The Jarzynski equality in action: a pedagogical example

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A. Introduction

The Jarzynski equality [1] has become an important tool for measuring the free energies of nana-scale systems. For understanding the derivation of the equality, it may be helpful to have a transparent example that illustrates how it works. To that end, this note carries out the derivation for a simple Hamiltonian. The Hamiltonian describes a particle at position x and momentum p in a harmonic oscillator well, coupled by another spring stretched to a movable point y :

$$H(x,p,y) = \frac{p^2}{2m} + \frac{1}{2}k_1 x^2 + \frac{1}{2}k_2(x-y)^2. \tag{1}$$

The free energy $F(y,\beta)$ of the system is given by

$$e^{-\beta F} = \int dx\, dp\, \rho_c(x,p,y,\beta) \tag{2}$$

where

$$\rho_c = e^{-\beta H(x,p,y)} \tag{3}$$

is the canonical statistical phase-space density at temperature $T = 1/\beta$. I will use the symbol ρ_c for canonical densities and a plain ρ for densities defined differently.

The integrals are trivial to evaluate the free energy for Eq. (1). The result is

$$e^{-\beta F} = \frac{2\pi}{\beta}\sqrt{\frac{m}{k_1+k_2}} \exp\left(-\beta \frac{k_1 k_2}{k_1+k_2}\frac{y^2}{2}\right). \tag{4}$$

B. Stretching the spring

Now let us change the state of the system by increasing y. I assume that y depends linearly on time,

$$y(t) = at \tag{5}$$

The resulting time-dependent Hamiltonian equation of motion can be solved exactly. The phase-space coordinates evolve in time according to

$$x(t) = x_m \sin(\omega t + \phi) + \frac{k_2}{k_1+k_2} at \tag{6}$$

and

$$p(t) = m\omega\, x_m cos(\omega t + \phi) + \frac{k_2}{k_1+k_2} a \tag{7}$$

where $\omega = \sqrt{(k_1+k_2)/m}$. The amplitude x_m and the phase ϕ are determined by the initial conditions $x(0), p(0)$,

$$x(0) = x_m \sin(\phi) \tag{8}$$

$$p(0) = x_m m\,\omega \cos(\phi) - \frac{k_2}{k_1+k_2} a \tag{9}$$

I now assume that the second spring is stretched to a length y_0 in a time $\tau = y_0/a$. At the end of the stretch the coordinates are

$$x(\tau) = x_m \sin(\omega\tau + \phi) - \frac{k_2}{k_1+k_2} y_0 \tag{10}$$

$$p(\tau) = x_m m\,\omega \cos(\omega\tau + \phi) - \frac{k_2}{k_1+k_2}\frac{y_0}{\tau}. \tag{11}$$

Now we ask, what happens to the phase-space density under this transformation? The answer is very simple: by Liouville's theorem the density remains constant, ie.

$$\rho(x,p,y_0) = \rho_c(x',p',0,\beta) = e^{-\beta H(x',p',0)} \tag{12}$$

where $x,p = x(\tau),p(\tau)$ and $x',p' = x(0),p(0)$ in Eqs. (6,7). This differs from the canonical density at $t=\tau$, given by $\exp(-H(x,p,y_0)\beta))$. We can construct the canonical density at $t=\tau$ by correcting the exponent:

$$\rho_c(x,p,y_0,\beta) = e^{-\beta\Delta E}\rho_c(x',p',0,\beta) \tag{13}$$

where ΔE is the difference in energies of the system initially at x',p' and finally at x,p,

$$\Delta E = H(x,p,y_0) - H(x',p',0). \tag{14}$$

Now a crucial observation: the energy difference can be computed as the work W done by stretching the second spring from $y=0$ to y_0. The work is calculated by integrating the force in the second spring with respect to y. This is carried out as follows.

$$W = \int_0^\tau dt\; k_2\,(y(t) - x(t))\,\frac{dy}{dt} \tag{15}$$
$$= k_2 a \frac{x_m}{\omega}\left(\cos(\omega\tau+\phi) - \cos(\phi)\right) + \frac{a^2 k_1 k_2}{2(k_1+k_2)}\tau^2$$

The result can be shown by straightforward algebra to be equal to the energy difference calculated from Eq. (14). It could hardly come out otherwise. Anyway, The result is Jarzynski's relation,

$$e^{-\beta F(y_0,\beta)} = \int dx dp\, e^{-\beta W}\rho_c(x,p,0,\beta). \tag{16}$$

To apply the equation, one samples the canonical ensemble at $y = 0$, weighing each sample by the work done to stretch the second spring.

[1] C. Jarzynski, Phys. Rev. Lett. **78 2690 (1997).**