CHEM/CHPH/PHYS 703, C. Jarzynski, Spring 2020 Final Exam

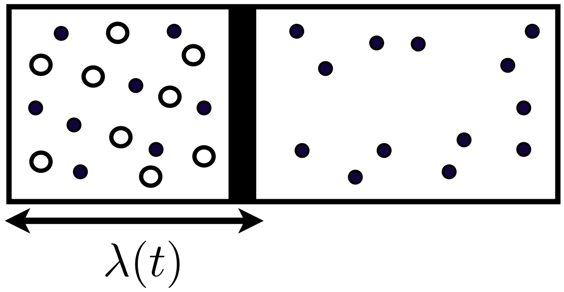
Due *Tuesday, May 19 by 5pm*

This exam consists of four problems, each worth **20 points**. You may use your own notes and any material available on the course website, including solutions to problem sets. Also, feel free to look up standard mathematical formulas such as the Stirling approximation for factorials. However, aside from the cases mentioned in the previous two sentences, do not consult any other resources (online or otherwise) and do not discuss these problems among yourselves or with anyone else. If you have any questions regarding what is being asked in the problems, please contact me by email.

Choose two of the problems, solve them elsewhere, write and scan a **clean** version of your solutions for those problems, and submit your answers electronically using ELMS.

Please do not turn in solutions for all four problems – I will only grade two of them! Of course, you are encouraged to try to solve all four on your own, and after May 19th I will post the solutions for all four problems to the course website.

Problem 1.



Consider a two-component dilute gas in a box containing a partition. There are N_A particles of type A (filled circles) and N_B particles of type B (open circles). The former are able to pass through small pores in the piston, whereas the latter are confined to the region to its left. The position of the piston, λ, is varied quasi-statically, reducing the volume to the left of the piston from V_0 to V_1.

(a) [**6 pts**] Assuming the mixture of gases to be ergodic, use the ergodic adiabatic invariant to show that the work performed on the mixture during this process is:

$$W = \left[\left(\frac{V_0}{V_1} \right)^{2N_B/3N} - 1 \right] E_0 \equiv \alpha E_0 \tag{1}$$

where E_0 is the initial energy of the gas and $N = N_A + N_B$.

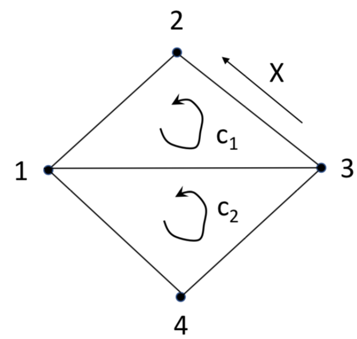
Now imagine the gas is equilibrated with an external reservoir at temperature T, with the volume of the left chamber fixed at V_0. The reservoir is then removed and the partition is moved quasi-statically to the left, until the volume of the left chamber becomes V_1. Let W denote the work performed on the gas, during one realization of this process. This process is repeated infinitely many times, always first equilibrating the gas with a thermal reservoir.

(b) [**7 pts**] Solve for the work distribution $\rho(W)$, and verify that it satisfies $\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$, where $\beta^{-1} = k_B T$, and $\Delta F = F_1 - F_0$ is the free energy difference between the equilibrium states, at temperature T, corresponding to the initial and final locations of the partition.

(c) [**7 pts**] If the process described above is now considered to be the *forward* process, then define a *reverse* process in which the volume of the left chamber is increased, from V_1 to V_0, after initial equilibration at temperature T. Solve for the corresponding work distribution, and show that the forward and reverse work distributions satisfy

$$\frac{\rho_F(+W)}{\rho_R(-W)} = e^{\beta(W - \Delta F)}\,. \tag{2}$$

Problem 2.



Consider the network shown above, which appears on pages 10-11 of the April 21 lecture notes on Thermodynamic Forces (posted online). This network describes a four-state system in contact with a thermal reservoir at temperature T. Let E_i denote the energy of the i'th state, with $i = 1, 2, 3, 4$. The labels c_1 and c_2 denote the cycles $1-3-2-1$ and $1-4-3-1$, defined so that counter-clockwise (CCW) is the positive direction around each cycle.

Let $\mathcal{R}$ denote a 4×4 transition rate matrix with elements R_{ij}. Imagine that detailed balance is broken by a thermodynamic force applied along the edge connecting states 2 and 3, and suppose this force points from 3 to 2. All other edges satisfy detailed balance. In other words,

$$\frac{R_{23}}{R_{32}} = \frac{\exp(-\beta E_2)}{\exp(-\beta E_3)} \cdot e^{\beta X} \quad , \quad X > 0 \tag{3}$$

but for all other connected pairs we have $R_{ij}/R_{ji} = \exp[-\beta(E_i - E_j)]$. Under these conditions the system relaxes to a steady state with currents $\mathcal{J}_1^s$ and $\mathcal{J}_2^s$ along the cycles c_1 and c_2.

(a) [**15 pts**] Prove that both $\mathcal{J}_1^s$ and $\mathcal{J}_2^s$ are positive, in other words the net current around each cycle is CCW. You may use the following result (see p. 16 of April 21 lecture notes):

$$\sum_{\text{n}=1}^{2} A_n \mathcal{J}_n^s > 0 \tag{4}$$

where A_n is the affinity for cycle c_n. Since detailed balance is broken this is a strict inequality.

(b) [**5 pts**] The steady-state current from state 1 to state 3 is given by $J_{31}^s = \mathcal{J}_1^s - \mathcal{J}_2^s$. Determine whether J_{31}^s is positive or negative.

Problem 3.

When a Brownian particle with mass m and friction coefficient γ, in one degree of freedom, is subjected to a time-periodic force $\alpha \sin(\omega t)$, it evolves to a time-periodic state in which the mean position of the particle is given by

$$\langle q \rangle(t) = \frac{\alpha}{\omega} \frac{\sin(\omega t - \phi)}{\sqrt{\gamma^2 + m^2\omega^2}} + A \quad , \quad \tan\phi = -\frac{\gamma}{m\omega} \tag{5}$$

where A is an irrelevant constant offset that is determined by initial conditions.

Now consider a pair of Brownian particles, of equal mass m, attracted by a harmonic force of stiffness $k = m\omega_0^2$. The equations of motion for these particles are given by:

$$m\ddot{q}_1 = -k(q_1 - q_2) - \gamma\dot{q}_1 + \xi_1(t) \tag{6a}$$

$$m\ddot{q}_2 = -k(q_2 - q_1) - \gamma\dot{q}_2 + \xi_2(t) + \alpha\sin(\omega t) \tag{6b}$$

where ξ_1 and ξ_2 are noise terms satisfying $\langle \xi_i(0)\xi_j(t)\rangle = 2D\delta(t)\delta_{ij}$. Note that the time-periodic force acts only on particle 2.

(a) **[15 pts]** For the dynamics given by Eq. 6, solve for the time-dependent mean position of the second particle, $\langle q_2 \rangle(t)$, in the long-time limit. Feel free to use Eq. 5, if you find it convenient, and feel free to ignore any constant offsets determined by initial conditions, like the quantity A appearing in Eq. 5.

(b) **[5 pts]** Evaluate your results for $\langle q_2 \rangle(t)$ in the two limits $k \to 0$ and $k \to \infty$, with all other parameters (m, γ, α, ω, D) held fixed. Compare with Eq. 5 and comment briefly on why the results you obtain in these limits make sense, physically.

Problem 4.

Consider diffusive motion with drift on a circle of perimeter L, described by the Langevin equation $\dot{x} = v + \xi(t)$, with $0 \le x < L$ and periodic boundary conditions. At the ensemble level, the Fokker-Planck equation is

$$\frac{\partial f}{\partial t} = -v \frac{\partial f}{\partial x} + D \frac{\partial^2 f}{\partial x^2} \equiv \hat{\mathcal{L}} f \qquad , \qquad \text{with constants } v, D > 0 \quad . \tag{7}$$

(a) [**4 pts**] Solve for the eigenvalues and eigenstates of $\hat{\mathcal{L}}$ and its adjoint $\hat{\mathcal{L}}^\dagger$. In the complex plane, sketch the locations of the eigenvalues of $\hat{\mathcal{L}}$.

(b) [**4 pts**] For an initial probability distribution $f(x, 0) = L^{-1} \left[1 + a \cos(2n\pi x/L) \right]$, where n is an integer and $0 < a < 1$, solve for $f(x, t)$ for $t \ge 0$.

Now imagine a particle making random transitions on a one-dimensional lattice with N sites, lattice spacing d, and periodic boundary conditions. These transitions are described by a Poisson process, where α is the probability rate for the particle to jump one site to the left, and β is the probability rate to jump one site to the right.

(c) [**4 pts**] Write down the transition rate matrix $\mathcal{R}$ for this process, and solve for its eigenvalues and left and right eigenvectors.

(d) [**4 pts**] In the appropriate large-N limit, these discrete-state dynamics reduce to the diffusive dynamics of parts (a) and (b) above. Provide explicit expressions showing how the parameters N, d, α and β that describe the discrete-state dynamics relate to the parameters L, v and D that describe the diffusive dynamics.

Now imagine a modified process on this N-site lattice, in which the transitions occur at times t_0, t_1, $t_2 \cdots$, with $t_n = n\gamma^{-1}$. Each transition is either one step to the right, with probability p, or to the left, with probability $q = 1 - p \ne p$. The quantity

$$\sigma = \frac{n_{\rm R} - n_{\rm L}}{\tau} \ln \frac{p}{q} \tag{8}$$

represents the time-averaged entropy production rate over an interval of duration τ, where $n_{\rm R}$ (or $n_{\rm L}$) is the number of transitions to the right (or left). The theory of large deviations suggests that the probability distribution for σ takes the form $P_\tau(\sigma) \sim e^{-\tau I(\sigma)}$.

(e) [**4 pts**] Solve for the large deviation function $I(\sigma) = \lim_{\tau \to \infty} -(1/\tau) \ln P_\tau(\sigma)$ and show that it obeys the steady-state fluctuation theorem, $I(\sigma) - I(-\sigma) = -\sigma$.