Introduction to Nonequilibrium Work Theorems

Lectures I and II - derivations

[I presented Lectures I and II as chalkboard talks, and I do not have a set of accompanying transparencies or pdf / power point files. The derivations below are more or less the ones that I worked through during those two lectures; the derivation of the Crooks fluctuation theorem is additional material, since I ran out of time and was not able to present that during Lecture I as originally intended. These notes are meant as a concise summary of the analysis in Lecture I and II, rather than a self-contained exposition of the material.]

Setup

Thermodynamic process:

(1) start in equilibrium at temperature T, work parameter $\lambda = A$

(2) vary the work parameter from A to B using a protocol λ_t $(0 \leq t \leq \tau)$

Repeating this procedure, we obtain an ensemble of realizations of the process.

Macroscopic.

$W \geq \Delta F \equiv F_B - F_A$ (Clausius inequality). $W = \Delta F$ when the process is reversible and isothermal. E.g. reversible expansion / compression of dilute gas:

$$W_{\rm isoth} = -n\beta^{-1} \ln \frac{V_B}{V_A} = \Delta F \quad , \quad W_{\rm adiab} = \left[\left(\frac{V_B}{V_A} \right)^{-2/3} - 1 \right] \frac{3}{2} n\beta^{-1} > \Delta F \tag{1}$$

Microscopic.

$$\text{microstate} \quad : \quad x = (\mathbf{r}_1, \mathbf{r}_2, \cdots ; \mathbf{p}_1, \mathbf{p}_2, \cdots) = (q,p) \tag{2}$$

$$\text{Hamiltonian} \quad : \quad H(x,\lambda) = \text{Hamiltonian} \tag{3}$$

Equilibrium state :

$$p_\lambda^{\rm eq}(x) = \frac{1}{Z_A} e^{-\beta H(x,\lambda)} \quad , \quad Z_\lambda = \int dx\, e^{-\beta H(x,\lambda)} \quad , \quad F_\lambda = -\beta^{-1} \ln Z_\lambda \tag{4}$$

Work performed during a given realization:

$$W = \int_0^\tau dt\, \dot{\lambda} \frac{\partial H}{\partial \lambda}(x_t, \lambda_t) \tag{5}$$

Average over realizations:

$$\langle W \rangle \equiv \int dW\, \rho(W)\, W \geq \Delta F \tag{6}$$

Forward ($A \to B$) and *reverse* ($B \to A$) processes,

$$\lambda_t^R = \lambda_{\tau-t}^F \tag{7}$$

Predictions:

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F} \tag{8}$$

$$\frac{\rho^F(+W)}{\rho^R(-W)} = e^{\beta(W-\Delta F)} \tag{9}$$

$$\left\langle \delta(x - x_t) e^{-\beta w_t} \right\rangle = \frac{1}{Z_A} e^{-\beta H(x,A)} \tag{10}$$

where $\langle \cdots \rangle$ denotes an average over infinitely many realizations of the process in question; β^{-1} is the temperature at which the system is initially prepared; $\Delta F = F_B - F_A$; $\rho^{F/R}(W)$ is the distribution of work values for the forward/reverse process; and w_t is the work performed up to time t during a given realization.

Isolated Hamiltonian systems

Prepare system in equilibrium, then remove reservoir. The system subsequently evolves under Hamilton's equations:

$$\dot{x} = (\dot{q}, \dot{p}) = \left(\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q} \right) \quad , \qquad \mathrm{div}(\dot{x}) = 0 \qquad \text{(Liouville)} \tag{11}$$

In this case $x_t = x_t(x_0)$ (deterministic evolution) and

$$W = W(x_0) = H(x_\tau(x_0), B) - H(x_0, A) \tag{12}$$

Evaluate $\langle e^{-\beta W} \rangle$:

$$\left\langle e^{-\beta W} \right\rangle = \int dx_0 \, p_A^{\mathrm{eq}}(x_0) \, e^{-\beta W(x_0)} \tag{13}$$

$$= \frac{1}{Z_A} \int dx_0 \, e^{-\beta H(x_\tau(x_0),B)} \tag{14}$$

$$= \frac{1}{Z_A} \int dx_\tau \, e^{-\beta H(x_\tau,B)} = \frac{Z_B}{Z_A} = e^{-\beta \Delta F} \tag{15}$$

Note change of variables, $dx_0 \to dx_\tau \, |\partial x_\tau / \partial x_0|^{-1} = dx_\tau$, using Liouville's theorem.

For the Crooks fluctuation theorem assume time-reversal invariance: $H(x, \lambda) = H(x^*, \lambda)$, where $(q, p)^* \equiv (q, -p)$. Conjugate pairs: if $X = \{x_t\}$ is a solution of Hamilton's equations for the forward process, then $X^\dagger = \{x_t^\dagger\}$ is a solution for the reverse process, where

$$x_t^\dagger = x_{\tau-t}^* \tag{16}$$

For such a conjugate pair, the work values are opposite:

$$W^F(x_0) = -W^R(x_0^\dagger) \tag{17}$$

Useful identity:

$$\frac{p_A^{\rm eq}(x_0)}{p_B^{\rm eq}(x_0^\dagger)} = \frac{Z_B}{Z_A}\,\frac{\exp[-\beta H(x_0,A)]}{\exp[-\beta H(x_0^\dagger,B)]} = e^{\beta(W^F-\Delta F)}, \tag{18}$$

since $x_0^\dagger = x_\tau$. Equivalently:

$$\frac{P^F[X]}{P^R[X^\dagger]} = e^{\beta(W^F-\Delta F)} \tag{19}$$

Now define an indicator function

$$\Theta^F(x_0,W,dW) \;=\; 1 \qquad \text{if}\left|W^F(x_0)-W\right| \le \frac{dW}{2} \tag{20}$$

$$\;=\; 0 \qquad \text{otherwise}, \tag{21}$$

and similarly Θ^R for the reverse process. Note that

$$\Theta^R(x_0^\dagger,-W,dW) = \Theta^F(x_0,W,dW) \tag{22}$$

For dW infinitesimal,

$$\rho^F(W)\,dW \;=\; \int dx_0\, p_A^{\rm eq}(x_0)\,\Theta^F(x_0,W,dW) \tag{23}$$

$$=\; \int dx_0\, e^{\beta(W^F-\Delta F)}\, p_B^{\rm eq}(x_0^\dagger)\,\Theta^F(x_0,W,dW) \tag{24}$$

$$=\; e^{\beta(W-\Delta F)}\int dx_0^\dagger\, p_B^{\rm eq}(x_0^\dagger)\,\Theta^R(x_0^\dagger,-W,dW) \tag{25}$$

$$=\; e^{\beta(W-\Delta F)}\,\rho^F(-W)\,dW \tag{26}$$

Define

$$f(x,t) \;=\; \Big\langle \delta(x-x_t)\Big\rangle = \lim_{\epsilon\to 0}\lim_{N\to\infty}\Big\langle \delta_\epsilon(x-x_t)\Big\rangle_N \tag{27}$$

$$h(x,w,t) \;=\; \Big\langle \delta(x-x_t)\,\delta(w-w_t)\Big\rangle \tag{28}$$

$$g(x,t) \;=\; \Big\langle \delta(x-x_t)\,\exp(-\beta w_t)\Big\rangle = \int dw\, e^{-\beta w}\, h(x,w,t), \tag{29}$$

where

$$w_t = \int_0^t ds\,\dot\lambda\,\frac{\partial H}{\partial\lambda}(x_s,\lambda_s) \tag{30}$$

Liouville (continuity) equation for f:

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial q}(\dot q f) - \frac{\partial}{\partial p}(\dot p f) = \frac{\partial H}{\partial q}\frac{\partial f}{\partial p} - \frac{\partial H}{\partial p}\frac{\partial f}{\partial q} = \{H,f\} \tag{31}$$

For h we have

$$\frac{\partial h}{\partial t} = -\frac{\partial}{\partial q}(\dot{q}h) - \frac{\partial}{\partial p}(\dot{p}h) - \frac{\partial}{\partial w}(\dot{w}h) = \{H, h\} - \dot{\lambda}\frac{\partial H}{\partial \lambda}\frac{\partial h}{\partial w} \tag{32}$$

This gives us for g:

$$\frac{\partial g}{\partial t} = \int dw\, e^{-\beta w}\left(\{H, h\} - \dot{\lambda}\frac{\partial H}{\partial \lambda}\frac{\partial h}{\partial w}\right) \tag{33}$$

$$= \{H, g\} - \dot{\lambda}\frac{\partial H}{\partial \lambda}\int dw\, e^{-\beta w}\frac{\partial h}{\partial w} \tag{34}$$

$$= \{H, g\} - \beta\dot{\lambda}\frac{\partial H}{\partial \lambda}\int dw\, e^{-\beta w} h = \{H, g\} - \beta\dot{\lambda}\frac{\partial H}{\partial \lambda} g \tag{35}$$

Initial conditions: $g(x,0) = f(x,0) = Z_A^{-1}\exp[-\beta H(x, A)]$ (since $w_0 = 0$). Solution:

$$g(x,t) = \frac{1}{Z_A}\exp[-\beta H(x, \lambda_t)] \tag{36}$$

using $\{H, e^{-\beta H}\} = 0$.

Feynman-Kac approach for stochastic dynamics

Propagator:

$$K(x,t|x_0,t_0) = \int dX\, P[X|x_0,t_0] \tag{37}$$

$$\frac{\partial}{\partial t}K(x,t|x_0,t_0) = \int dx'\, R_t(x' \to x)\, K(x',t|x_0,t_0) \equiv \mathcal{L}_t K \tag{38}$$

$\int dX$ is over all paths from (x_0, t_0) to (x, t), and $P[X|x_0, t_0]$ is the conditional probability of observing a path X, given (x_0, t_0). For a function $\omega(x, t)$, define

$$G(x,t|x_0,t_0) \equiv \int dX\, P[X|x_0,t_0]\, e^{\Omega[X]}, \tag{39}$$

where

$$\Omega[X] = \int dt\, \omega(x_t, t) \tag{40}$$

for a trajectory $X = \{x_t\}$.

$$G(x,t+dt|x_0,t_0) = \int dx'\, G(x,t+dt|x',t)\, G(x',t|x_0,t_0) \tag{41}$$

But

$$G(x,t+dt|x',t) = \int dX\, P[X|x',t]\, e^{\Omega[X]} \tag{42}$$

$$\approx e^{\omega(x',t)\,dt}\, K(x,t+dt|x',t) \tag{43}$$

$$\approx (1 + \omega\, dt)\left[\delta(x - x') + dt\, R_t(x' \to x)\right] \tag{44}$$

Therefore

$$G(x,t+dt|x_0,t_0) \approx \int dx'\,(1+\omega\,dt)\left[\delta(x-x') + dt\,R_t(x'\to x)\right]G(x',t|x_0,t_0) \quad (45)$$

$$\approx (1+\omega\,dt+dt\,\mathcal{L}_t)\,G(x,t|x_0,t_0) \quad (46)$$

$$\frac{\partial G}{\partial t} = (\mathcal{L}_t+\omega)\,G \qquad (\text{Feynman}-\text{Kac theorem}) \quad (47)$$

Apply this result to the nonequilibrium work context ...

Assume Markov process + balanced dynamics:

$$\frac{\partial}{\partial t}f(x,t) = \int dx'\,R_\lambda(x' \;\to\; x)\,f(x',t) = \mathcal{L}_\lambda f \quad (48)$$

$$\mathcal{L}_\lambda \exp[-\beta H(x,\lambda)] \;=\; 0 \quad (49)$$

Then

$$g(x,t) \equiv \left\langle \delta(x-x_t)\,e^{-\beta w_t}\right\rangle \quad (50)$$

$$= \int dx_0\,p_A^{\rm eq}(x_0)\int dX\,P[X|x_0,0]\,\exp(-\beta w_t) \quad (51)$$

$$= \int dx_0\,p_A^{\rm eq}(x_0)\,G(x,t|x_0,0), \quad (52)$$

using $\omega = -\beta\dot\lambda\,(\partial H/\partial\lambda)$, $\Omega = -\beta w_t$. Then the F-K theorem tells us:

$$\frac{\partial g}{\partial t} = \left(\mathcal{L}_\lambda - \beta\dot\lambda\frac{\partial H}{\partial\lambda}\right)g, \quad (53)$$

whose solution is $g(x,t) = Z_A^{-1}\exp[-\beta H(x,\lambda_t)]$.

Importance of ordering of limits: illustrative example

[See Pressé and Silbey, J. Chem. Phys. **124**, 054117 (2006)]

Ideal gas of N particles in box. Initially the potential energy is zero in the left half of the box, and "infinite" in the right half. Then the potential in the right half is suddenly dropped to zero. Since all the particles are in the left half of the box, we get $W=0$, hence $\langle e^{-\beta W}\rangle = 1$, which is not equal to $e^{-\beta\Delta F} = 2^N$.

Do this carefully. Let $U_0 \gg k_BT$ denote the initial potential in the right half of the box (zero in the left half). Then the work during one realization is

$$W = -nU_0, \quad (54)$$

where n is the number of particles found in the right half of the box (when sampling from the canonical distribution). Hence

$$\left\langle e^{-\beta W}\right\rangle = p_0 + p_1e^{\beta U_0} + p_2e^{2\beta U_0} + \cdots + p_Ne^{N\beta U_0} = \sum_{n=0}^{N} p_n\epsilon^{-n}, \quad (55)$$

where $\epsilon = e^{-\beta U_0} \ll 1$, and p_n is the probability that n particles are initially found in the right half of the box. (Since $p_0 \gg p_1 \gg \cdots \gg p_N$ and $1 \ll \epsilon^{-1} \ll \cdots \ll \epsilon^{-N}$, the above sum is a competition between the rapid decrease of p_n and the rapid increase of ϵ^{-n}.) Explicitly,

$$p_n = \binom{N}{n} \left(\frac{\epsilon}{1+\epsilon}\right)^n \left(\frac{1}{1+\epsilon}\right)^{N-n}, \tag{56}$$

where $\epsilon/(1+\epsilon)$ is the probability that a given particle is initially found in the right half of the box. Hence

$$p_n \epsilon^{-n} = \binom{N}{n} \left(\frac{1}{1+\epsilon}\right)^N, \tag{57}$$

which gives us

$$\left\langle e^{-\beta W} \right\rangle = \sum_{n=0}^{N} p_n \epsilon^{-n} = \left(\frac{2}{1+\epsilon}\right)^N \to 2^N = e^{-\beta \Delta F}, \tag{58}$$

as $U_0 \to \infty$. Thus we obtain agreement when we *first* take the limit of infinitely many realizations, and *then* $U_0 \to \infty$.

Note that $p_n \epsilon^{-n}$ is peaked at $n = N/2$ (Eq.57), thus the largest contribution to $\langle e^{-\beta W} \rangle$ comes from those (extremely rare!) realizations for which half the particles are found in the right half of the box. This illustrates the central result discussed in Lecture III.