) = \int_0^\infty P(x,t)\mathrm{d}t$$

By applying the operator $\mathcal{L}_x$ on both sides of this relation, we get:

$$\mathcal{L}_x U_1(x) = \int_0^\infty \mathcal{L}_x P(x,t)\mathrm{d}t = \int_0^\infty \frac{\partial P}{\partial t}\mathrm{d}t = -P(x,0) = -\delta(x)$$

where we have used (31). Using the expression (32) for $\mathcal{L}_x$, it is easy to solve:

$$U_1(x) = \frac{e^{-\phi(x)/kT}}{D}\int_x^{x_1} e^{\phi(y)/kT}\left[\int_0^y \delta(z)\mathrm{d}z\right]\mathrm{d}y$$

Now we can express the mean escape time:

$$\begin{aligned}\tau &= \int_{-x_1}^{x_1} U_1(x)\mathrm{d}x = 2\int_0^{x_1} U_1(x)\mathrm{d}x \\ &= \frac{1}{D}\int_0^{x_1} e^{-\phi(x)/kT}\left[\int_x^{x_1} e^{\phi(y)/kT}\mathrm{d}y\right]\mathrm{d}x\end{aligned}$$

[1] Solution written by Thierry Savin (2003). Used with permission.

[2] The function $U_1(x)$ is denoted $g_0(x)$ in Lecture 18 notes from 2005, and some of this derivation can also be found there.

By partial integration:

$$\tau = \frac{1}{D}\left[\left(\int_0^x e^{-\phi(y)/kT}\mathrm{d}y\right)\left(\int_x^{x_1} e^{\phi(y)/kT}\mathrm{d}y\right)\right]_0^{x_1} + \frac{1}{D}\int_0^{x_1} e^{\phi(x)/kT}\left[\int_0^x e^{-\phi(y)/kT}\mathrm{d}y\right]\mathrm{d}x$$

To get finally:

$$\boxed{\tau = \frac{1}{D}\int_0^{x_1}\mathrm{d}x\, e^{\phi(x)/kT}\int_0^x \mathrm{d}y\, e^{-\phi(y)/kT}}$$

(b) Kramers Mean Escape Rate. We use the saddle-point asymptotics to evaluate the integrals as $kT \to 0$.

$$\int_0^x e^{-\phi(y)/kT}\mathrm{d}y \sim \frac{1}{2}\sqrt{\frac{2\pi kT}{\phi''(0)}}e^{-\phi(0)/kT} = \sqrt{\frac{\pi kT}{2K_0}}$$

So that:

$$\int_0^{x_1}\mathrm{d}x\; e^{\phi(x)/kT}\int_0^x \mathrm{d}y\; e^{-\phi(y)/kT} \sim \sqrt{\frac{\pi kT}{2K_0}}\int_0^{x_1} e^{\phi(x)/kT}\mathrm{d}x$$

with:

$$\int_0^{x_1} e^{\phi(x)/kT}\mathrm{d}x \sim \frac{1}{2}\sqrt{-\frac{2\pi kT}{\phi''(x_1)}}e^{\phi(x_1)/kT} = \sqrt{\frac{\pi kT}{2K_1}}e^{E/kT}$$

Finally:

$$\boxed{R = \frac{1}{\tau} \sim R_0(T) = \frac{2D\sqrt{K_0K_1}}{\pi kT}e^{-E/kT} \propto e^{-E/kT}}$$

(c) First Correction to the Kramers Escape Rate. In the next derivation, we will use the following relation:

$$\begin{aligned}\int_{-\infty}^{+\infty} e^{-ax^2+bx^3+cx^4}\mathrm{d}x &\sim \int_{-\infty}^{+\infty}\left(1+bx^3+cx^4+\frac{b^2x^6}{2}\right)e^{-ax^2}\mathrm{d}x \\ &= \sqrt{\frac{\pi}{a}}\left(1+\frac{3}{4}\frac{c}{a^2}+\frac{15}{16}\frac{b^2}{a^3}\right)\end{aligned}$$

Using saddle-point asymptotics with the previous formula:

$$\int_0^x e^{-\phi(y)/kT}\mathrm{d}y \sim \frac{1}{2}\sqrt{\frac{2\pi kT}{\phi''(0)}}\left(1-\frac{kT}{8}\frac{\phi^{(4)}(0)}{\left[\phi''(0)\right]^2}+\frac{5kT}{24}\frac{\left[\phi^{(3)}(0)\right]^2}{\left[\phi''(0)\right]^3}\right)e^{-\phi(0)/kT}$$

Since the well is symmetric, $\phi^{(3)}(0) = 0$, we end up with:

$$\int_0^x e^{-\phi(y)/kT}\mathrm{d}y \sim \sqrt{\frac{\pi kT}{2K_0}}\left(1-\frac{kT}{8}\frac{M_0}{K_0^2}\right)$$

with $M_0 = \phi^{(4)}(0)$. The same way:

$$\int_0^{x_1} e^{\phi(x)/kT}\mathrm{d}x \sim \frac{1}{2}\sqrt{-\frac{2\pi kT}{\phi''(x_1)}}\left(1+\frac{kT}{8}\frac{\phi^{(4)}(x_1)}{\left[\phi''(x_1)\right]^2}-\frac{5kT}{24}\frac{\left[\phi^{(3)}(x_1)\right]^2}{\left[\phi''(x_1)\right]^3}\right)e^{\phi(x_1)/kT}$$

that we write:

$$\int_0^{x_1} e^{\phi(x)/kT}\mathrm{d}x \sim \sqrt{\frac{\pi kT}{2K_1}}\left(1+\frac{kT}{8}\frac{M_1}{K_1^2}-\frac{5kT}{24}\frac{L_1^2}{K_1^3}\right)e^{E/kT}$$

with $L_1=\phi^{(3)}(x_1)$ and $M_1=\phi^{(4)}(x_1)$. We write then:

$$\begin{aligned}\tau &\sim \frac{1}{R_0(T)}\left(1-\frac{kT}{8}\frac{M_0}{K_0^2}\right)\left(1+\frac{kT}{8}\frac{M_1}{K_1^2}-\frac{5kT}{24}\frac{L_1^2}{K_1^3}\right)\\ &\sim \frac{1}{R_0(T)}\left[1+\frac{kT}{8}\left(\frac{M_1}{K_1^2}-\frac{M_0}{K_0^2}-\frac{5}{3}\frac{L_1^2}{K_1^3}\right)\right]\end{aligned}$$

that is:

$$\boxed{R(T)\sim R_0(T)\left[1-\frac{kT}{8}\left(\frac{M_1}{K_1^2}-\frac{M_0}{K_0^2}-\frac{5}{3}\frac{L_1^2}{K_1^3}\right)\right]}$$

with:

$$\begin{aligned}K_0&=\phi''(0) & & & M_0&=\phi^{(4)}(0)\\ K_1&=-\phi''(x_1) & L_1&=\phi^{(3)}(x_1) & M_1&=\phi^{(4)}(x_1)\end{aligned}$$