Lecture 12

[Integrated fluctuation theorems]

Recall that $\frac{p^F(R)}{p^R(-R)} = e^R$, then

$$p^F(R)\, e^{-R} = p^R(-R),$$

$$\int_{-\infty}^{\infty} dR\, p^F(R)\, e^{-R} \equiv \langle e^{-R}\rangle_F \overset{R\to -R}{=} \int_{-\infty}^{\infty} d(-R)\, p^R(-R) = 1,$$

or $\underbrace{\langle e^{-R}\rangle_F = 1}$

Likewise, $\frac{p^F(Y)}{p^R(-Y)} = e^Y \Rightarrow \underbrace{\langle e^{-Y}\rangle_F = 1}$

No explicit reference to the reverse process, just expectation values over an ensemble of forward paths.

Using Jensen's inequality, $\langle e^y\rangle \geq e^{\langle y\rangle}$, we obtain: $\underbrace{\langle e^{-R}\rangle_F}_{=1} \geq e^{-\langle R\rangle_F}$, or

$$0 \geq -\langle R\rangle_F \Rightarrow \underbrace{\langle R\rangle_F \geq 0}.$$

Likewise, $\underbrace{\langle Y\rangle_F \geq 0}$.

Focusing on the 'R-theorem' (the arguments are the same with Y), we observe that in larger systems / longer paths we expect

$p^F(R)$ to be tightly peaked around $\langle R\rangle_F$. However, by the same argument $p^F(R)\,e^{-R} = p^R(-R)$ will be tightly peaked around $-\langle R\rangle_F$ (!) Thus, if $\langle R\rangle_F \gg 0$, a typical path will contribute $e^{-R} \simeq e^{-\langle R\rangle_F} \simeq 0$ to $\langle e^{-R}\rangle_F$. One needs atypical forward paths with $R \simeq -\langle R\rangle_F$ to produce non-zero $p^F(R)\,e^{-R}$ and actually observe the fluctuation theorem in simulations.

What is the minimal number of forward paths needed to observe the effect? Imagine $M-1$ non-contributing paths with $R \approx \langle R\rangle_F$ and 1 contributing path with $R \simeq -\langle R\rangle_F$:

$$\underbrace{\langle e^{-R}\rangle_F}_{=1} \simeq \frac{1}{M}\left[(M-1)\,e^{-\langle R\rangle_F} + e^{\langle R\rangle_F}\right] \simeq \frac{e^{\langle R\rangle_F}}{M}, \text{ or}$$

$$M \simeq e^{\langle R\rangle_F} \gg 1 \quad \text{if } \langle R\rangle_F \gg 0.$$

Thus, M can easily become exponentially large.

Physical applications

1. Consider a system in contact with a thermal reservoir at temp. T, then

SS = equil.: $p^s = e^{\beta(F - \mathcal{U})}$, or

(with F = free en., $\mathcal{U}$ = internal energy)

$$\varphi(\vec{x};\lambda) = \beta\,\mathcal{U}(\vec{x};\lambda) - \beta F(\lambda).$$

DB holds: $\vec{A} = 0$, $\vec{J}^s = 0$.

Then
$$Y^F = \int_F dt\, \dot{\lambda}_t^F \frac{\partial \varphi}{\partial \lambda} = \beta \int_F dt\, \dot{\lambda}_t^F \frac{\partial \mathcal{U}}{\partial \lambda} -$$
$$- \beta \int_F d\lambda \frac{dF}{d\lambda} = \beta \underbrace{\int_F dt\, \dot{\lambda}_t^F \frac{\partial \mathcal{U}}{\partial \lambda}}_{\text{total work } W \text{ done on the system}} - \beta \underbrace{\Delta F}_{F(\vec{x}_\tau) - F(\vec{x}_{-\tau})} \circleddash$$

$$\circleddash\ \beta(\underbrace{W - \Delta F}_{\equiv W_{diss}}),$$ dissipated work

Here,
$$R^F = Y^F + \int_F d\vec{x} \cdot \vec{A} = Y^F.$$

Finally, $\langle e^{-Y} \rangle_F = 1$ yields

$$\langle e^{-\beta(W - \Delta F)} \rangle = 1, \text{ or}$$

$$\underline{\underline{\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}}}. \Leftarrow \text{confirmed in single-molecule experiments}$$

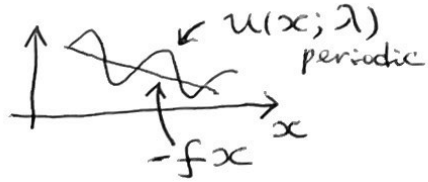
(2.) Consider 1D non-conservative dynamics:

non-conservative ~~acting changing constant~~ force: $f = f(\lambda)$

$$\gamma \dot{x} = \underbrace{-\frac{\partial u}{\partial x}}_{\text{conservative force}} + \tilde{f} + \xi(t)$$

$\gamma > 0$, $f > 0$

conservative force periodic $\Rightarrow$



$$\langle \xi(t)\,\xi(t') \rangle = 2\overbrace{\gamma^{-1} k_B T}^{= G}\,\delta(t-t')$$

Consider $\lambda = \underset{\text{const}}{\lambda}(t)$: system evolves to a ~~through a quasistatic sequence of~~ SS with $p_s = e^{-\varphi(x;\lambda)}$.

In this case,

$$A = 2\underbrace{\Gamma}_{=\frac{1}{2\gamma^{-1}k_B T}} \overbrace{F}^{=\gamma^{-1}[f - \frac{\partial u}{\partial x}]} + \underbrace{\varphi'}_{=\frac{\partial \varphi}{\partial x}} = \beta\left[f - \frac{\partial u}{\partial x}\right] + \frac{\partial \varphi}{\partial x}$$

If $f = 0$, $\varphi = \beta u$ and $A = 0 \Rightarrow f \neq 0$ makes $\varphi \neq \beta u$ (SS $\neq$ eq).

One can identify
$$Q = \beta^{-1} \int dx\, A$$
with 'housekeeping heat', that is,

i.e., increase in reservoir's entropy

[heat absorbed by the external reservoir = 'thermodynamic price' to keep the system away from equilibrium.

This is a random quantity that on average grows linearly with time (i.e., path length 2τ)

(3.) Recall the example with a moving quadratic trap +
(2D) + tangential current.
('vortex')

When $f(q)>0$, the particle is subject to a counter-clockwise force
(a) around $\vec{r}_\lambda$. Consider $\lambda = \text{const}(t)$ first.

Then $\int d\vec{x}\cdot \underbrace{\vec{A}}_{= f(q)\hat{\theta}} = \int dt\, \dot{\vec{r}}_t \cdot \hat{\theta} f(q_t) \equiv C[X]$, circulation of path X

Here, $C[X] = R[X]$ since $Y[X]=0$.

Thus, $\frac{p(C)}{p(-C)} = e^{C}$;

$p(C)$ = prob. of observing circulation C, with initial conditions sampled from SS

by previous arguments,

Since $\langle C \rangle > 0$

$p(C) > p(-C)$ ⇒ the particle tends to flow with the vortex (i.e, external tangential force)

However, $-\langle C\rangle$ must be observed for $\langle e^{-C}\rangle_F = 1$ to hold.
at some point

(b) Now consider $\dot{\lambda}_t \neq 0$, $f(q_\theta) = 0$.

Then $\vec{A} = 0$, $\vec{J}^s = 0$.

In this case, $R = Y = \int dt\, \dot{\lambda}_t \frac{\partial \varphi}{\partial \lambda}$

$$\varphi \sim \frac{k q_\theta^2}{2} = \frac{k}{2} \overbrace{|\vec{r}_t - \underbrace{\vec{r}_\lambda}_{= (\lambda, 0)}|^2}^{= (x_t - \lambda_t)^2 + y_t^2}.$$

Then $\frac{\partial \varphi}{\partial \lambda} = k(x_t - \lambda) \times (-1)$, yielding

note that $z = \text{const}(\lambda)$ here

$$R = -k \int d\lambda (x_t - \lambda_t) = \text{total external work } \text{exerted on the particle by the moving well}$$

(c) Finally, consider $\dot{\lambda}_t \neq 0$, $f(q_\theta) > 0$.

$$\underset{\text{counter-clockwise}}{\mathcal{I}_\lambda \to + f(q_\theta)}, \quad \underset{\text{clockwise}}{\hat{\mathcal{I}}_\lambda \to - f(q_\theta)}$$

If we use $\mathcal{I}_\lambda$ for both $\overset{\text{forward}}{F}$ and $\overset{\text{reverse}}{R}$ processes, the particle is always dragged counter-clockwise and therefore 'goes with the current' in F but 'against the current' in R. Then we use

$$R = Y + C \quad \text{and} \quad \frac{p^F(+R)}{p^F(-R)} = e^R.$$

However, we can also consider a situation in which we switch to $\hat{\mathcal{I}}_\lambda$ (clockwise current) in R, so that the particle 'goes with the flow' in both F and R.

Then we need to use Y, <u>not</u> R:

$$\frac{p^F(+Y)}{p^F(-Y)} = e^Y .$$

G is no longer needed in this setup.