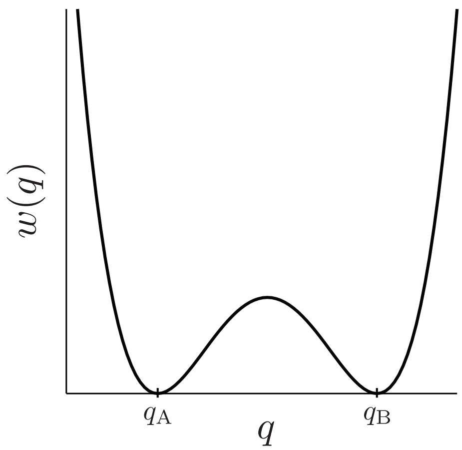
1. **Splitting probabilities from the Smoluchowski equation**

A coordinate q evolves stochastically on a bistable potential $w(q)$, such as the one sketched below.



The stable states A and B, with characteristic values $q_{\rm A}$ and $q_{\rm B}$ of the order parameter, might correspond to reactants and products of a chemical reaction. Here we will focus on the splitting probability $\phi_{\rm B}(q_0)$, i.e., the fraction of trajectories initiated from q_0 that reach $q_{\rm B}$ before $q_{\rm A}$.

In class we sketched a calculation of $\phi_{\rm B}$ that begins with the Smoluchowski equation,

$$\frac{\partial p(q,t)}{\partial t} = -\frac{\partial}{\partial q} J(q,t) \tag{1}$$

where

$$J(q,t) = -De^{-\beta w(q)}\frac{\partial}{\partial q}\left(e^{\beta w(q)} p(q,t)\right) \tag{2}$$

is the flux of probability at position q and time t, and D is the diffusion coefficient for dynamics along q.

(i) The splitting probability $\phi_{\rm B}(q_0)$ can be written in terms of the solution to Eqs. 1-2,

$$\phi_{\rm B} = \int_0^\infty dt\, J(q_{\rm B}, t), \tag{3}$$

with boundary conditions:

$$p(q,0) = \delta(q-q_0), \qquad p(q_{\rm A},t) = 0, \qquad p(q_{\rm B},t) = 0.$$

Provide a physical explanation for Eq. 3 and each of these boundary conditions.

(ii) As a first step towards calculating $\phi_{\rm B}(q_0)$, integrate Eq. 1 over all times (from $t=0$ to $t=\infty$). Simplify your result using the specified initial condition $p(q,0)$ and the fact that, over time, our boundary conditions steadily remove probability from the interval $q_{\rm A} < q < q_{\rm B}$.

(iii) Integrate your result from part (ii) over the coordinate q. Take $q_{\rm B}$ as the upper limit of this integration; for the lower limit use an arbitrary value q. In your result, you should be able to identify the splitting probability $\phi_{\rm B}(q_0)$.

(iv) Multiply your result from part (iii) by the inverse Boltzmann factor $e^{\beta w(q)}$, and integrate once again over q. This time, take $q_{\rm A}$ and $q_{\rm B}$ as the limits of integration. A simple rearrangement should then yield Onsager's result:

$$\phi_{\rm B}(q_0) = \int_{q_{\rm A}}^{q_0} dq\, e^{\beta w(q)} \Bigg/ \int_{q_{\rm A}}^{q_{\rm B}} dq\, e^{\beta w(q)} \tag{4}$$

(v) Consider the idealized case of a harmonic barrier:

$$w(q) = -\frac{1}{2} m\omega^2 q^2 \tag{5}$$

Setting $q_{\rm A} = -\infty$ and $q_{\rm B} = \infty$, evaluate the splitting probability using Eq. 4. Your answer should involve the error function

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dz\, e^{-z^2}$$

and/or the complementary error function

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} dz\, e^{-z^2} = 1 - \mathrm{erf}(x).$$

(vi) For the harmonic barrier model, plot $\phi_{\rm B}(q_0)$ as a function of q_0, over a range that encompasses most of the crossover between its limiting values. Identify the width of this crossover, say, the range of q_0 over which $\phi_{\rm B}(q_0)$ lies between 0.1 and 0.9. There is no need to be very precise with these values. The goal is to determine the rough scale of the crossover range.

(vii) Give a physical interpretation for the crossover range you found in part (vi).

2. **Numerically integrating the overdamped Langevin equation**

We have performed several exact calculations based on Langevin dynamics of very simple systems. Here you will derive and implement basic methods for advancing Langevin dynamics numerically, as required for systems with complicated potentials.

We will focus on the Langevin equation in the overdamped limit:

$$\gamma \dot{q} = -\frac{dw}{dq} + \eta, \qquad \langle \eta(t)\eta(t')\rangle = 2k_{\rm B}T\gamma\delta(t-t'),$$

All quantities here are dimensionless, e.g., the coordinate q is implicitly expressed relative to some length scale ℓ. The simplest approach to integrating this equation of motion (known as the Euler method) assumes that the force $F(q) = -dw/dq$ does not vary during the time step Δt.

(i) Let q_t be the value of q at the beginning of an integration time step, $q_{t+\Delta t}$ be the value of q at the end of the step, and $F_t = F(q_t)$. Taking the force to be constant (i.e., $F = F_t$) for all times between t and $t + \Delta t$, derive an equation relating $q_{t+\Delta t}$ to q_t, F_t, Δt, γ, and an integrated random force R defined as

$$R = \gamma^{-1} \int_t^{t+\Delta t} dt'\, \eta(t').$$

(ii) Show that $\langle R^2 \rangle = 2D\Delta t$, where $D = k_{\rm B}T/\gamma$.

(iii) Consider a Brownian particle, whose position q evolves through the overdamped Langevin equation, subject to a constant force $\bar{F}$. Its average drift velocity over a period t,

$$\bar{v} = \frac{\langle (q_t - q_0)\rangle}{t},$$

is proportional to the driving force,

$$\bar{v} = \mu \bar{F}.$$

Using your result from parts (i) and (ii), show that the mobility μ is related simply to the particle's diffusion constant, specifically, $\mu = \beta D$.

In the remaining parts of this problem, we will consider the specific case of a bistable potential

$$w(q) = (q+1)^2(q-1)^2, \tag{6}$$

which features minima at $q_{\mathrm{A}} = -1$ and $q_{\mathrm{B}} = 1$.

(iv) Write a computer program that implements the Euler method of part (i) to advance dynamics with this potential. As model parameters take $D = 1$ and $k_{\mathrm{B}}T = 0.4$, and use an integration time step $\Delta t = 0.001$. Plot q as a function of time over an interval long enough to exhibit ≈ 10 transitions from one basin to the other.

(v) From a single trajectory of 10^7 time steps, make a histogram $H(q)$ of values of q. Plot it alongside the expected Boltzmann distribution $p_{\mathrm{eq}}(q)$. Both of these quantities should be normalized such that $\int dq\, H(q) = \int dq\, p_{\mathrm{eq}}(q) = 1$. (In order to normalize $p_{\mathrm{eq}}(q)$, you will need to compute the corresponding partition function numerically.)

(vi) Repeat the calculation of part (v) for temperatures $k_{\mathrm{B}}T = 0.2$, $k_{\mathrm{B}}T = 0.1$, and $k_{\mathrm{B}}T = 0.05$. Describe how and why the agreement between $H(q)$ and $p_{\mathrm{eq}}(q)$ changes with temperature (for a single trajectory of length 10^7 time steps).

(vii) Repeat the calculation of part (v) with larger time steps $\Delta t = 0.01$, $\Delta t = 0.02$, and $\Delta t = 0.03$. Describe how and why the agreement between $H(q)$ and $p_{\mathrm{eq}}(q)$ changes with step size.

3. **Splitting probabilities from a computer**

   This problem combines results from the previous two questions, to determine splitting probabilities for the potential given in Eq. 6. In all cases set the diffusion coefficient to unity, $D = 1$.

   (i) For temperature $k_{\mathrm{B}}T = 0.1$, use Eq. 4 to calculate $\phi_{\mathrm{B}}(q_0)$ numerically for a range of coordinate values between q_{A} and q_{B}. Plot your result for the splitting probability as a function of q_0.

   (ii)Also for temperature $k_{\mathrm{B}}T = 0.1$, use computer simulations to determine $\phi_{\mathrm{B}}(q_0)$ for several values of q_0 between q_{A} and q_{B}. For each value of q_0, generate a large number of trajectories initiated with $q = q_0$, advancing time until q reaches either q_{A} or q_{B}. Plot your simulation result for the splitting probability as a function of q_0. Are your simulation results consistent with Eq. 4?

   (iii) Repeat the calculations of parts (i) and (ii) for temperatures $k_{\mathrm{B}}T = 0.2$ and $k_{\mathrm{B}}T = 0.4$.

   (iv) How accurate is the harmonic barrier approximation for this potential? To address this question, perform a second-order Taylor expansion of $w(q)$ about its maximum at $q = 0$ and determine an appropriate value of $m\omega^2$. Then use your result from part (v) of question 1 to estimate $\phi_{\mathrm{B}}(q_0)$ for values of q_0 between q_{A} and q_{B}. Carry out this calculation for the temperatures $k_{\mathrm{B}}T = 0.1$, $k_{\mathrm{B}}T = 0.2$, and $k_{\mathrm{B}}T = 0.4$. In each case plot the harmonic estimate together with your numerical evaluation of Eq. 4. Why is the approximation better in some cases than others?