Probability

1. *Random deposition:* A mirror is plated by evaporating a gold electrode in vaccum by passing an electric current. The gold atoms fly off in all directions, and a portion of them sticks to the glass (or to other gold atoms already on the glass plate). Assume that each column of deposited atoms is independent of neighboring columns, and that the average deposition rate is d layers per second.

(a) What is the probability of m atoms deposited at a site after a time t? What fraction of the glass is not covered by any gold atoms?

• This is an example of a Poisson process, for which the probability of m deposition events at average rate d is

$$p(m) = \frac{(dt)^m e^{-dt}}{m!}.$$

The fraction of the glass that is not covered by gold atoms can be obtained by $p(0)$, that is,

$$p(0) = e^{-dt}.$$

An explicit derivation of this follows: First note that in a given time interval Δt, the probability for an atom to stick to a site is Δp. We will eventually send both to zero. In this case, the probability for a column at a site to have m atoms in time t would be,

$$p(m) =_{(t/\Delta t)} C_m (\Delta p)^m (1 - \Delta p)^{t/\Delta t - m}.$$

So the average number of layers made in time t would be for $N \equiv t/\Delta t$,

$$\sum_{n=0}^{N} n \cdot_N C_n (\Delta p)^n (1 - \Delta p)^{N-n} = N\Delta p = \frac{\Delta p}{\Delta t} t = dt.$$

Hence the relation, $\Delta p = d\Delta t$. Note that this relation was obtained without any assumptions on $\Delta t, \Delta p$. Now let's obtain $p(m)$ as we send $\Delta t, \Delta p \to 0$

$$p(m) = \lim_{\Delta t \to 0} \frac{(t/\Delta t)(t/\Delta t - 1) \cdots (t/\Delta t - m + 1)}{m!} (\Delta p)^m (1 - \Delta p)^{t/\Delta t - m}.$$

Rearranging the terms we get,

$$p(m) = \lim_{\Delta t \to 0} \frac{(t\Delta p/\Delta t) \cdots (t\Delta p/\Delta t - (m-1)\Delta p)}{m!} (1 - \Delta p)^{t/\Delta t - m}.$$

Inserting, $\Delta t = d\Delta p$ we get,

$$p(m) = \lim_{\Delta p \to 0} \frac{(dt)^m}{m!}(1-\Delta p)^{dt/\Delta p} = \frac{(dt)^m e^{-dt}}{m!}.$$

(b) What is the variance in the thickness?

- We need $\langle m^2 \rangle$, which is,

$$\langle m^2 \rangle = \sum_{m=0}^{\infty} m^2 p(m) = \sum \frac{m(m-1)}{m!}(dt)^m e^{-td} + \sum \frac{m}{m!}(dt)^m e^{-td} = (dt)^2 + dt$$

Since,

$$\langle m \rangle = \sum_{m=0}^{\infty} \frac{m}{m!}(dt)^m e^{-td} = dt.$$

the variance in the thickness is,

$$\langle m^2 \rangle - \langle m \rangle^2 = dt.$$

Note that all cumulants of this Poisson process are equal to dt.

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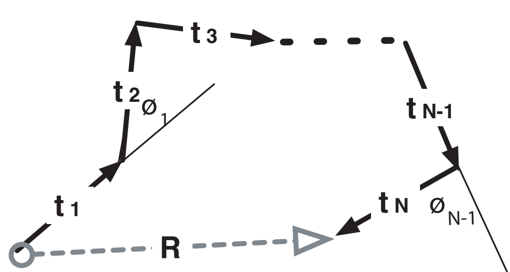
2. *Semi-flexible polymer in two dimensions* Configurations of a model polymer can be described by either a set of vectors $\{\mathbf{t}_i\}$ of length a in two dimensions (for $i = 1, \cdots, N$), or alternatively by the angles $\{\phi_i\}$ between successive vectors, as indicated in the figure below.



The polymer is at a temperature T, and subject to an energy

$$\mathcal{H} = -\kappa \sum_{i=1}^{N-1} \mathbf{t}_i \cdot \mathbf{t}_{i+1} = -\kappa a^2 \sum_{i=1}^{N-1} \cos\phi_i \quad ,$$

where κ is related to the bending rigidity, such the probability of any configuration is proportional to $\exp(-\mathcal{H}/k_B T)$.

(a) Show that $\langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle \propto \exp\left(-|n-m|/\xi\right)$, and obtain an expression for the *persistence length* $\ell_p = a\xi$. (You can leave the answer as the ratio of simple integrals.)

• In terms of the angles, the dot product can be written as

$$\mathbf{t}_m \cdot \mathbf{t}_n = a^2 \cos\left(\phi_m + \phi_{m+1} + \cdots + \phi_{n-1}\right) = a^2 \Re e^{i(\phi_m + \phi_{m+1} + \cdots + \phi_{n-1})}.$$

Note that the angles $\{\phi_n\}$ are *independent variables*, distributed according to the Boltzmann weight

$$p\left[\{\phi_n\}\right] \propto \prod_{n=1}^{N-1} \exp\left(\frac{\kappa a^2}{k_B T}\cos\phi_n\right) \qquad .$$

Hence the average of the product is the product of averages, and

$$\langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle = a^2 \Re \prod_{k=m}^{n-1} \left\langle e^{i\phi_n} \right\rangle = a^2 \left[\frac{\int d\phi \cos\phi \; e^{\frac{\kappa a^2}{k_B T}\cos\phi}}{\int d\phi \; e^{\frac{\kappa a^2}{k_B T}\cos\phi}}\right]^{|n-m|} \qquad .$$

The persistence length is thus given by

$$\ell_p = \frac{a}{\ln\left[\int d\phi \; e^{\frac{\kappa a^2}{k_B T}\cos\phi} \Big/ \int d\phi \; \cos\phi \; e^{\frac{\kappa a^2}{k_B T}\cos\phi}\right]}.$$

(b) Consider the end–to–end distance $\mathbf{R}$ as illustrated in the figure. Obtain an expression for $\langle R^2 \rangle$ in the limit of $N \gg 1$.

• Using $\mathbf{R} = \sum_{n=1}^{N-1} \mathbf{t}_n$, we obtain

$$\langle R^2 \rangle = \sum_{m,n} \langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle = \sum_{m,n} a^2 e^{-|n-m|/\xi}.$$

The above sum decays exponentially around each point. Ignoring corrections from end effects, which are asymptotically negligible for $N \to \infty$, we obtain

$$\langle R^2 \rangle \simeq a^2 N \left[1 + 2\frac{e^{-1/\xi}}{1 - e^{-1/\xi}}\right] = a^2 N \coth\frac{1}{2\xi}.$$

(c) Find the probability $p(\mathbf{R})$ in the limit of $N \gg 1$.

• Since $\mathbf{R} = \sum_{n=1}^{N-1} \mathbf{t}_n$, we can use the central limit theorem to conclude that in the limit of $N \to \infty$, the probability distribution $p(\mathbf{R})$ approaches a Gaussian form. Thus, we just need to evaluate the mean and variance of $\mathbf{R}$. Since the mean $\langle \mathbf{R} \rangle = 0$ by symmetry, the variance is equal to $\left\langle R^2 \right\rangle$ calculated in part (b). Noting that in two dimensions, $\left\langle R_x^2 \right\rangle = \left\langle R_y^2 \right\rangle = \left\langle R^2 \right\rangle/2$, the properly normalized Gaussian form is

$$p(\mathbf{R}) = \frac{1}{\pi \left\langle R^2 \right\rangle} \exp\left[-\frac{\mathbf{R}\cdot\mathbf{R}}{\left\langle R^2 \right\rangle}\right].$$

(d) If the ends of the polymer are pulled apart by a force $\mathbf{F}$, the probabilities for polymer configurations are modified by the Boltzmann weight $\exp\left(\frac{\mathbf{F}\cdot\mathbf{R}}{k_B T}\right)$. By expanding this weight, or otherwise, show that

$$\langle \mathbf{R} \rangle = K^{-1}\mathbf{F} + \mathcal{O}(F^3) \quad ,$$

and give an expression for the Hookian constant K in terms of quantities calculated before.
• Let us indicate by $\langle\rangle_0$ averages taken for $\mathbf{F} = 0$. Then the average of $\mathbf{R}$ at finite $\mathbf{F}$ is given by

$$\langle \mathbf{R} \rangle = \frac{\left\langle \mathbf{R} e^{\beta \mathbf{F}\cdot\mathbf{R}} \right\rangle_0}{\left\langle e^{\beta \mathbf{F}\cdot\mathbf{R}} \right\rangle_0} \quad ,$$

where $\beta = 1/(k_B T)$. The exponential factors can now be expanded in powers of F. Noting that zero-force averages of odd powers of R are zero by symmetry, we obtain

$$\langle R_\mu \rangle = \beta F_\nu \left\langle R_\nu R_\mu \right\rangle_0 + \mathcal{O}(F^3) \quad .$$

By symmetry $\left\langle R_\nu R_\mu \right\rangle_0 = \delta_{\mu\nu} \left\langle R^2 \right\rangle_0 /2$, where $\left\langle R^2 \right\rangle_0$ is the zero-force expression calculated in the previous part. Thus,

$$\langle \mathbf{R} \rangle = K^{-1}\mathbf{F} + \mathcal{O}(F^3) \quad \text{, with} \quad K = \frac{2k_B T}{\left\langle R^2 \right\rangle_0}.$$

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3. *Foraging:* Typical foraging behavior consists of a random search for food, followed by a quick return to the nest. For this problem, assume that the nest is at the origin, and the search consists of a random walk *in two dimensions* around the nest. For a random walk it can be shown that the probability density to be a distance r, at a time t after leaving the origin, is given by (in terms of a diffusion constant D)

$$p(r|t) = \frac{r}{2Dt} \exp\left(-\frac{r^2}{4Dt}\right) .$$

(a) Assume that durations of search segments are exponentially distributed, i.e. with probability $p(t) \propto e^{-t/\tau}$. What is the probability to find the searcher at a distance r just before it retuns to the nest? Use saddle-point integration to find the asymptotic probability for large r.

• The forager observed at position r, may have left the nest at an earlier time t with probability $p(t) = e^{-t/\tau}/\tau$, leading to the joint probability $p(r,t) = p(r|t)p(t)$. Integrating the latter over all times t leads to the unconditional probability

$$p(r) = \int_0^\infty \frac{dt}{\tau}\,\frac{r}{2Dt}\exp\left(-\frac{r^2}{4Dt} - \frac{t}{\tau}\right).$$

For large r, we can use the saddle point method to evaluate the integral. The maximum of the exponent occurs for $r^2/(4D\bar{t}^2) - 1/\tau = 0$, i.e. for $\bar{t} = \sqrt{\tau/D}r/2$, resulting in

$$p(r) \propto \exp\left(-\frac{r}{\sqrt{D\tau}}\right).$$

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4. *Jensen's inequality and Kullback–Liebler divergence:* A convex function $f(x)$ always lies above the tangent at any point, i.e. $f(x) \geq f(y) + f'(y)(x-y)$ for all y.

(a) Show that for a convex function $\langle f(x)\rangle \geq f(\langle x\rangle)$.

• Using the presented condition for a convex function, we find

$$\langle f(x)\rangle = \int dx\; p(x)f(x) \geq \int dx\; p(x)\left[f(y) + f'(y)(x-y)\right] = f(y) + f'(y)(\langle x\rangle - y).$$

Choosing $y = \langle x\rangle$, the second term above vanishes, leading to

$$\langle f(x)\rangle \geq f(\langle x\rangle).$$

(b) The *Kullback–Liebler divergence* of two probability distributions $p(x)$ and $q(x)$ is defined as $D(p|q) \equiv \int dx\;\; p(x)\ln\left[p(x)/q(x)\right]$. Use Jensen's inequality to prove that $D(p|q) \geq 0$.

• The Kullback–Liebler divergence can be rearranged as

$$-D(p|q) = \int dx\; p(x) \ln \left[\frac{q(x)}{p(x)}\right] = \langle \ln \left[\frac{q(x)}{p(x)}\right] \rangle.$$

Noting that $-\ln(x)$ is a convex function, we can now use Jensen's inequality to find

$$D(p|q) = -\langle \ln \left[\frac{q(x)}{p(x)}\right] \rangle \geq -\ln \langle \left[\frac{q(x)}{p(x)}\right] \rangle = -\ln \left[\int dx\; p(x) \frac{q(x)}{p(x)} \right] = -\ln 1 = 0,$$

since $\int dx\; q(x) = 1$.

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5. *The book of records:* Consider a sequence of random numbers $\{x_1, x_2, \cdots, x_n, \cdots\}$; the entry x_n is a *record* if it is larger than all numbers before it, i.e. if $x_n > \{x_1, x_2, \cdots, x_{n-1}\}$. We can then define an associated sequence of indicators $\{R_1, R_2, \cdots, R_n, \cdots\}$ in which $R_n = 1$ if x_n is a record, and $R_n = 0$ if it is not (clearly $R_1 = 1$).

(a) Assume that each entry x_n is taken independently from the same probability distribution $p(x)$. [In other words, $\{x_n\}$ are *IIDs* (independent identically distributed).] Show that, irrespective of the form of $p(x)$, there is a very simple expression for the probability P_n that the entry x_n is a record.

• Consider the n–entries $\{x_1, x_2, \cdots, x_n\}$. Each one of them has the same probability to be the largest one. Thus the probability that x_n is the largest, and hence a record, is $P_n = 1/n$.

(b) The records are entered in the *Guinness Book of Records.* What is the average number $\langle S_N \rangle$ of records after N attempts, and how does it grow for $N \gg 1$? If the number of trials, e.g. the number of participants in a sporting event, doubles every year, how does the number of entries asymptotically grow with time.

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$$\langle S_N \rangle = \sum_{n=1}^{N} P_n = \sum_{n=1}^{N} \frac{1}{n} \approx \ln N + \gamma + \mathcal{O}\left(\frac{1}{N}\right) \quad \text{for} \quad N \gg 1,$$

where $\gamma \approx 0.5772\ldots$ is the Euler number. Clearly if $N \propto 2^t$, where t is the number of years,

$$\langle S_t \rangle \approx \ln N(t) = t \ln 2.$$

(c) Prove that $\langle R_n R_m \rangle_c = 0$ for $m \neq n$. (The record indicators indicators $\{R_n\}$ are in fact *independent* random variables, though not identical, which is a stronger statement than the vanishing of the covariance.)

• $\langle R_n R_m \rangle = 1 \cdot P_n \cdot P_m$ while $\langle R_n \rangle = 1 \cdot P_n$, hence yielding,

$$\langle R_n R_m \rangle_c = P_n P_m - P_n \cdot P_m = 0.$$

This is by itself not sufficient to prove that the random variables R_n and R_m are independent variables. The correct proof is to show that the joint probability factorizes, i.e. $p(R_n, R_m) = p(R_n)p(R_m)$. Let us suppose that $m > n$, the probability that x_m is the largest of the random variables up to m is $1/m$, irrespective of whether some other random number in the set was itself a record (the largest of the random numbers up to n). The equality of the conditional and unconditional probabilities is a proof of independence.

(d) **(Optional)** Compute all moments, and the first three cumulants of the total number of records S_N after N entries. Does the central limit theorem apply to S_N?

• We want to compute $\langle e^{-ikS_N} \rangle$. This satisfies,

$$\langle e^{-ikS_N} \rangle = \frac{e^{-ik}}{N} \langle e^{-ikS_{N-1}} \rangle + \frac{N-1}{N} \langle e^{-ikS_{N-1}} \rangle = \frac{e^{-ik} + N - 1}{N} \langle e^{-ikS_{N-1}} \rangle,$$

since the probability for aquiring an additional phase $-ik$ is $P_N = 1/N$. Since $\langle e^{-ikS_1} \rangle = e^{-ik}$, by recursion we obtain,

$$\langle e^{-ikS_N} \rangle = \frac{1}{N!} \prod_{n=1}^{N} (e^{-ik} + n - 1) = \frac{1}{N!} \sum_{n=0}^{N} S_1(N, n) e^{-ikn},$$

where $S_1(n, m)$ denotes the unsigned Stirling number of the first kind. Expanding the exponent, we obtain,

$$\langle e^{-ikS_N} \rangle = \frac{1}{N!} \sum_{n=0}^{N} S_1(N, n) \sum_{m=0}^{\infty} \frac{n^m (-ik)^m}{m!} = \sum_{m=0}^{\infty} \frac{(-ik)^m}{m!} \left[\frac{1}{N!} \sum_{n=0}^{N} S_1(N, n) n^m \right].$$

Hence we obtain the mth moment,

$$\langle S_N^m \rangle = \frac{1}{N!} \sum_{n=0}^{N} S_1(N, n) n^m.$$

The first three cumulants can be obtained using the moments, but the easier way to obtain them is by using the fact that $S_N = R_1 + \cdots + R_N$ and that R_n are independent variables. Due to the independence of R_n,

$$\langle S_N^m \rangle_c = \sum_{n=1}^{N} \langle R_n^m \rangle_c .$$

From this, and the fact that for any m, $\langle R_n^m \rangle = 1/n$, we easily obtain,

$$\langle S_N \rangle_c = \sum_{n=1}^{N} \langle R_n \rangle_c = \sum_{n=1}^{N} \frac{1}{n},$$

$$\langle S_N^2 \rangle_c = \sum_{n=1}^{N} \langle R_n^2 \rangle_c = \sum_{n=1}^{N} (\frac{1}{n} - \frac{1}{n^2}),$$

$$\langle S_N^3 \rangle_c = \sum_{n=1}^{N} \langle R_n^3 \rangle_c = \sum_{n=1}^{N} (\frac{1}{n} - \frac{3}{n^2} + \frac{2}{n^3}).$$

The central limit theorem applies to S_N since R_n are independent variables. Seeing this in another way is to observe that for large N,

$$\langle S_N^m \rangle_c = \sum_{n=1}^{N} \langle R_n^m \rangle_c < \sum_{n=1}^{N} \langle R_n^m \rangle = \sum_{n=1}^{N} \frac{1}{n} \approx \ln N + \mathcal{O}\left(1\right).$$

Since the variance is of order $\ln N$, all the higher moments can be disregarded: if we define a new variable $\phi_N = S_N/\sqrt{\ln N}$, its mean grows as $\sqrt{\ln N}$, its variance is order of 1, while all higher order cumulants vanish as powers of $(\ln N)^{-1/2}$ as $N \to \infty$.

(e) **(Optional)** The first record, of course occurs for $n_1 = 1$. If the third record occurs at trial number $n_3 = 9$, what is the mean value $\langle n_2 \rangle$ for the position of the second record? What is the mean value $\langle n_4 \rangle$ for the position of the fourth record?

- The probability for $n_2 = n$ and $n_3 = 9$ is,

$$(1 - R_2) \cdots (1 - R_{n-1}) R_n (1 - R_{n+1}) \cdots (1 - R_8) R_9 = \frac{1}{72(n-1)}.$$

Hence $\langle n_2 \rangle_{n_3=9}$ can be obtained by,

$$\langle n_2 \rangle = \frac{\sum_{n_2=2}^{8} n_2 \cdot \frac{1}{72(n_2-1)}}{\sum_{n_2=2}^{8} \frac{1}{72(n_2-1)}} = \frac{1343}{363} \approx 3.70.$$

As for $\langle n_4 \rangle$, for given value of x_3, define, $P(x_3) = \int_{x_3}^{\infty} dx p(x)$. Then we get for a given value of x_3,

$$\langle n_4 \rangle_{x_3=a} = \sum_{n=10}^{\infty} n \cdot (1 - P(a))^{n-10} P(a) = \frac{9P(a)}{1-(1-P(a))} + \frac{P(a)}{(1-(1-P(a)))^2} = 9 + \frac{1}{P(a)}.$$

Hence we obtain $\langle n_4 \rangle$ by,

$$\langle n_4 \rangle = \frac{\int_{-\infty}^{\infty} dap(a)(9 + 1/P(a))}{\int_{-\infty}^{\infty} dap(a)} = \int_0^1 dP(9 + \frac{1}{P}) \to \infty,$$

where we used the fact that $p(a) = -dP(a)/da$.

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6. *Jarzynski equality:* In equilibrium at a temperature T, the probability that a macroscopic system is in a microstate μ is $p(\mu) = \exp\left[-\beta\mathcal{H}(\mu)\right]/Z$, where $\mathcal{H}(\mu)$ is the energy of the microstate, $\beta = 1/(k_B T)$, and the normalization factor is related to the free energy by $-\beta F = \ln Z$. We now change the macroscopic state of the system by performing external work W, such that the new state is also in equilibrium at temperature T. For example, imagine that the volume of a gas in changed by moving a piston as $L(t) = L_1 + (L_2 - L_1)t/\tau$. Depending on the protocol (e.g. the speed $u = (L_2 - L_1)/\tau$), the process may be close to or far from reversible. Nonetheless, the Jarzynski equality relates the probability distribution for the work W to the *equilibrium* change in free energy!

(a) Assume that the process by which work is performed is fully deterministic, in the sense that for a given protocol, any initial microstate μ will evolve to a specific final microstate μ'. The amount of work performed $W(\mu)$ will vary with the initial microstate, and there is thus a probability distribution $p_f(W)$ which can be related to the equilibrium $p(\mu)$. The energy of the final microstate, however, is precisely $\mathcal{H}'(\mu') = \mathcal{H}(\mu) + W(\mu)$. Time reversal symmetry implies that if we now instantaneously reverse all the momenta, and proceed according to the reversed protocol, the time-reversed microstate $\overline{\mu'}$ will deterministically evolve back to microstate μ, and the work $-W(\mu)$ is recovered. However, rather than doing so, we first allow the system to equilibrate into its new macrostate at temperature T, before reversing the protocol to recover the work. The recovered work $-W$ will now be a function of the selected microstate, and distributed according to a different probability $p_b(-W)$, related to $p'(\mu') = \exp\left[-\beta\mathcal{H}'(\mu')\right]/Z'$. It is in general not possible to find $p_f(W)$

or $p_b(-W)$. However, by noting that the probabilities of a pair of time-reversed microstates are exactly equal, show that their ratio is given by

$$\frac{p_f(W)}{p_b(-W)} = \exp\left[\beta(W + F - F')\right].$$

While you were guided to prove the above result with specific assumptions, it is in fact more generally valid, and known as the *work–fluctuation theorem.*

- $p_f(W)$ can be defined such that,

$$p_f(W)dW = \sum_{W(\mu)=W} p(\mu)d\mu.$$

Also,

$$p_b(-W)dW = \sum_{W'(\mu')=-W} p'(\mu')d\mu'.$$

We used $W(\mu)$ to denote the work done on the microstate μ in the forward process, and $W'(\mu')$ to denote the work done on the microstate μ' in the backward process. Note that there is a one to one correspondence between initial microstates μ such that $W(\mu) = W$ and final microstates μ' with $W'(\mu') = -W$, since each μ is mapped to a μ' by a given protocol. Also, since the density of microstates do not change by thermodynamic processes, it is safe to say that at a given microstate μ, $d\mu = d\mu'$. Hence we may write,

$$p_b(-W)dW = \sum_{W'(\mu')=-W} p'(\mu')d\mu' = \sum_{W(\mu)=W} p'(\mu'(\mu))d\mu.$$

Therefore,

$$\frac{p_f(W)}{p_b(-W)} = \frac{\sum_{W(\mu)=W} p(\mu)d\mu}{\sum_{W(\mu)=W} p'(\mu'(\mu))d\mu}.$$

Now since for each μ,

$$\frac{p(\mu)d\mu}{p'(\mu'(\mu))d\mu} = \frac{Z'}{Z}\exp(-\beta(\mathcal{H}(\mu) - \mathcal{H}'(\mu'))) = \exp(\beta(W + F - F')),$$

we finally obtain,

$$\frac{p_f(W)}{p_b(-W)} = \exp(\beta(W + F - F')).$$

(b) Prove the *Jarzynski equality*

$$\Delta F \equiv F' - F = -k_B T \ln \left\langle \mathrm{e}^{-\beta W} \right\rangle \equiv -k_B T \ln \left[\int dW p_f(W) \mathrm{e}^{-\beta W} \right].$$

This result can in principle be used to compute equilibrium free energy differences from an ensemble of non-equilibrium measurements of the work. For example, in *Liphardt, et. al., Science* **296**, *1832 (2002),* the work needed to stretch a single RNA molecule was calculated and related to the free energy change. However, the number of trials must be large enough to ensure that the averaged exponential, which is dominated by rare events, is accurately obtained.

• From the previous problem,

$$p_f(W)e^{-\beta W} = p_b(-W)e^{\beta(F-F')} = p_b(-W)e^{-\beta\Delta F}.$$

Integrating both sides with respect to W, and using $\int dW p_b(-W) = 1$ we get,

$$\langle e^{-\beta W} \rangle = e^{-\beta\Delta F}.$$

Taking the logarithm of both sides and sorting out the terms we get,

$$\Delta F = -k_B T \ln\langle e^{-\beta W} \rangle.$$

(c) Use the Jarzynski equality to prove the familiar thermodynamic inequality

$$\langle W \rangle \geq \Delta F \qquad .$$

• Since $\exp(-\beta W)$ is a convex function of W, for any distribution $p(W)$ with $p(W) \geq 0$ and $\int dW p(W) = 1$,

$$\langle e^{-\beta W} \rangle = \int dW p(W) \exp(-\beta W) \geq \exp(-\beta \int dW p(W) W) = e^{-\beta\langle W \rangle}.$$

Hence we obtain,

$$\Delta F = -\frac{1}{\beta} \ln\langle e^{-\beta W} \rangle \leq -\frac{1}{\beta} \ln e^{-\beta\langle W \rangle} = \langle W \rangle.$$

(d) Consider a cycle in which a work $W-\omega$ is performed in the first stage, and work $-W$ is returned in the reversed process. According to the second law of thermodynamics, the net gain ω must be positive. However, within statistical physics, it is always possible that this condition is violated. Use the above results to conclude that the probability of violating the second law decays with the degree of violation according to

$$P_{\text{violating second law}}(\omega>0)\le \mathrm{e}^{-\beta\omega}.$$

• Let us define $\overline{p}(\omega)$ as the *probability density* to violate the second law by $\omega>0$. Since the same ω can be obtained for different choices of W, we have

$$\overline{p}(\omega)=\int dW p_f(W-\omega)p_b(-W).$$

By the relation obtained in (a), we get,

$$\frac{p_f(W-\omega)p_b(-W)}{p_b(-W+\omega)p_f(W)}=\frac{\exp(\beta(W-\omega+F-F'))}{\exp(\beta(W+F-F'))},$$

which yields,

$$p_f(W-\omega)p_b(-W)=p_b(-W+\omega)p_f(W)\exp(-\beta\omega),$$

hence,

$$\overline{p}(\omega)=\int dW p_b(-W+\omega)p_f(W)\exp(-\beta\omega)=\overline{p}(-\omega)\exp(-\beta\omega).$$

The cumulative probability of violating the second law by ω *or more* is now obtained as

$$P(\omega)=\int_\omega^\infty \omega'\overline{p}(\omega')=\int_\omega^\infty \omega'\overline{p}(-\omega')\exp(-\beta\omega')<\exp(-\beta\omega)\int_\omega^\infty \omega'\overline{p}(-\omega')<\exp(-\beta\omega).$$

The first inequality is because for all ω' in the integrand, $\exp(-\beta\omega')<\exp(-\beta\omega)$, and the second since any cumulative probability is less than one.

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7. *Dice:* **(Optional)** A dice is loaded such that 6 occurs twice as often as 1.

(a) Calculate the unbiased probabilities for the 6 faces of the dice.

• We want to find p_i that maximizes, $S=-\sum p_i\ln p_i$ with the constraints, $p_6=2p_1$ and $\sum p_i=1$. Since for a fixed sum, $\sum p_i=1-3p_1$, $-\sum_{i=2,\cdots,5}p_i\ln p_i$ is maximized by $p_2=p_3=p_4=p_5$, our problem reduces to maximizing,

$$S(p_1)=-p_1\ln p_1-2p_1\ln 2p_1-(1-3p_1)\ln\frac{1-3p_1}{4}.$$

Differentiating this with respect to p_1, we get,

$$\frac{dS}{dp_1} = 3\ln\left(\frac{1-3p_1}{2^{8/3}p_1}\right).$$

Note that this has only one zero and its sign changes from + to − at that zero. The maximum value of S is obtained for at that zero which is,

$$p_1 = \frac{1}{2^{8/3}+3}.$$

Hence we obtain,

$$p_1 = \frac{1}{2^{8/3}+3}, \quad p_2 = p_3 = p_4 = p_5 = \frac{1-3p_1}{4} = \frac{2^{2/3}}{2^{8/3}+3}, \quad p_6 = 2p_1 = \frac{2}{2^{8/3}+3}.$$

(b) What is the information content (in bits) of the above statement regarding the dice?

• By definitiion of the information content,

$$I = \ln_2 6 + \sum_{i=1}^{6} p_i \ln_2 p_i = \ln_2 6 + \ln_2 \frac{2^{2/3}}{3+2^{8/3}} = \frac{5}{3} + \ln_2 \frac{3}{3+2^{8/3}},$$

which is about 0.03 bits.

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8. (Optional) *Approach to equilibrium:* For a dynamical system described by parameters $\mathbf{x} = \{x_i\}$, we can define time dependent correlation functions $C_{ij}(t) = \langle x_i(t)x_j(0)\rangle$.

(a) Show that time translational invariance ($C(t) = C(t+\tau)$), combined with time reversal symmetry ($C(t) = C(-t)$)– both characteristics of equilibrium– implies $C_{ij}(t) = C_{ji}(t)$.

• By time translation through $\tau = -t$, we obtain $C_{ij}(t) = \langle x_i(t)x_j(0)\rangle = \langle x_i(t-t)x_j(0-t)\rangle$, and then by time reversal $\langle x_i(0)x_j(-t)\rangle = \langle x_i(0)x_j(t)\rangle = \langle x_j(t)x_i(0)\rangle = C_{ji}(t)$.

(b) If the equilibrium weight for small fluctuations is Gaussian distributed, with density function

$$c = \sqrt{\frac{\det[K]}{(2\pi)^n}} \exp\left[-\frac{1}{2}\sum_{mn} K_{ij}x_ix_j\right] \quad ,$$

relate $C_{ij}(0)$ to the (positive definite) matrix $[K]$.

• The Gaussian average is related to the inverse matrix by $\langle x_ix_j\rangle = (K^{-1})_{ij}$. Since equilibrium corresponds to equal time average, $C_{ij}(0) = \langle x_ix_j\rangle = (K^{-1})_{ij}$.

(c) Conjugate variables (forces) are defined by $J_\alpha = -\frac{\partial \ln p(\mathbf{x})}{\partial x_\alpha}$. Show that $\langle J_\alpha x_\beta \rangle = \delta_{\alpha\beta}$.

• From the Gaussian form of $p(\mathbf{x})$, it is easy to obtain

$$J_\alpha = -\frac{\partial \ln p(\mathbf{x})}{\partial x_\alpha} = K_{\alpha\gamma} x_\gamma \,,$$

and hence

$$\langle J_\alpha x_\beta \rangle = K_{\alpha\gamma} \langle x_\gamma x_\beta \rangle = K_{\alpha\gamma} (K^{-1})_{\gamma\beta} = \delta_{\alpha\beta} \,.$$

(d) In a generalized form of gradient descent, relaxation to equilibrium follows $\dot{x}_i = -\mu_{i\alpha} J_\alpha = -\mu_{i\alpha} K_{\alpha\beta} x_\beta$, where $\{\mu_{ab}\}$ are *kinetic coefficients*. By considering $\dot{C}_{ij}(t=0)$ show that the matrix μ must be symmetric. (This is an example of an Onsager relation).

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$$\dot{C}_{ij}(t) = \langle \dot{x}_i(t) x_j(0) \rangle = -\mu_{i\alpha} \langle J_\alpha(t) x_j(0) \rangle \,.$$

At $t = 0$, the above expectation value is the equal time average, which according to the earlier result gives

$$\dot{C}_{ij}(t=0) = -\mu_{i\alpha} \langle J_\alpha(0) x_j(0) \rangle = -\mu_{i\alpha} \delta_{\alpha j} = -\mu_{ij} \,.$$

Similar manipulations lead to $\dot{C}_{ji}(t=0) = -\mu_{ji}$, and since $C_{ij}(t) = C_{ji}(t)$, $-\mu_{ij} = -\mu_{ji}$, and the matrix μ must be symmetric to be consistent with time reversal in equilibrium.

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9. (Optional) *Simpson's paradox:* A recent study of COVID-19 case fatality rates (cfrs) notes a seemingly strange result:[‡] comparing a large-scale study from China with reports from Italy, it finds that cfrs are lower in Italy for every age group, but higher overall. The following examples demonstrate how this can happen.

(a) Let's divide the population of two countries (A and B) into two age classes, say young (y) and old (o). The probabilities of covid fatality for both age demographics are higher for country A, and arranged according to $p_o^A > p_o^B > p_y^A > p_y^B$. Show that the country A as a whole can still end up with lower cfrs if its population is older.

• Just consider the extreme limit in which country B is entirely composed of elderly, while country A has only the young. Since $p_o^B > p_y^A$, cfrs is larger in B.

[‡] J. von Kugelgen, L. Gresele, Max and B. Scholkopf, IEEE Transactions on Artificial Intelligence **2**, 18-27 (2021); DOI: 10.1109/TAI.2021.3073088.

(b) Use the same principle to construct a fake demonstration of violation of the second law of thermodynamics as follows. An equal number of Carnot and non-Carnot engines are paired together; each pair operating with the same input/output sources (possibly different from other pairs). The same quantity of heat Q is separately distributed amongst the Carnot engines, and also amongst the non-Carnot engines. It is found that the net work produced by the non-Carnot engines is larger than that produced by the Carnot engines. How is this possible?

• Some of the engine pairs operate between temperatures allowing for higher efficiency than others. For example, with two input/output temperatures, we could arrange for $\eta_C^{(1)} > \eta_{NC}^{(1)} > \eta_C^{(2)} > \eta_{NC}^{(2)}$ analogous to the probabilities in the previous part.

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