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

PROBLEM 1

(a) The ergodic adiabatic invariant is the volume of phase space enclosed by the energy shell E:

$$\Omega(E, V; N_A, N_B, V_{tot}) = V^{N_B} \cdot V_{tot}^{N_A} \cdot \omega(E) \tag{1}$$

where V_{tot} is the fixed total volume of the container, and $\omega(E)$ is the volume of momentum-space enclosed by a surface of constant kinetic energy E:

$$\begin{aligned}
\omega(E) &= \int d^{3N_A} p_A \int d^{3N_B} p_B \, \theta\left(E - \frac{p_A^2}{2m_A} - \frac{p_B^2}{2m_B}\right) & (2)\\
&= (2m_A)^{3N_A/2}(2m_B)^{3N_B/2} \int d^{3N_A} q_A \int d^{3N_B} q_B \, \theta\left(E - q_A^2 - q_B^2\right) & (3)\\
&= (2m_A)^{3N_A/2}(2m_B)^{3N_B/2} \int d^{3N} q \, \theta\left(E - q^2\right) & (4)\\
&= (2m_A)^{3N_A/2}(2m_B)^{3N_B/2} \frac{(\pi E)^k}{k\Gamma(k)} \equiv cE^k \quad , \quad k = \frac{3N}{2} & (5)
\end{aligned}$$

Here, $\mathbf{p}_A$ is the $3N_A$-dimensional momentum vector for the collection of A particles, and $\mathbf{p}_B$ is defined analogously. Thus

$$\Omega(E, V; N_A, N_B, V_{tot}) = cV^{N_B} V_{tot}^{N_A} E^{3N/2} \tag{6}$$

During the process described in the problem, Ω remains constant while V is changed quasi-statically from V_0 to V_1. If the initial and final energies are E_0 and E_1, we have:

$$cV_0^{N_B} V_{tot}^{N_A} E_0^{3N/2} = cV_1^{N_B} V_{tot}^{N_A} E_1^{3N/2} \tag{7}$$

hence

$$E_1 = \left(\frac{V_0}{V_1}\right)^{2N_B/3N} E_0 \tag{8}$$

Since there is no exchange of energy with a heat bath, the first law gives us

$$W = E_1 - E_0 = \left[\left(\frac{V_0}{V_1}\right)^{2N_B/3N} - 1\right] E_0 \equiv \alpha E_0 \tag{9}$$

(b) From the Boltzmann distribution we get the following distribution of initial energies:

$$P(E_0) = \beta e^{-\beta E_0} \frac{(\beta E_0)^{k-1}}{\Gamma(k)} \theta(E_0) \tag{10}$$

where $\theta(\cdot)$ is the unit step function. Combining this with Eq. 9 gives us

$$\rho(W) = \int \mathrm{d}E_0 P(E_0)\,\delta(W - \alpha E_0) = \frac{\beta}{\alpha^k} e^{-\beta W/\alpha} \frac{(\beta W)^{k-1}}{\Gamma(k)} \theta(W) \tag{11}$$

Next, we evaluate

$$\begin{aligned}
\left\langle e^{-\beta W} \right\rangle &= \int_{-\infty}^{+\infty} \mathrm{d}W\, \rho(W) e^{-\beta W} && (12)\\
&= \frac{1}{\alpha^k} \frac{1}{\Gamma(k)} \int_0^{\infty} \mathrm{d}y\, e^{-sy} y^{k-1} && (13)\\
&= \frac{1}{(\alpha s)^k} \frac{1}{\Gamma(k)} \int_0^{\infty} \mathrm{d}x\, e^{-x} x^{k-1} && (14)\\
&= \frac{1}{(\alpha+1)^k} = \left(\frac{V_1}{V_0}\right)^{N_B} = e^{-\beta \Delta F} && (15)
\end{aligned}$$

using the substitutions $y = \beta W$, $s = 1 + \alpha^{-1}$ and $x = sy$, and using $\Delta F = N_B \beta^{-1} \ln(V_0/V_1)$.

(c) From above we have

$$\rho_F(W) = \frac{\beta}{\alpha^k} e^{-\beta W/\alpha} \frac{(\beta W)^{k-1}}{\Gamma(k)} \theta(W) \tag{16}$$

and for the reverse process we obtain (by a similar calculation)

$$\rho_R(W) = \frac{\beta}{\gamma^k} e^{\beta W/\gamma} \frac{(-\beta W)^{k-1}}{\Gamma(k)} \theta(-W) \tag{17}$$

where

$$\gamma = \left[1 - \left(\frac{V_1}{V_0}\right)^{2N_B/3N}\right] \tag{18}$$

Therefore for $W > 0$ we obtain

$$\frac{\rho_F(+W)}{\rho_R(-W)} = \left(\frac{\gamma}{\alpha}\right)^k e^{-\beta W(\alpha^{-1} - \gamma^{-1})} = e^{\beta(W - \Delta F)} \tag{19}$$

using $\alpha^{-1} - \gamma^{-1} = -1$ and $(\gamma/\alpha)^k = e^{-\beta \Delta F}$.

PROBLEM 2

(a) First calculate the affinities for cycles c_1 and c_2, using the information about the R_{ij}'s provided in the problem:

$$A_1 = \ln \frac{R_{23}R_{12}R_{31}}{R_{32}R_{21}R_{13}} = \beta X > 0 \quad , \quad A_2 = \ln \frac{R_{41}R_{34}R_{13}}{R_{14}R_{43}R_{31}} = 0 \tag{20}$$

Therefore the inequality $\sum_n A_n \mathcal{J}_n^s > 0$ immediately gives us

$$\mathcal{J}_1^s > 0 \tag{21}$$

which implies

$$J_{12}^s > 0 \quad , \quad J_{23}^s > 0, \tag{22}$$

i.e. steady-state current flows from 3 to 2 to 1. To determine the sign of $\mathcal{J}_2^s$, let's separately consider two possibilites:

<u>Case 1</u>: $J_{31}^s = R_{31}\pi_1 - R_{13}\pi_3 > 0$.

$$R_{31}\pi_1 > R_{13}\pi_3 \tag{23}$$

$$\frac{\pi_1}{\pi_3} > \frac{R_{13}}{R_{31}} = e^{\beta(E_3 - E_1)} \tag{24}$$

$$\pi_1 e^{\beta E_1} > \pi_3 e^{\beta E_3} \tag{25}$$

Next we will show that the value of $\pi_4 e^{\beta E_4}$ falls between $\pi_1 e^{\beta E_1}$ and $\pi_3 e^{\beta E_3}$, i.e.

$$\pi_1 e^{\beta E_1} > \pi_4 e^{\beta E_4} > \pi_3 e^{\beta E_3} \tag{26}$$

We show this by contradiction. First suppose that

$$\pi_4 e^{\beta E_4} \geq \pi_1 e^{\beta E_1} > \pi_3 e^{\beta E_3} \tag{27}$$

Then

$$\frac{\pi_4}{\pi_1} \geq e^{\beta(E_1 - E_4)} = \frac{R_{41}}{R_{14}} \tag{28}$$

hence

$$J_{14}^s = R_{14}\pi_4 - R_{41}\pi_1 \geq 0 \tag{29}$$

By similar arguments, Eq. 27 gives

$$J_{34}^s > 0 \tag{30}$$

These results imply that probability is flowing out of state 4:

$$\frac{d}{dt}\pi_4 = J^s_{41} + J^s_{43} = -J^s_{14} - J^s_{34} < 0 \tag{31}$$

which is incompatible with a steady state. Thus Eq.27 leads to a contradictory result. Analogously, if we suppose that $\pi_1 e^{\beta E_1} > \pi_3 e^{\beta E_3} \geq \pi_4 e^{\beta E_4}$ then we get the contradictory result $d\pi_4/dt > 0$. Eq. 26 is thus established by process of elimination.

From Eq. 26 we get:

$$\pi_1 e^{\beta(E_1-E_4)} \; > \; \pi_4 > \pi_3 e^{\beta(E_3-E_4)} \tag{32}$$

$$\pi_1 \frac{R_{41}}{R_{14}} \; > \; \pi_4 > \pi_3 \frac{R_{43}}{R_{34}} \tag{33}$$

which implies

$$J^s_{41} \; = \; R_{41}\pi_1 - R_{14}\pi_4 > 0 \tag{34}$$

$$J^s_{34} \; = \; R_{34}\pi_4 - R_{43}\pi_4 > 0 \tag{35}$$

Thus, in Case 1, the steady-state current flows from 1 to 4 to 3, hence $\mathcal{J}^s_2 > 0$.

Case 2: $J^s_{31} = R_{31}\pi_1 - R_{13}\pi_3 \leq 0$.
Equivalently,

$$J^s_{13} \geq 0. \tag{36}$$

In the steady state we must have

$$0 = \frac{d}{dt}\pi_1 = J^s_{12} + J^s_{13} + J^s_{14} \tag{37}$$

which implies (since $J^s_{13} \geq 0$ and $J^s_{12} > 0$ – see Eq. 22) $J^s_{14} < 0$, i.e.

$$J^s_{41} > 0. \tag{38}$$

We similarly have $0 = d\pi_4/dt = J^s_{41} + J^s_{43}$, hence $J^s_{43} < 0$, equivalently

$$J^s_{34} > 0. \tag{39}$$

Eqs. 36, 38 and 39 can be rewritten as follows:

$$R_{13}\pi_3 \; \geq \; R_{31}\pi_1 \tag{40}$$

$$R_{41}\pi_1 \; > \; R_{14}\pi_4 \tag{41}$$

$$R_{34}\pi_4 \; > \; R_{43}\pi_3 \tag{42}$$

Multiplying together the left sides of these inequalities, as well as the right sides, we get (after cancellation of the common factor $\pi_1\pi_3\pi_4$)

$$R_{13}R_{41}R_{34} > R_{31}R_{14}R_{43} \tag{43}$$

which implies $A_2 > 0$, which contradicts Eq. 20. Thus Case 2 is incompatible with the statement of the problem.

We conclude that Case 1 must apply, and in that situation we have shown that $\mathcal{J}_2^s > 0$.

(b) Since Case 1 must be true, we have $J_{31}^s > 0$.

PROBLEM 3

(a) Introducing

$$M = 2m \quad , \quad Q = \tfrac{q_1+q_2}{2} \quad , \quad \eta = \xi_1 + \xi_2 \tag{44}$$

$$\mu = \frac{m}{2} \quad , \quad q = q_2 - q_1 \quad , \quad \zeta = \frac{\xi_2 - \xi_1}{2} \tag{45}$$

we can rewrite the equations of motion in decoupled form:

$$M\ddot{Q} = -2\gamma\dot{Q} + \alpha\sin(\omega t) + \eta \tag{46}$$

$$\mu\ddot{q} = -kq - \frac{\gamma}{2}\dot{q} + \frac{\alpha}{2}\sin(\omega t) + \zeta \tag{47}$$

Eq. 46 describes a Brownian particle of mass $M = 2m$ and friction coefficient 2γ, driven by a force $\alpha\sin(\omega t)$. Using Eq. 5 of the problem, with $m \to 2m$ and $\gamma \to 2\gamma$, we get

$$\langle Q\rangle(t) = \frac{\alpha}{2\omega}\frac{\sin(\omega t - \phi)}{\sqrt{\gamma^2 + m^2\omega^2}} \quad , \quad \tan\phi = -\frac{\gamma}{m\omega} \tag{48}$$

in the long-time limit (ignoring the offset A).

Introducing $p = \mu\dot{q}$, we can rewrite Eq. 47 as follows

$$\dot{q} = \frac{p}{\mu} \quad , \quad \dot{p} = -kq - \frac{\gamma}{2\mu}p + \frac{\alpha}{2}\sin(\omega t) + \zeta \tag{49}$$

Using cumulant distribution functions, one can show that the mean values $\langle q\rangle$ and $\langle p\rangle$ obey

$$\frac{d}{dt}\langle q\rangle = \frac{\langle p\rangle}{\mu} \quad , \quad \frac{d}{dt}\langle p\rangle = -k\langle q\rangle - \frac{\gamma}{2\mu}\langle p\rangle + \frac{\alpha}{2}\sin(\omega t) \tag{50}$$

Taking a periodic-in-time *ansatz* $\langle q\rangle(t) = C\sin(\omega t - \Phi)$ and solving for Φ and C, we get

$$\langle q\rangle(t) = \frac{\alpha}{\omega}\frac{\sin(\omega t - \Phi)}{\sqrt{\gamma^2 + (r-1)^2m^2\omega^2}} \quad , \quad \tan\Phi = \frac{\gamma}{(r-1)m\omega} \quad , \quad r = \frac{k}{\mu\omega^2} \tag{51}$$

Combining these results with $q_2 = Q + (q/2)$ gives us

$$\langle q_2\rangle(t) = \frac{\alpha}{2\omega}\left[\frac{\sin(\omega t - \phi)}{\sqrt{\gamma^2 + m^2\omega^2}} + \frac{\sin(\omega t - \Phi)}{\sqrt{\gamma^2 + (r-1)^2m^2\omega^2}}\right] \tag{52}$$

(b) Eq. 52 gives

$$\lim_{k\to 0}\langle q_2\rangle(t) = \frac{\alpha}{\omega}\frac{\sin(\omega t - \phi)}{\sqrt{\gamma^2 + m^2\omega^2}} \quad \text{and} \quad \lim_{k\to\infty}\langle q_2\rangle(t) = \frac{\alpha}{\omega}\frac{\sin(\omega t - \phi)}{\sqrt{4\gamma^2 + 4m^2\omega^2}} \tag{53}$$

For $k \to 0$ the masses become uncoupled and q_2 moves like a Brownian particle of mass m and friction coefficient γ. For $k \to \infty$ the two particles become tethered infinitely strongly, acting as a single Brownian particle of mass $2m$ and friction coefficient 2γ.

PROBLEM 4

(a) We have:

$$\hat{\mathcal{L}} = -v\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2} \quad , \quad \hat{\mathcal{L}}^\dagger = +v\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2} \tag{54}$$

Substituting a plane-wave *ansatz* e^{ikx} we get

$$\hat{\mathcal{L}}e^{ikx} = (-Dk^2 - ikv)e^{ikx} \quad , \quad \hat{\mathcal{L}}^\dagger e^{ikx} = (-Dk^2 + ikv)e^{ikx} \tag{55}$$

Periodic boundary conditions impose the quantization conditions $kL = 2\pi n$ where n is an integer, hence the eigenstates and eigenvalues are:

$$\lambda_n = -Dk_n^2 - ik_n v \quad , \quad k_n = \frac{2\pi n}{L} \tag{56}$$

To make a bi-orthonormal basis set, we can write

$$\phi_n(x) = \frac{1}{L}e^{ik_n x} \quad , \quad \alpha_n(x) = e^{-ik_n x} \tag{57}$$

where $\phi_n(x)$ and $\alpha_n(x)$ are eigenstates of $\hat{\mathcal{L}}$ and $\hat{\mathcal{L}}^\dagger$, respectively, for the eigenvalue λ_n.

(b)

$$f(x,0) = \phi_0(x) + \frac{a}{2}\left[\phi_n(x) + \phi_{-n}(x)\right] \tag{58}$$

$$f(x,t) = \phi_0(x) + \frac{a}{2}\phi_n(x)e^{\lambda_n t} + \phi_{-n}(x)e^{\lambda_{-n} t} \tag{59}$$

$$= \frac{1}{L} + \frac{a}{L}e^{-Dk_n^2 t}\cos[k_n(x - vt)] \tag{60}$$

(c) The transition matrix is tri-diagonal, apart from the element β in the upper right and α in the lower left:

$$\mathcal{R} = \begin{pmatrix} -\alpha-\beta & \alpha & & & \beta \\ \beta & -\alpha-\beta & & & \\ & \beta & \ddots & \alpha & \\ & & & -\alpha-\beta & \alpha \\ \alpha & & & \beta & -\alpha-\beta \end{pmatrix} \tag{61}$$

The $(n+1)$'th column is the same as the n'the column, only shifted downward by one element. Such matrices are called *circulant matrices*.

The right eigenvectors of $\mathcal{R}$ are

$$\mathbf{u}_n = \frac{1}{N}\begin{pmatrix} 1 \\ e^{-in\nu} \\ e^{-2in\nu} \\ \vdots \\ e^{-i(N-1)n\nu} \end{pmatrix} \quad , \quad \nu = \frac{2\pi}{N} \quad , \quad 0 \le n < N \tag{62}$$

The left eigenvectors are the transpose and complex conjugates of the $\mathbf{u}_n$'s, without the factor $1/N$. These eigenvectors can be guessed (after some trial and error) by analogy with those of part (a) above. They are also known to be the eigenvectors of any circulant matrix.

From the eigenvalue equation $\mathcal{R}\mathbf{u}_n = \lambda_n \mathbf{u}_n$, using Eqs. 61 and 62 we get

$$\lambda_n = -(\alpha+\beta) + (\alpha+\beta)\cos(n\nu) + i(\beta-\alpha)\sin(n\nu) \tag{63}$$

(d) With N lattice sites and lattice spacing d, the total length of the lattice is given by

$$L = Nd. \tag{64}$$

Over a time interval τ, let $\Delta = (n_R - n_L)\cdot d$ denote the net displacement of the particle, where n_R and n_L are the number of steps to the right and to the left. Both n_R and n_L satisfy Poisson statistics, hence we have (see Eq. 31 of "Math tools"):

$$\langle n_L\rangle = \sigma^2_{n_L} = \alpha\tau \quad , \quad \langle n_R\rangle = \sigma^2_{n_R} = \beta\tau \tag{65}$$

From these expressions, and using the fact that n_R and n_L are uncorrelated, we get

$$\langle\Delta\rangle = (\beta-\alpha)\tau d \tag{66}$$

$$\sigma^2_\Delta = \langle(n_R-n_L)^2\rangle d^2 - \langle n_R - n_L\rangle^2 d^2 = (\beta+\alpha)\tau d^2 \tag{67}$$

Setting $\langle\Delta\rangle = v\tau$ and $\sigma^2_\Delta = 2D\tau$ we get

$$v = (\beta-\alpha)d \quad , \quad D = \frac{1}{2}(\beta+\alpha)d^2 \tag{68}$$

As a consistency check, substituting Eqs. 64 and 68 into Eq. 56, we obtain

$$\lambda_n = -\frac{1}{2}(\beta+\alpha)\frac{4\pi^2 n^2}{N^2} - i(\beta-\alpha)\frac{2\pi n}{N} = -\frac{1}{2}(\beta+\alpha)(n\nu)^2 - i(\beta-\alpha)n\nu \tag{69}$$

which converges to Eq. 63 if we fix n and let N become very large.

(e) The total number of steps during an interval of duration τ is:

$$K = \gamma\tau \tag{70}$$

The probability that the system takes n steps to the right and $(K-n)$ steps to the left is:

$$P(n) = \frac{K!}{n!\,(K-n)!}\, p^n\, q^{K-n} \tag{71}$$

The time-averaged entropy production rate is:

$$\sigma = \frac{2n-K}{\tau}\,\Delta s \;\in\; [-\gamma\Delta s, +\gamma\Delta s] \qquad , \qquad \Delta s \equiv \ln\frac{p}{q} \tag{72}$$

Taking $|\sigma| \leq \gamma\Delta s$, we have

$$\begin{aligned} P_\tau(\sigma) &= \sum_{n=0}^{K} \frac{K!}{n!\,(K-n)!}\; p^n\, q^{K-n}\cdot\delta\left[\sigma - \frac{\Delta s}{\tau}(2n-K)\right] \\ &\approx \sum_{n=0}^{K}\left(\frac{K}{n}\right)^n\left(\frac{K}{K-n}\right)^{K-n}\; p^n\, q^{K-n}\cdot\delta\left[\sigma - \frac{\Delta s}{\tau}(2n-K)\right] \\ &\approx K\int_0^1 \mathrm{d}x\,\left(\frac{p}{x}\right)^{Kx}\left(\frac{1-p}{1-x}\right)^{K(1-x)}\cdot\delta\left[\sigma - \gamma\Delta s\,(2x-1)\right] \end{aligned} \tag{73}$$

using Stirling's approximation and defining $x \equiv n/N$. After integrating we get

$$\begin{aligned} P_\tau(\sigma) &\approx \frac{K}{2\gamma\Delta s}\left(\frac{p}{\bar{x}}\right)^{K\bar{x}}\left(\frac{1-p}{1-\bar{x}}\right)^{K(1-\bar{x})} \qquad , \qquad \bar{x} \equiv \frac{\gamma\Delta s + \sigma}{2\gamma\Delta s} \\ &= \frac{\tau}{2\Delta s}\left(\frac{p}{\bar{x}}\right)^{\gamma\tau\bar{x}}\left(\frac{1-p}{1-\bar{x}}\right)^{\gamma\tau(1-\bar{x})} \end{aligned} \tag{74}$$

The large deviation function is:

$$\begin{aligned} I(\sigma) &= \lim_{\tau\to\infty} -\frac{1}{\tau}\ln P_\tau(\sigma) = \gamma\bar{x}\ln\frac{\bar{x}}{p} + \gamma(1-\bar{x})\ln\frac{1-\bar{x}}{1-p} \\ &= \gamma\cdot\frac{\gamma\Delta s+\sigma}{2\gamma\Delta s}\ln\left(\frac{\gamma\Delta s+\sigma}{2p\gamma\Delta s}\right) + \gamma\cdot\frac{\gamma\Delta s-\sigma}{2\gamma\Delta s}\ln\left(\frac{\gamma\Delta s-\sigma}{2q\gamma\Delta s}\right) \\ &= \frac{\gamma}{2}\ln\left[\frac{\gamma^2\Delta s^2-\sigma^2}{4\gamma^2\Delta s^2 pq}\right] + \frac{\sigma}{2\Delta s}\ln\left[\frac{\gamma\Delta s+\sigma}{\gamma\Delta s-\sigma}\right] - \frac{\sigma}{2} \quad . \end{aligned} \tag{75}$$

On the last line, the first two terms are even in σ, therefore $I(\sigma) - I(-\sigma) = -\sigma$.