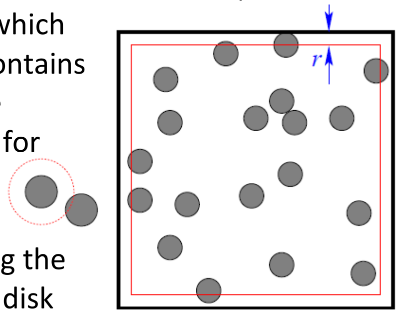
Advanced Statistical Mechanics (Part III Minor Topic): Examples

1. Hard sphere gas

Consider the two-dimensional ideal gas of atoms having a small radius ***r***. If we make the potential energy infinite inside this radius (hard spheres, or rather – disks in 2D), the potential energy is simple (zero unless the spheres overlap, which is forbidden). A two-dimensional $L \times L$ box with hard walls contains a gas of N hard disks of radius $r \ll L$. The disks are dilute; the summed area $N\pi r^2 \ll L^2$. Let A be the effective area allowed for the disks in the box (see sketch): $A = (L-2r)^2$.



(a) The area allowed for the second disk is $A-\pi(2r)^2$, ignoring the small correction when the excluded region around the first disk overlaps the excluded region near the walls of the box. What is the allowed 2N-dimensional volume in configuration space, of allowed zero energy configurations of hard disks, in this dilute limit?

(b) What is the configurational entropy for the hard disks? Here, simplify your answer so that it does not involve a sum over N terms, but valid to first order in the area of the disks πr^2. Show, for large N, that it is well approximated by $S = Nk_B\,(\text{const} + \ln(A/N - b))$, with b representing the effective excluded area due to the other disks. What is the value of b, in terms of the area of the disk?

(c) Find the pressure for the hard-disk gas in the large N approximation. Does it reduce to the ideal gas law for $b = 0$?

2. Density of states of a classical ideal gas

Consider an ideal gas, which could be monoatomic or diatomic (e.g. He or H_2). Consider the density of states, defined as $\Omega(E)\delta E = \int d\Gamma$ over the shell with energies $(E, E+\delta E)$ with $\delta E \to 0$, or equivalently as $\Omega(E) = \int d\Gamma\, \delta[E - \mathcal{H}(p,q)]$. Note that the equilibrim entropy of the microcanonical state is: $S(E) = k_B \ln \Omega(E)$.

Show that for an ideal monoatomic gas of N particles: $\Omega_1(E) \propto E^{3N/2}$.

3. Lagrange method in thermodynamics

Lagrange multipliers allow one to find the extremum of a function $f(\boldsymbol{x})$ given a constraint $g(\boldsymbol{x}) = g_0$. One sets the derivative of $f(\boldsymbol{x}) + \lambda[g(\boldsymbol{x}) - g_0]$ with respect to x to zero. The derivatives with respect to components of $\boldsymbol{x}$ then include terms involving λ, which act to enforce the constraint. Solving for $\boldsymbol{x}(\lambda)$, substituting back, and then setting the derivative with respect to λ to zero determines λ.

Let us use Lagrange multipliers to find the maximum of the non-equilibrium entropy:
$S = -k_B \int \rho(\mathbb{P},\mathbb{Q}) \ln \rho(\mathbb{P},\mathbb{Q}) = -k_B\, \mathrm{Tr}(\rho \log \rho) = -k_B \sum_i p_i \ln p_i$
constraining the normalisation, energy, and number. You may use whichever form of the entropy you prefer; the first continuous form will demand some calculus of variations; the last, discrete, form is the most straightforward.

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(a) Microcanonical. Using a Lagrange multiplier to enforce the normalisation $\sum_i p_i = 1$, show that the probability distribution that extremizes the entropy is a constant (the microcanonical distribution).

(b) Canonical. Integrating over all $\mathbb{P}$ and $\mathbb{Q}$, use another Lagrange multiplier to fix the mean energy <E> = $\sum_i E_i p_i$. Show that the canonical distribution maximizes the entropy given the constraints of normalisation and fixed energy.

(c) Grand canonical. Summing over different numbers of particles N and adding the constraint that the average number is <N> = $\sum_i N_i p_i$, show that you get the grand canonical distribution by maximizing the entropy.

4. Poisson 1

For a Poisson process, the expected waiting time between events is 0.5 minutes. What is the probability that 10 or fewer events occur during a 10-minute time span? What is the probability that the waiting time between two consecutive events is at least 1 minute?

5. Poisson 2

Consider a process of forming a queue in the canteen. It starts at t = 0 when the canteen opens, and the students arrive at a rate k_0.
Given the cross-section size of each student is *a*, and the distance from the counter to the door is *L*, what is the probability that the growing queue will reach the door in the time t?

We now wish to calculate the average time it would take for the queue to reach the Door, using either the discrete, or the continuous representation of this stochastic process. (*Remember the rule of sums:* $\sum_{m=0}^{N}(U_m - U_{m+1}) = U_0 - U_{N+1}$)

6. Fluctuation-dissipation in two-level system

Consider kinetics of a first-order reaction between species A and B ($A \leftrightharpoons B$) described by two rate constants:

$$\frac{d[A]}{dt} = -k_1[A] + k_2[B], \quad \frac{d[B]}{dt} = -k_2[B] + k_1[A]$$

In equilibrium, the detailed balance will have: $k_1[A]_{\text{eq}} = k_2[B]_{\text{eq}}$. If we define the deviation from equilibrium as Δ ($[A]= [A]_{\text{eq}} + \Delta$, $[B] = [B]_{\text{eq}} - \Delta$), then it is easy to see that this deviation decays with time:

$$\frac{d\Delta}{dt} = -(k_1 + k_2)\Delta$$

According to the Onsager regression hypothesis (1931), small fluctuations decay on the average in exactly the same way as macroscopic deviations from equilibrium. Then the time correlation function of fluctuations is

$$\langle \Delta(t_1)\Delta(t_2)\rangle = \langle \Delta^2\rangle_{\text{eq}} e^{-(k_1+k_2)|t_1-t_2|}$$

If the transitions between two states are affected by a random noise (a Wiener term ξ(t) added to the equation for Δ), find the fluctuation-dissipation condition that is necessary to ensure the correct equilibrium behaviour.

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7. Share prices in different markets

Let us the price of a given share, S, that evolves in a market according to the Geometric Brownian Motion equation

$$\frac{dS}{S} = \mu\, dt + \sigma\, dW_t$$

where μ is the expected rate of return, σ is the variance of market fluctuations, and W_t is the Wiener stochastic process with the zero mean and the variance $\langle dW_t^2 \rangle = dt$.

(a) Follow the Ito calculus discussed in the lectures to confirm the solution of this SDE:

$$S(t) = S_0 e^{\left[\mu - \frac{\sigma^2}{2}\right]t + \sigma W_t}$$

(b) Plot several realisations of this share price for a market with μ=1, and.σ=0.5, 1, 1.5, and 2, using the suggested Python code (or otherwise).

8. Exploring Black-Scholes hedging

Suppose there are only two possible investments: a risky asset (which we will call a stock) and cash (a risk-free investment). Let us assume, for simplicity, that the rate of growth of the risk-free asset is r=0. Initially the stock is worth S_0. The stock could have one of two values at the expiration date of the option: $S_+ > S_-$. We can borrow and lend any amount of cash at the prevailing interest rate (that is, zero) and can buy or sell stock (even if we do not own any; this is called *selling short*). There are no transaction costs.

The value of the option on its expiration date can also take one of two values: if the option allowed the buyer to purchase the stock at the price S_f , with $S_+ > S_f > S_-$, then the value of the option at the expiration date will either be $V_+ = S_+ - S_f$, or $V_- = 0$ (since in the latter case the buyer would choose not to exercise the option).

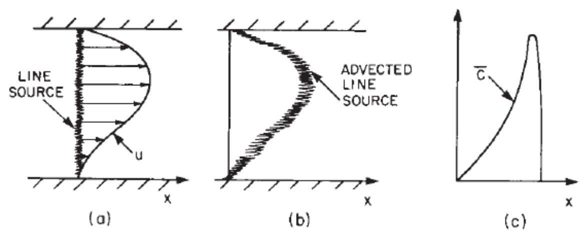
Let V_0 be the fair initial price of the option that we wish to determine. Consider a portfolio Π that includes the option and a certain amount of the stock (which Black and Scholes determined as α=-dV/dS). Initially the value is $\Pi_0 = V_0 + \alpha\, S_0$. At the expiration date the final portfolio value will either be $(V_+ + \alpha\, S_+)$ or $(V_- + \alpha\, S_-)$.

(a) What value of α makes these two final portfolio values equal (i.e. eliminate risk)? What do the signs of your answer suggest? What is this common final value Π_F ?

(b) What initial value V_0 of the option makes the initial value of the portfolio equal to the final value?

9. Convection diffusion

If a streak of die is put initially straight across a channel of fluid in steady uniform flow, after some time the die streak will become curved due to the transverse variation of velocity, and also becomes thicker due to



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diffusion in all directions. After sufficiently long time lateral diffusion of the die will be complete and the die distribution is nearly uniform across the channel. Convective diffusion will continue as a one-dimensional process along the long circular pipe. We wish to predict the effective diffusivity in the last phase.

The velocity profile along the pipe is known: $u(r) = u_0(1 - r^2/a^2),\ \text{for } 0 < r < a$. The concentration in the channel is governed by the convestion-diffusion equation

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x}(u \cdot c) = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right)$$

There are three time scales here: diffusion time across the pipe radius a, convection time across L, and diffusion time across L. Their ratios are $\frac{a^2}{D}:\frac{L}{u_0}:\frac{L^2}{D}$, and we focus attention to processes in the longitudinal direction long after lateral diffusion is complete. If we scale the variables: $x = Lx', r = ar', u = u_0 u', \text{and } t = (L/u_0)t'$, then in the non-dimensional (primed) variables the diffusion equation takes the form:

$$\frac{u_0 a}{D}\frac{a}{L}\left(\frac{\partial c}{\partial t'} + u' \cdot \frac{\partial c}{\partial x'}\right) = \frac{a^2}{L^2}\frac{\partial^2 c}{\partial x'^2} + \frac{1}{r'}\frac{\partial}{\partial r'}\left(r'\frac{\partial c}{\partial r'}\right) \qquad (*)$$

with the boundary conditions ${\partial c}/{\partial r'} = 0$ at $r' = 0,1$. The ratio Pe = $(u_0 a/D)$ is called the Peclet number, which we should take ~1. On the other hand, $a/L = \varepsilon \ll 1$. Note that the two relevant timescales are in the ratio $\varepsilon : 1$, which allows separation these time scales in the equation (and eventually averaging over the fast process). Continue working with non-dimensional scaled variables (the primes are suppressed in what follows).

(a) Introduce the time scales as $t_0 = t, t_1 = \varepsilon t$, and consider the concentration dependent on these times as if they were independent: $c = c(t_0, t_1)$. Show that

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial t_0} + \varepsilon\frac{\partial c}{\partial t_1}$$

(b) Introduce the multiple scale expansion $c = c_0 + \varepsilon c_1 + \varepsilon^2 c_2 + \cdots$ and write the perturbation equations that emerge from eq.(*) in O(ε^0), O(ε^1), and O(ε^2). Show that the O(ε^0) solution is: $c_0(x, t_0, t_1)$.

(c) Define the averaging over the pipe cross-section as $\langle h \rangle = \frac{1}{\pi}\int_0^1 h \cdot 2\pi r\, dr$ (in non-dimensional units). By subtracting the O(ε^1) equation from its average, show that

$$\text{Pe}\cdot(u(r) - \langle u \rangle)\frac{\partial c_0}{\partial x} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_1}{\partial r}\right)$$

According to the result of part (c), define the r-dependence of $c_1(r)$ as

$$c_1 = \text{Pe} \cdot \left({\partial c_0}/{\partial x}\right)B(r)$$

Therefore, turning to the O(ε^2) equation and replacing c_1 in it, we can obtain

$$\text{Pe} \cdot \frac{\partial c_0}{\partial t_1} + \text{Pe}^2 \cdot (u(r) - \langle u \rangle)B(r)\frac{\partial^2 c_0}{\partial x^2} = \frac{\partial^2 c_0}{\partial x^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_2}{\partial r}\right)$$

(d) By averaging the above equation over the pipe cross-section find the effective diffusion coefficient of the die along the pipe, which is the constant in

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$$\mathrm{Pe}\cdot\frac{\partial c_0}{\partial t_1}=D_{\mathrm{eff}}\frac{\partial^2 c_0}{\partial x^2}$$

Finally, in order to re-construct the full time derivative, we need to take the averaged O(ε^1) equation, and combine with the above to obtain:

$$\mathrm{Pe}\cdot\left(\frac{\partial c_0}{\partial t_0}+\varepsilon\frac{\partial c_0}{\partial t_1}\right)+\mathrm{Pe}\cdot\langle u\rangle\frac{\partial c_0}{\partial x}=\varepsilon D_{\mathrm{eff}}\frac{\partial^2 c_0}{\partial x^2}$$

(e) In the original dimensional units, show that the effective coefficient of diffusion along the pipe is equal to

$$D_{\mathrm{eff}}=D\left[1+\frac{1}{192}\left(\frac{u_0 a}{D}\right)^2\right]$$

10.Escape in both directions

Consider simple 1D diffusion of a particle on an interval between two absorbing boundaries at 0 and L, starting at a position x_0 between them. Calculate the mean time of the particle escape, in either direction.

[*You may choose the method of images, or the method of eigenfunctions on an interval*]

11. Multi-variable Ornstein Uhlenbeck process 1

Let us consider an illustration of an Ornstein-Uhlenbeck process with different variables: the Brownian motion of a classical harmonic oscillator, described by the Hamilton's equations of motion

$$\frac{d\boldsymbol{x}}{dt}=\frac{\boldsymbol{p}}{m};\qquad\qquad \frac{d\boldsymbol{p}}{dt}=-m\omega^2\boldsymbol{x}-\gamma\frac{\boldsymbol{p}}{m}+\eta(t)$$

(a) Present these equations in the canonical form $\dot{\boldsymbol{q}}=-\boldsymbol{\Theta}\cdot\boldsymbol{q}+\boldsymbol{\eta}(t)$, and write the matrix expressions for $\boldsymbol{q},\boldsymbol{\eta},\boldsymbol{\Theta}$, and $\boldsymbol{M}=\langle\boldsymbol{q}\boldsymbol{q}\rangle$**.**

(b) Using the equipartition equilibrium expressions for $\langle\boldsymbol{x}^2\rangle$ and $\langle\boldsymbol{p}^2\rangle$, verify the fluctuation-dissipation relation in the matrix form $\boldsymbol{Q}\cdot\boldsymbol{M}+\boldsymbol{M}\cdot\boldsymbol{Q}^T=\boldsymbol{\sigma}\cdot\boldsymbol{\sigma}^T$ (as in lecture notes).

(c) Let us illustrate the non-Markov nature of this oscillator. Write the {standard solution} of the equation for $\boldsymbol{p}(t)$, and thus show that the equation for $\boldsymbol{x}(t)$ will take the form

$$\frac{d\boldsymbol{x}}{dt}=-\int_{-\infty}^{t}g(t-s)\,\boldsymbol{x}(s)\,ds+\eta_x(t)$$

(d) Carry out the calculation to demonstrate the non-Markov version of the fluctuation-dissipation theorem: $\langle\boldsymbol{\eta}_x(t)\boldsymbol{\eta}_x(t')\rangle=\langle\boldsymbol{x}^2\rangle_{\mathrm{eq}}\cdot g(t-t')$

(e) Verify how in the limit of very high friction γ, the memory function $g(t)$ reduces to a delta function: $g(\tau)=[m\omega^2/\gamma]\,\delta(\tau)$, and the coordinate variable $\boldsymbol{x}(t)$ follows the ordinary Langevin SDE.

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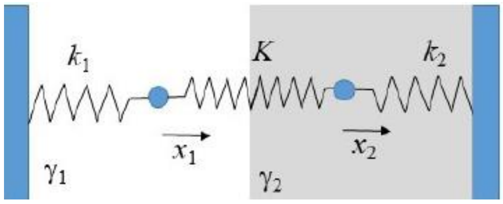
12. Multi-variable Ornstein Uhlenbeck process 2

Consider two Brownian particles, coupled by a spring with constant *K*, each confined by a harmonic potential of spring constants $k_{1;2}$ respectively, each embedded in a different medium with the friction constants $\gamma_{1;2}$ respectively. The particles are coupled by another spring: see figure.

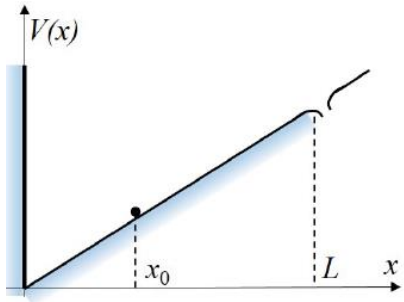


a) Write the coupled overdamped Langevin equations for this system, assuming isothermal conditions.

b) Derive the multi-variable fluctuation-dissipation relation for the system

c) Derive the expressions for equilibrium mean square fluctuation for each of the particles, and the equilibrium correlation function $\langle x_1 x_2 \rangle_{eq}$, and comment on the limiting cases of these expressions.

13. MFPT in linear potential



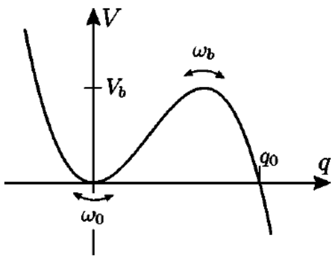
Brownian particle diffuses in a linear potential $V = \alpha\, x$ for $x > 0$, as illustrated in the figure (initial position: x_0 at t = 0). The absorbing 'sink' is located a distance *L* from the origin, with only x > 0 allowed.

a) Write down the standard solution of the Smoluchowski equation in this linear potential, $P(x;\, t\, |x_0;\, t_0)$

b) Calculate the mean first-passage time for the particle to reach the 'sink'.

c) Explore and discuss the limiting cases of your solution: the limit $\alpha \to 0$, the limit $x_0 \to L$, and when does the crossover to the 'long distance L' regime occurs.

14. Escape over or under the barrier



Consider a particle trapped in a metastable state described by the potential energy $V(q)$ shown in the sketch (which makes it the Kramers escape problem in classical physics). A good model for such a potential is the cubic: $V(q) = \frac{1}{2} K q^2 (1 - q/q_0)$. Let us consider a particle of mass m trapped, and escaping from this metastable state.

a) First of all, assuming the high barrier [$V_b/k_B T$ <<1] and overdamped motion [γ^2/mK <<1], reproduce the classical Kramers solution for the thermally-activated escape rate k, whether via the constant-flux or via the mean first-passage time methods.

b) Our interest here is to examine the crossover between the thermally-activated escape and the quantum tunnelling under the barrier. The first estimate of the crossover temperature (Goldansky 1959) suggests: $k_B T_0 = \hbar\omega_b/2\pi$. Estimate this crossover temperature for a hydrogen atom, and for a benzene ring, when the potential spring

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constant taking a 'typical' value K = 10 J/m^2 (arising from the potential height V_b=4 kcal/mol (170 meV), and a distance q_0=2 Angström).

c) The more accurate estimate of the crossover temperature (Hänggi and Weiss 1985) shows that it depends on the friction constant γ: $k_B T_0 = (\hbar\omega_b/2\pi)\left(\sqrt{1+a^2} - a\right)$, with the non-dimensional ratio $a = \gamma/2m\omega_b$. Show how this temperature changes for a hydrogen atom in the potential above, for a=0, 0.5 and 2.

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