I. PROJECT: THERMODYNAMICS AT STRONG COUPLING

1. Hamiltonian of closed total system is given by

$$H_{tot}(\xi, \lambda) = H_s(\xi^s, \lambda) + H_i(\xi) + H_b(\xi^b), \tag{1}$$

where λ is a protocol. If $|H_i| \ll |H_s|, |H_b|$, we call it weak coupling limit, otherwise it is called strong coupling. Then the probability distribution is generally given by $\rho(\xi) = \rho(\xi^s)\rho(\xi^b|\xi^s)$, not by a product state of system and heat bath. If the total system is prepared as cannonical distribution with β,

$$\rho_{eq}(\xi) = \frac{e^{-\beta H_{tot}(\xi,\lambda)}}{Z}, \tag{2}$$

where $Z = \text{tr}\left[e^{-\beta H_{tot}(\xi)}\right]$, the marginal and conditional distribution are given by

$$\rho_{eq}(\xi^s) = \frac{e^{-\beta H_s(\xi^s,\lambda)}\text{tr}_b\left[e^{-\beta\left(H_b(\xi^b)+H_i(\xi)\right)}\right]}{Z} \tag{3}$$

$$\rho_{eq}(\xi^b|\xi^s) = \frac{e^{-\beta\left(H_b(\xi^b)+H_i(\xi)\right)}}{\text{tr}_b\left[e^{-\beta\left(H_b(\xi^b)+H_i(\xi)\right)}\right]}. \tag{4}$$

Find $\rho_{eq}(\xi^s)$ for two cases:

- Single harmonic oscillator coupled to the harmonic bath:

$$H_s = \frac{P^2}{2M} + \frac{M\Omega_s^2}{2}X^2$$
$$H_b + H_i = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m_i} + \frac{m_i w_i^2}{2}\left(X - x_i\right)^2\right]$$

- Harmormin dumbbell coupled to the harmonic bath:

$$H_s = \frac{P_1^2 + P_2^2}{2M} + \frac{M\Omega_s^2}{2}\left(X_1 - X_2\right)^2$$
$$H_b + H_i = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m_i} + \frac{m_i w_{1i}^2}{2}\left(X_1 - x_i\right)^2 + \frac{m_i w_{2i}^2}{2}\left(X_2 - x_i\right)^2\right]$$

2. Defining an effective Hamiltonian $H_\Delta(\xi^s, \beta)$ like

$$H_\Delta(\xi^s, \beta) = -\beta^{-1}\ln\frac{\text{tr}_b\left[e^{-\beta\left(H_b(\xi^b)+H_i(\xi)\right)}\right]}{Z_b}, \tag{5}$$

where $Z_b = \mathrm{tr}_b\left[e^{-\beta H_b(\xi^b)}\right]$, one can rewrite the margianl distribution,

$$\rho_{eq}(\xi^s) = \frac{e^{-\beta(H_s(\xi^s,\lambda)+H_\Delta(\xi^s,\beta))}}{Z_s}, \tag{6}$$

where $Z_s = ZZ_b^{-1}$. From $Z = Z_sZ_b$, one can construct additive thermodynamic relations in equilibrium:

$$F_{tot}(\lambda) = F_s(\lambda) + F_b \tag{7}$$

$$\langle E_{tot}(\xi,\lambda)\rangle = \langle E_s(\xi^s,\lambda,\beta)\rangle + \langle E_b(\xi^b)\rangle_b \tag{8}$$

$$\langle S_{tot}(\xi)\rangle = \langle S_s(\xi^s)\rangle + \langle S_b(\xi^b)\rangle_b, \tag{9}$$

where $\langle\cdots\rangle_b \equiv Z_b^{-1}\mathrm{tr}\left[\cdots e^{-\beta H_b}\right]$. Find the energy and entropy functionals, i.e., E_s, E_b, S_s and S_b in terms of Hamiltonians and distributions and calculate system's energy and entropy for above two examples.

3. Changing the protocol λ, one can supply work to the total system and generally the total system is driven out of equilibrium. For a specific path $\xi_1(\lambda_1) \to \xi_2(\lambda_2)$, work W is given by the change of total Hamiltonian

$$W = H_{tot}(\xi_2,\lambda_2) - H_{tot}(\xi_1,\lambda_1). \tag{10}$$

We define the internal enegy change of system using $E_s(\xi^s,\lambda)$ on the path $\xi_1(\lambda_1) \to \xi_2(\lambda_2)$ with constant β (initial equilibrium temperature). Then heat q can be defined as an additive quantity,

$$q = [H_{tot}(\xi_2,\lambda_2) - H_{tot}(\xi_1,\lambda_1)] - [E_s(\xi_2^s,\lambda_2) - E_s(\xi_1^s,\lambda_1)] \tag{11}$$

Now we define an additive entropy production ΔS_{tot} on a single path $\xi_1 \to \xi_2$,

$$\Delta S_{tot} = S_s(\xi_2^s) - S_s(\xi_1^s) + \beta q, \tag{12}$$

where S_s has been defined in 2. Note that S_s also has an explicit function of β, but β is also constant here. Prove $\langle\Delta S_{tot}\rangle \geq 0$ when we start from equilibrium state for $H_{tot}(\lambda_1)$ with β and change the protocol to λ_2 in the isolated total system, using the Jarzinski equality.

[1] U. Seifert, Phys. Rev. Lett. **116**, 020601 (2016).

[2] M. F. Gelin and M. Thoss, Phys. Rev. E **79**, 051121 (2009).