

Jarzynski's equality illustrated by simple examples

Humberto Híjar¹ and José M Ortiz de Zárate²

¹ Facultad de Ciencias, Universidad Nacional Autónoma de México, México DF, Mexico

² Departamento de Física Aplicada I, Universidad Complutense, Madrid, Spain

E-mail: jmortizz@fis.ucm.es

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Abstract

The Jarzynski theorem is perhaps the most recently discovered simple general formula in elementary statistical physics. In this paper, written with a pedagogical aim, we illustrate the physical concepts under the Jarzynski and related results by a detailed calculation with a representative example. The physics of the model is sufficiently transparent so that it becomes suitable to incorporate in a general course of statistical physics.

1. Introduction

The Jarzynski theorem is perhaps the most recently discovered simple general formula in elementary statistical physics [1]. In its most common expression it is formulated as

$$\langle e^{-W/k_B T} \rangle = e^{-\Delta F/k_B T}. \quad (1)$$

Equality (1) refers to two different equilibrium thermodynamic states of an arbitrary system which we refer to as the initial and the final state. These two states must have the same temperature T , but differ in some other thermodynamic variable so that there is a difference in the Helmholtz free energy ΔF between them. For instance, in a regular fluid system, the variable distinguishing the two states can be the volume V . From a microscopic point of view, the variable discriminating between the two states enters as an external parameter in the Hamiltonian of the system. It is known from elementary thermodynamics that when the system is driven from the initial to the final state by a *reversible* process, a work W is performed so that $W = -\Delta F$ (isothermal process). If, in contrast, the process connecting initial and final states is *irreversible*, the work W differs in general from the free-energy difference. Of course, there are many irreversible processes (potentially infinity) connecting the initial and the final states (only one isothermal reversible, though), and in each of these processes the work performed will be different. Therefore, one can treat the ensemble of possible processes

statistically. As discussed in elementary thermodynamics treatises, by virtue of the second law, the average work must verify

$$\langle W \rangle \geq \Delta F. \quad (2)$$

Actually, in thermodynamics books, equation (2) is written without the brackets implying that it must hold for *all* processes. We know, however, that the second law is of statistical nature so that there can be exceptions (very infrequently) and interpreting equation (2) statistically is more rigorous. Indeed, one of the virtues of the Jarzynski equality is that it gives meaning to the average in equation (2). As we hope to illustrate in this paper, Jarzynski teaches us how to consistently perform these kind of averages, opening up the possibility of doing statistical physics not only of states but also of *processes*.

Now we are in a position to understand the physical significance of equation (1). In accordance with the second law of thermodynamics, the work performed in an irreversible process connecting two isothermal equilibrium states (temperature T) of an arbitrary system satisfies inequality (2). However, it can be rigorously demonstrated that the average ($e^{-W/k_B T}$) satisfies equation (1), which is an equality. A rigorous formal derivation can be found in the original papers [1, 2]. Here, our goal is to show Jarzynski's theorem in action through a simple example. We note here that due to the well-defined concavity of the exponential function, equation (1) implies equation (2).

Many theoretical developments based on the Jarzynski equality have appeared during the last decade. Many of them represent equivalent formulations adopting different perspectives. Most noted is the so-called Crooks theorem [3], usually formulated as

$$\frac{P_F(W)}{P_B(-W)} = \exp[(W - \Delta F)/k_B T], \quad (3)$$

where the left-hand side is the ratio of the probability of work W when going from the initial to the final state (forward probability) to the probability of work $-W$ when going from the final to the initial state (backward probability). The equivalence of the Jarzynski and Crooks formulations can be readily demonstrated [3]. Among other theoretical developments we mention extensions to cover the Langevin dynamics, when the system is in equilibrium with a thermal bath [4]. Also equation (1) has been used to formulate nonequilibrium entropies that could be related to extrema principles [5]. As we discuss later, Jarzynski's original result is based on a canonical ensemble; especially interesting is the not so trivial extension to microcanonical ensembles that might be relevant to adiabatic processes [6]. All this and the related work has generated in the last 10 years a new sub-field inside nonequilibrium statistical physics that is usually referred to as *nonequilibrium work theorems*.

Jarzynski's and related nonequilibrium work theorems are not only theoretically interesting, because they have found many practical applications in research. Originally, Jarzynski proposed his result as a simple and computationally advantageous way of calculating free energies in molecular simulations, and indeed it was successfully employed with this aim [7]. More recently, for instance, nonequilibrium work theorems have been used to computationally estimate free energy differences in a solution of charged particles in water [8], or the surface tension of magnetic domains in the Ising model [9]. Another important field where equation (1) has successfully been used is single-molecule experiments. This application was originally done by Liphardt *et al* [10], who used equation (1) to experimentally estimate the free-energy difference between the open and the close state of an RNA hairpin. Subsequently, it has been used to interpret similar experiments [11].

We should mention that the Jarzynski result has faced some criticism in the scientific literature [12]. Most criticisms were not about the detailed kind of calculations we will present here, but about the definition and interpretation of work based on thermodynamics

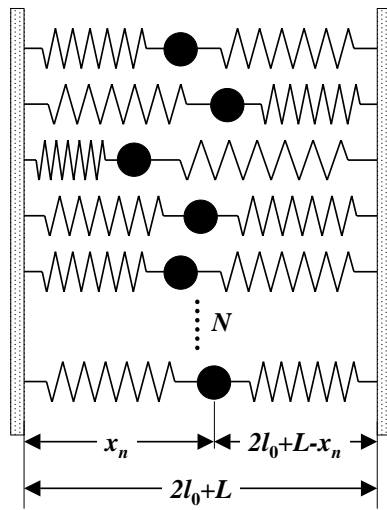


Figure 1. Schematic representation of the system under consideration in section 2. There are N particles of mass m connected by harmonic springs to two bounding walls. All springs are identical, with the constant k and equilibrium length l_0 .

grounds. The objections raised appear to be rebutted in our opinion [13]. We will comment more on these issues of thermodynamic work and heat at the end of the paper, but a complete understanding of nonequilibrium work theorems may still require some more scientific debate.

We now stop commenting on Jarzynski's and related results because our purpose here is not a systematic review. The goal of this paper is to illustrate the Jarzynski and Crooks fluctuation theorems by detailed calculations using simple representative examples. Of course, the Jarzynski and Crooks theorems are exact and hold for any system. The interest of performing a detailed calculation is purely pedagogical. In the example that we examine in detail here, the (irreversible) work probability distribution can be readily calculated analytically. Most importantly, in our example the central physical insight behind these results is clearly shown, namely that in an isothermal process starting at an equilibrium state the work performed depends on the initial phase space position of the system within the corresponding canonical distribution. Furthermore, our example here is based on one of the typical model systems often used to teach the introductory courses of statistical physics, being sufficiently transparent to incorporate in one of these elementary courses, effortlessly exposing the students to cutting-edge research.

2. Two plates joined by springs

Let us consider a system of N identical particles of mass m which are joined to two parallel plates by a set of $2N$ springs. The setup under consideration is shown schematically in figure 1. All the springs are equal, with the constant k and equilibrium length l_0 , and the corresponding potentials are assumed to be harmonic.

The Hamiltonian of the mechanical system depicted in figure 1 is readily expressed as

$$H(p_n, q_n) = \sum_{n=1}^N \frac{p_n^2}{2m} + \frac{m\omega^2}{2} [(x_n - l_0)^2 + (x_n - L - l_0)^2], \quad (4)$$

where $\omega^2 = k/m$ is the frequency corresponding to the set of $2N$ identical springs and $2l_0 + L$ is the distance between the bounding plates. The position of the n particle is measured by its distance x_n to the left plane, p_n being the corresponding momentum. We note in equation (4) the dependence of the Hamiltonian on the extensive parameter L ; Jarzynski's equality refers to the changes in the free energy of the system when L is varied. From Hamiltonian (4) the equations of motion of the individual particles follow:

$$m \frac{d^2 x_n}{dt^2} = -2k(x_n - l_0) + kL. \quad (5)$$

If the system is in equilibrium at temperature T , the free energy of the system $F(L, T)$ can be easily obtained from a canonical distribution, since all integrals are Gaussian. It results in

$$F(L, T) = -Nk_B T \left[\ln \left(\frac{k_B T}{\sqrt{2}\hbar\omega} \right) - \frac{m\omega^2 L^2}{4k_B T} \right], \quad (6)$$

where k_B is the Boltzmann constant. In equations (4)–(6) it is implicitly assumed that the particles move in one dimension and can occupy any position $x_n \in \{-\infty, +\infty\}$. The model can be complicated by introducing, for instance, impervious walls or more spatial dimensions. Any complication introduced into the model does not affect the validity of Jarzynski's result, so for the illustration goals intended here it is preferable to keep the model (and the calculations) as simple as possible. All the thermodynamics of the system can be deduced from equation (6), which gives the Helmholtz free energy in terms of its natural variables. In particular, the free-energy difference between a final state with $L = L_1$ and an initial state with $L = L_0$, appearing on the right-hand side of Jarzynski's equality (1), will be given by

$$\Delta F = N \frac{m\omega^2}{4} (L_1^2 - L_0^2). \quad (7)$$

To verify Jarzynski's theorem for our system we can imagine that at $t = 0$ the right wall starts to move with a uniform velocity V , so that $L(t) = (L_0 + Vt)\theta(t)$, where $\theta(t)$ is a step function. By substituting $L(t)$ into the equations of motion, equation (5), it is relatively easy to obtain the general solution of the corresponding differential equation, namely

$$x_n(t) = A_{n,0} \cos(\sqrt{2}\omega t + \theta_{n,0}) + l_0 + \frac{1}{2}(L_0 + Vt), \quad \text{for } t > 0. \quad (8)$$

The integration constants $A_{n,0}$ and $\theta_{n,0}$ are related to the position and linear momentum of the n -particle at $t = 0$. Let us consider next the energy of the n -particle for $t > 0$, which will be given by

$$E_n(t) = \frac{1}{2}m[\dot{x}_n(t)]^2 + \frac{1}{2}k[x_n(t) - l_0]^2 + \frac{1}{2}k[x_n(t) - l_0 - L(t)]^2. \quad (9)$$

The work W_n required to move the n -particle from its position at $t = 0$ to its position at time t will be given by the difference between the corresponding energies. Some simple algebra allows us to express it as

$$W_n = E_n(t) - E_n(0) = \phi(t) - p_0 \frac{V}{2} (1 - \cos \sqrt{2}\omega t) - \left(x_0 - l_0 - \frac{1}{2}L_0 \right) \frac{m\omega V}{\sqrt{2}} \sin \sqrt{2}\omega t, \quad (10)$$

where p_0 and x_0 are the linear momentum and the position of the n -particle at $t = 0$, respectively. The function $\phi(t)$ in equation (10) is given by

$$\begin{aligned} \phi(t) &= \frac{mV^2}{4} \left[1 + \omega^2 t \left(t + \frac{2L_0}{V} \right) - \cos \sqrt{2}\omega t \right], \\ &= \frac{m\omega^2}{4} \left[L_1^2 - L_0^2 + \frac{V^2}{\omega^2} (1 - \cos \sqrt{2}\omega t) \right], \end{aligned} \quad (11)$$

where $L_1 = L_0 + Vt$ is the position reached by the right wall after a time t has elapsed. The total work W required to move the left wall to its location at time t will be obtained by adding all the contributions of the individual particles $W = \sum_n W_n$. As is well known, the initial positions and velocities of the particles at a given temperature are the stochastic variables, with the probability distribution given by the canonical ensemble. Consequently, the work required to move the left wall will be a stochastic variable also. The probability distribution $P(W)$ of the stochastic variable W can be easily calculated by averaging over initial positions and velocities of the particles, namely

$$P_F(W) = \left\langle \delta \left(W - \sum_{n=1}^N W_n \right) \right\rangle = \int_{-\infty}^{\infty} \frac{dq}{2\pi} \exp[iqW] \langle \exp[-iqW_n] \rangle^N, \quad (12)$$

where we represented the delta function as an integral, and used the fact that the system under consideration is ideal, so that averages are the same for any particle. For later use, we have introduced the subindex 'F' to denote the *forward* work probability distribution.

The average contained in equation (12) can be exactly calculated for the simple dynamics under consideration here, since all integrals are Gaussian. Indeed, using equation (10) and the canonical ensemble with Hamiltonian (4) evaluated at $L = L_0$, one obtains

$$\begin{aligned} \langle \exp[-iqW_n] \rangle &= \frac{\beta\omega}{\sqrt{2\pi}} e^{\frac{1}{4}\beta m\omega^2 L_0^2} e^{-iq\phi} \int_{-\infty}^{\infty} dp_0 \exp \left[-\frac{\beta p_0^2}{2m} + iq \frac{V}{2} p_0 (1 - \cos(\sqrt{2}\omega t)) \right] \\ &\quad \times \int_{-\infty}^{\infty} dx_0 \exp \left[-\frac{\beta m\omega^2}{2} (x_0 - l_0)^2 - \frac{\beta m\omega^2}{2} (x_0 - l_0 - L_0)^2 \right. \\ &\quad \left. + iq \frac{m\omega V}{\sqrt{2}} \left(x_0 - l_0 - \frac{L_0}{2} \right) \sin(\sqrt{2}\omega t) \right] \\ &= \exp \left[-iq\phi - q^2 \frac{mV^2}{4\beta} (1 - \cos \sqrt{2}\omega t) \right], \end{aligned} \quad (13)$$

where, as usual, $\beta = 1/k_B T$. Next, substituting into equation (12), one obtains a Gaussian probability distribution for the work performed when the right plate moves, namely

$$P_F(W) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{(W - N\phi)^2}{2\sigma^2} \right], \quad (14)$$

where the variance σ is given by

$$\sigma = \sqrt{N} \left[\frac{mV^2(1 - \cos \sqrt{2}\omega t)}{2\beta} \right]^{1/2}. \quad (15)$$

We note that the variance of the probability distribution $P_F(W)$ vanishes for times multiples of $\pi/\sqrt{2}\omega$. This strange feature is a consequence of the simplicity of our noninteracting model, and is also present in other ideal systems [14]. For systems with interaction this oscillatory behaviour in the moments of the work probability distribution is not present [15]. This feature will be discussed in more detail in section 3, where a slightly interacting variation of the current model will be considered.

Now we are in a position to readily verify Jarzynski's equality, namely

$$\langle e^{-\beta W} \rangle = \exp \left[\frac{\beta}{2} (\beta\sigma^2 - 2N\phi) \right] = \exp \left[-\frac{\beta}{4} Nm\omega^2 [L_1^2 - L_0^2] \right] = e^{-\beta\Delta F}, \quad (16)$$

where the difference between free energies is to be calculated from equation (6) by taking $L = L_0$ as the initial state and $L = L_1$ as the final state.

To verify the Crooks theorem, we have to study the process inverse to the one considered so far. This means that the left wall is initially at a position $x_W = L_1$ and moves with a uniform velocity $-V$, so that after some elapsed time t it reaches the position $x_W = L_0$. The solution of the equation of motion continues to be represented by (8) with the exchanges L_0 by L_1 and V by $-V$. With the same exchanges, equation (10) continues to represent the work required to move the n -particle backwards. Furthermore, since the average performed in equation (13) does not depend on the L_0 value, the probability distribution of work performed in the backward process will also be Gaussian, with the same variance σ as the forward process, but where the mean value will now be given by ϕ' , defined as

$$\phi'(t) = \frac{m\omega^2}{4} \left[L_0^2 - L_1^2 + \frac{V^2}{\omega^2} (1 - \cos \sqrt{2}\omega t) \right]. \quad (17)$$

Consequently, the Crooks theorem immediately follows

$$\begin{aligned} \frac{P_F(W)}{P_B(-W)} &= \frac{\exp\left[-\frac{(W-N\phi)^2}{2\sigma^2}\right]}{\exp\left[-\frac{(W+N\phi')^2}{2\sigma^2}\right]} = \exp\left[\beta\left(W - N\frac{m\omega^2}{4}(L_1^2 - L_0^2)\right)\right] \\ &= \exp[\beta(W - \Delta F)]. \end{aligned} \quad (18)$$

From our expression (14) for $P_F(W)$ it readily follows $\langle W \rangle = N\phi$. This result, in view of equation (11), agrees with the thermodynamic result (2), as expected.

To finalize this section, we discuss the quasi-static reversible limit, that is when the velocity V is very small. In that case the variance σ of the Gaussian probability work distribution (14) goes to zero. Consequently, the work distribution approaches a delta function

$$P_F(W) = \delta\left(W - N\frac{m\omega^2}{4}(L_1^2 - L_0^2)\right), \quad (19)$$

independent of the temperature. Of course this is the result expected on thermodynamic grounds. For a reversible (infinitely slow) isothermal process the work performed is equal to the free-energies difference, equation (7).

3. A slightly interacting model

We can introduce a little interaction in our model of harmonic oscillators, while maintaining it analytically tractable, by considering the system depicted in figure 2. The difference with the system of the previous section is that the two parallel plates are joined now by a chain of *two* particles. As before, they are connected by springs to the walls but now there exists a third spring connecting the two particles of a given pair. To have the same overall number of particles as in section 2, we assume that there are in this case $N/2$ pairs of particles joining the two planes. Furthermore, to facilitate the comparison with the results of the previous section, we assume in this section that the mass of the particles is $m' = (2/9)\sqrt{3}m$, and that the natural frequency of the springs is $\omega' = (3^{1/4}/\sqrt{2})\omega$.

The Hamiltonian of the system is now given by

$$H(p_n, q_n) = \sum_{n=1}^{N/2} \frac{p_{n1}^2}{2m'} + \frac{p_{n2}^2}{2m'} + \frac{m\omega^2}{6} [(x_{n1} - l_0)^2 + (x_{n2} - x_{n1} - l_0)^2 + (x_{n2} - L - 2l_0)^2], \quad (20)$$

where x_{n1} and x_{n2} are the positions of the first and the second particle of the n -pair measured with respect to the left wall, while p_{n1} and p_{n2} are the respective momenta. From Hamiltonian (20), the corresponding canonical partition function and free energy $F(L, T)$ can be readily

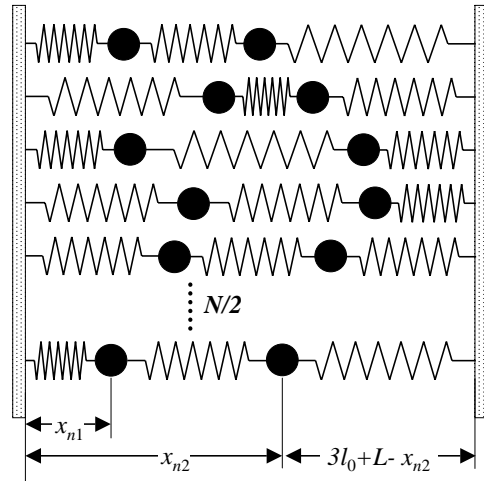


Figure 2. Schematic representation of the system under consideration in section 3. There are $N/2$ pairs of particles of mass m' connected by harmonic springs between them and to the two bounding walls. All springs are identical, with the constant k' and equilibrium length l_0 .

evaluated. Because of our choice for the ratio of masses m'/m and ratio of frequencies ω'/ω of the model of section 3 to the model of section 2, it turns out that the free energy corresponding to Hamiltonian (20) is exactly the same as the free energy corresponding to Hamiltonian (4), that was given by equation (6). Consequently, the free energy difference ΔF between two equilibrium states at the same temperature T and different values of L is still given by equation (7). Note that here, as in section 2, we continue to assume that particles move in one spatial dimension and can occupy any position $x_{n1}, x_{n2} \in \{-\infty, +\infty\}$. We note that this model is slightly more realistic than the simpler one considered before.

The equations of motion corresponding to Hamiltonian (20) are

$$\frac{d^2 x_{n1}}{dt^2} = -\frac{\sqrt{3}}{2} \omega^2 [(x_{n1} - l_0) - (x_{n2} - x_{n1} - l_0)], \quad (21)$$

$$\frac{d^2 x_{n2}}{dt^2} = -\frac{\sqrt{3}}{2} \omega^2 [(x_{n2} - x_{n1} - l_0) + (x_{n2} - 2l_0 - L)]. \quad (22)$$

These equations can be readily integrated for a linear wall protocol movement, i.e. when $L(t) = (L_0 + Vt)\theta(t)$, and positions and momenta at any time can be expressed in terms of the initial positions and momenta. Similar to equation (10) for the ideal model, the work W_n required to move a pair of particles from their initial state to the final state can be expressed as the corresponding energy difference. The explicit expression for W_n is obtained exactly and analytically from the solution of the equations of motion (21)–(22). This explicit expression is more complicated now than in the case of the simpler model of section 2, so we will not display it here. However we mention an important feature: as in equation (10) for the simpler ideal model, the work W_n depends linearly on the initial positions $x_{n1,0}, x_{n2,0}$ and momenta $p_{n1,0}, p_{n2,0}$.

The total work W required to move the right wall is expressed as a sum over pairs of W_n 's. Positions and momenta at the initial equilibrium state are the random variables distributed in accordance to a canonical ensemble. Hence, the total work W will also be an stochastic variable. The probability distribution of W can be computed in a fashion similar to

equation (12) for the simpler ideal model. Because W linearly depends on the initial position of momenta, the result turns out to be, again, a Gaussian distribution like in equation (14). However, for the slightly interacting model of this section, the mean ϕ' and the variance σ' differ from the previous results, namely

$$\phi' = \frac{\Delta F}{N} + \frac{m'}{36} V^2 [10 - 9 \cos(\omega't) - \cos(\sqrt{3}\omega't)] \quad (23)$$

$$\sigma' = \sqrt{N} \left\{ \frac{m' V^2}{18\beta} [10 - 9 \cos(\omega't) - \cos(\sqrt{3}\omega't)] \right\}^{1/2}. \quad (24)$$

Of course, the different values obtained for the mean and the variance of the Gaussian work distribution in the case of the slightly interacting model, do not affect the Jarzynski theorem, since

$$\frac{\beta}{2} [\beta(\sigma')^2 - 2N\phi'] = -\beta \Delta F, \quad (25)$$

see equation (16). A similar argument applies to the Crooks theorem or the limit of quasi-static process discussed at the end of section 2.

Regarding the time dependence of the variance, we observe that in this case σ' still features the oscillatory behaviour already encountered for the simpler ideal case in equation (15). However, when a little interaction is present, the variance is always positive for $t > 0$. We conclude, as anticipated after equation (15), that the strange vanishing of the variance found in section 2 is a consequence of the simplicity of the ideal model, and that when a slight interaction is added this feature disappears. Furthermore, if more interaction is added to the model (imagining, for instance, chains of more than two particles between the two rigid walls) the amplitude of the variance temporal oscillations is diminished. Eventually, for a realistic interaction, the periodic behaviour is irrelevant, and the variance becomes a monotonic function of time.

4. Concluding remarks

It is obvious in our examples that when the right wall starts to move, the system is driven outside of equilibrium. Note that in our developments it was implicitly assumed that while the wall is moving, the system is disconnected from the thermostat that initially kept the system in equilibrium at a temperature T . When the wall movement ends, the system is not in equilibrium, the thermostat has to be reconnected and some energy has to be exchanged between the system and the thermostat to regain equilibrium at the same initial temperature T . But the energy exchanged in this re-equilibration step does not modify our results, because from a thermodynamic point of view it has to be considered as heat, as long as the final position of the wall is not modified. This way of reasoning (disconnection from the heat reservoir, irreversible process and re-connection to the reservoir) is not uncommon in elementary thermodynamics. For instance, similar arguments are implicitly used when calculating the 'entropy of the universe' increase (or entropy production) in the irreversible expansions of a gas against a constant pressure p_0 and in contact with a reservoir. For a recent account of this sort of thermodynamics calculations see, for instance, section 2.1 of [16]. Of course, in real processes, actual disconnection from the heat reservoir may not be possible, and coupling with the reservoir (possibly leading to non-Hamiltonian dynamics) need to be explicitly included in the calculations. Nonequilibrium work theorems can be established even in the presence of coupling with a heat bath: the case of a Langevin dynamics was already mentioned in the

introduction [4], and more explicit consideration of some specific thermostats has also been discussed in the literature [17].

When working out our examples, we use a simple wall-movement protocol of uniform velocity. One can imagine more complicated protocols, involving acceleration and/or deceleration of the wall. Of course, review of the original derivations [1, 2] show that the Jarzynski identity holds independently of the protocol. However, the actual protocol may affect the form of the work probability distribution, which in our case of uniform wall velocity was a simple Gaussian, equation (13).

As a summary, we have illustrated the physical significance of Jarzynski's and related nonequilibrium work theorems by working out in detail a representative example. In our case the probability distribution of work performed when driving the system between two equilibrium isothermal states can readily be evaluated analytically, and the main physical insight contained in the Jarzynski equality is immediately apparent, namely that the work depends on the initial microstate within a canonical distribution of energies.

Before closing we should mention that exact calculations as the one presented in this paper are of course feasible for almost any ideal system of the sort used as examples in elementary statistical physics courses. Actually, explicit calculations with pedagogical aims have been presented for the ideal gas by Lua and Grosberg [14], or for the Jepsen gas by Bena *et al* [18]. Crooks and Jarzynski [15] considered a simple model of an interacting gas, and Jarzynski himself [19] used a system of perturbed harmonic oscillators, somewhat similar to what we considered here. The examples we have discussed in this paper are different (and simpler in our opinion) from the others already presented in the literature. In any case, our present calculations add to the effort of making nonequilibrium work theorems accessible to a wider audience.

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