

Exam 2

Due at 9:30am in lecture on Thursday April 14.

Directions: (i) Work independently, and do not discuss the exam with anyone. (ii) You may quote formulae from 2005 18.366 lecture notes and problem sets, but all other steps in your solutions should be derived in detail. (iii) You may consult the required and recommended books, but no other resources (books, web sites, etc.), except for mathematical reference book, such as Abramowitz and Stegun *Handbook of Mathematical Functions*. (iv) Late exams will not be accepted without a valid excuse.

1. **Electrochemical equilibrium.** Consider an electrolyte with positive and negative ions (charged particles in solution) of charges, $\pm e$, diffusion constants, D_{\pm} , and concentrations, $c_{\pm}(x)$, respectively. Instead of treating the electrical force between each ion pair, consider the “mean-field approximation” that each ion feels only an average electric force, $\mp e d\phi/dx$, with a mobility given by the Einstein relation. The electrostatic potential, $\phi(x)$, satisfies Poisson’s equation,

$$-\varepsilon \frac{d^2\phi}{dx^2} = e(c_+ - c_-)$$

where ε is the permittivity of the solvent (e.g. water). In this approximation, each ion moves independently in the self-consistent electric field, so $c_+(x)$ and $c_-(x)$ satisfy steady Fokker-Planck equations¹. Consider ions in solution near a charged surface, $x > 0$, with $c_{\pm}(\infty) = c_o$ and $\phi(\infty) = 0$ and $\phi(0) = -\zeta$ (the “zeta potential”).

- (a) Show that potential satisfies the dimensionless “Poisson-Boltzmann equation” (PBE),

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

where $\psi(y) = -e\phi(x)/kT$ and $y = x/\lambda$. What is λ ?

- (b) Solve the linearized PBE, and explain why λ is called the “screening length”.
 (c) Integrate the nonlinear PBE once to obtain the total interfacial charge,

$$q(\zeta) = -e \int_0^{\infty} (c_+ - c_-) dx.$$

- (d) *Extra credit:* Integrate again to obtain $\phi(x)$. ²

¹In electrochemistry, these are the “Nernst-Planck equations”.

²This is the famous solution of Gouy (1910) and Chapman (1914).

2. **First passage of a set of random walkers.** Consider N independent random walkers released from $x = x_0 > 0$, and let T_i be the first passage time to the origin ($1 \leq i \leq N$) with PDF $f_i(t)$. Approximate the PDF of the position of each walker by the solution to the diffusion equation,

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

- (a) Solve with $P(0, t) = 0$ to obtain the survival probability, $S_i(t)$ (that the i th walker has not yet reached the origin). [Hint: introduce an “image” source.] Show that $f_i(t) = -S_i'(t)$ is the Smirnov density, derived by other means in lecture.
- (b) Find the PDF $f(t)$ of the first passage time for the *set* of N walkers, $T = \min_{1 \leq i \leq N} T_i$, when one of them reaches the origin for the first time.
- (c) Show that $\langle T^m \rangle < \infty$ if and only if $N > 2m$. In particular, the expected first passage time is finite if and only if $N \geq 3$, as mentioned in class.
3. **Escape from a symmetric trap.** Consider a diffusing particle which feels a conservative force, $f(x) = -\phi'(x)$, in a smooth, symmetric potential, $\phi(x) = \phi(-x)$, causing a drift velocity, $v(x) = bf(x)$, where $b = D/kT$ is the mobility and D is the diffusion constant. If the particle starts at the origin, then PDF of the position, $P(x, t)$, satisfies the Fokker-Planck equation,

$$\frac{\partial P}{\partial t} + \frac{\partial}{\partial x}(v(x)P(x, t)) = D \frac{\partial^2 P}{\partial x^2},$$

with $P(x, 0) = \delta(x)$. Suppose that the potential has a minimum $\phi = 0$ at $x = 0$ with $\phi''(0) = K_0 > 0$ and two equal maxima $\phi = E > 0$ at $x = \pm x_1$ with $\phi''(x_1) = -K_1 < 0$. Let τ be the mean first passage time to reach one of the barriers at $x = \pm x_1$ (and then escape from the well with probability 1/2).

- (a) Derive the general formula

$$\tau = \frac{1}{D} \int_0^{x_1} dx e^{\phi(x)/kT} \int_0^x dy e^{-\phi(y)/kT}$$

- (b) In the low temperature limit, $kT/E \rightarrow 0$, calculate the leading-order asymptotics of the escape rate, $R = 1/2\tau \sim R_0(T)$, using the saddle-point method. Verify the classical result of Kramers: $R_0(T) \propto e^{-E/kT}$.
- (c) Calculate the first correction to the Kramers escape rate:

$$R(T) \sim R_0(T) \left(1 + a \frac{kT}{E} \right).$$