

Practical Applicability of the Jarzynski Relation in Statistical Mechanics: A Pedagogical Example[†]

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Received: September 30, 2004; In Final Form: December 2, 2004

We suggest and discuss a simple model of an ideal gas under the piston to gain an insight into the workings of the Jarzynski identity connecting the average exponential of the work over the nonequilibrium trajectories with the equilibrium free energy. We show that the identity is valid for our system, due to the very rapid molecules belonging to the tail of the Maxwell distribution. For the most interesting extreme, when the system volume is large, while the piston is moving with great speed (compared to thermal velocity) for a very short time, the necessary number of independent experimental runs to obtain a reasonable approximation for the free energy from averaging the nonequilibrium work grows exponentially with the system size.

1. Introduction

The celebrated Jarzynski identity is perhaps the most recently discovered^{1,2} simple general formula in elementary statistical mechanics:

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

(see below about sign convention). The claim of this charming simple formula is as follows. Suppose we have an arbitrary system and let us consider two states of this system specified by parameters, e.g. A_{initial} and A_{final} ; these could be volumes, magnetic fields, or just about anything else. If the system comes to thermodynamic equilibrium at A_{initial} , it has free energy $F(A_{\text{initial}}) = F_{\text{initial}}$; if the system is equilibrated at A_{final} , its free energy is $F(A_{\text{final}}) = F_{\text{final}}$. The difference of these free energies is $\Delta F = F_{\text{final}} - F_{\text{initial}}$. According to elementary thermodynamics, if we drive the system from an initial to a final state by a reversible process, such that the system remains at equilibrium at every stage, then we have to perform work, $-W$, which is equal to the free energy change: $-W = \Delta F$. If, on the other hand, the process is not reversible, then the second law of thermodynamics tells us that $\langle -W \rangle \geq \Delta F$. We know, of course, that the second law of thermodynamics is of a statistical nature and, therefore, from time to time, very infrequently, fluctuations occur in which $-W < \Delta F$. These fluctuations might be very rare, but with large W (strongly negative $-W$) their contribution to the average of $e^{W/k_B T}$ might be significant. The Jarzynski formula (1) tells us precisely that when all fluctuations, including those violating $-W \geq \Delta F$, are taken into account, then the average of $\langle e^{W/k_B T} \rangle$ reduces to $e^{-\Delta F/k_B T}$.

It is worth repeating that $-W$ is the work performed by an external force on the system; in other words, W is the work performed by the system itself. We use this sign convention (perhaps somewhat nonstandard), because it will make for positive W and save us some writing in interesting cases below.

The tempting use of this result is to circumvent in computer simulation or in real experiment the often painful stage of equilibrating the system. Instead, it should be possible to run the system many times without any worry of the equilibrium,

repeatedly measure the work, W , and still obtain the equilibrium information ΔF from the formula (1). The problem is that it requires exploration of all sorts of fluctuations along the way and measurement of the work W for every fluctuation.

There are already quite a number of works exploring various aspects of the Jarzynski formula. Papers^{3–5} address mathematical foundations of the Jarzynski identity in the context of fundamental statistical mechanics. Some authors describe the Jarzynski identity in terms of “transient violations of the second law of thermodynamics”.⁶ There is a history of cases when such fluctuation effects were mentioned under the name of “temporary violations of the second law”,^{7,8} but many people feel that it is incorrect terminologically to say that fluctuations violate the second law, even if temporarily. Here, we do not make any firm commitment to any terminology in this sense and just say that the Jarzynski identity is based on proper exploration of a representative set of fluctuations. Various ways to apply the Jarzynski relation in computer simulations and in experiments are discussed in refs 6 and 9–12 (see also the extensive literature cited in these works).

Nevertheless, we found that one aspect is missing in the current literature: namely, the pedagogical aspect. The Jarzynski formula appears so simple and so general that there ought to be a simple way to explain it and to gain an intuitive insight of it on a very elementary level. This motivated us to look for the simplest possible example in which the Jarzynski equation shows some nontrivial results. Since the conceptually simplest subject in statistical mechanics is undoubtedly the classical ideal gas, the goal of the present paper is to work out the application of the formula to the ideal gas. Of course, we shall find nothing really new in terms of factual results, but we hope for a good new insight.

2. Model and Formulation of the Seeming Paradox

Consider some amount of ideal gas in a vessel under a piston. Everything is supposed to be in accord with elementary physics textbooks: ideal thermoisolation, massless piston moving without any friction, etc. Suppose initially that the piston is some distance L from the bottom of the vessel and that the gas temperature is T . Let us now move the piston by some distance ΔL and stop it again, thus preparing the final state.

[†] Part of the special issue “David Chandler Festschrift”.

The following way of thinking seems quite logical from a physicist's point of view. To make the situation dramatic, let us suppose that we move the piston at a very high speed, much faster than the speed of sound in the gas or, in other words, much faster than the averaged thermal velocity of the molecules. Then we can roughly say that no molecules will be able to chase the piston while it is moving, no molecules will hit it, and there will be, therefore, no work. When the piston is stopped at the end, molecules start arriving and they do bombard the piston, but since the piston does not move at this stage, the work is still zero. This logic leads to the conclusion that in this case $W = 0$, implying $\langle e^{W/k_B T} \rangle = 1$, while obviously $\Delta F \neq 0$, which seems to contradict the Jarzynski identity (1).

To resolve this paradox, we have to remember the tail of the Maxwell distribution: however large the speed of a piston, there is still some probability of molecules moving fast enough to chase the piston and hit it while it is moving. This already suggests that the Jarzynski identity (1) has to do with the tails of the relevant distributions. To make this statement more precise, we shall compute the probability distribution of the work W for our elementary model. This is obviously much more than just computing the average involved in Jarzynski formula (1).

To make our article more pedagogical, we shall start with proving the very identity (1) for our specific system. We shall also relegate cumbersome calculations to the Appendix.

3. Calculations

3.1. Average Value of $e^{W/k_B T}$. Since we plan to consider an ideal gas, all molecules will contribute to both W and ΔF independently. Therefore, we can imagine the Jarzynski formula (1) rewritten as

$$\langle \langle e^{W_1/k_B T} \rangle \rangle^N = \langle e^{-\Delta F_1/k_B T} \rangle^N \quad (2)$$

where W_1 and ΔF_1 are the work and the free energy change per molecule. We see that, for the ideal gas, the quantities W_1 and ΔF_1 satisfy the Jarzynski formula looking identical with (1). We, therefore, restrict ourselves for simplicity to the "ideal gas" of just one molecule, and also for simplicity we suppress the index 1 in writing W and ΔF . Thus, we keep considering formula (1), but we think now about just one molecule in an ideal gas.

Furthermore, to simplify writing, we assume that the temperature is such that $k_B T = 1$, the mass of the molecule is $m = 1$, and the piston is moving during the time interval $\tau = 1$.

Figure 1 illustrates the system consisting of a thermally isolated cylinder, a piston moving at speed v_p , and a single molecule initially at position x with velocity v . The molecule bounces off the walls elastically; thus, we are concerned only with the one-dimensional motion indicated. The space-time diagram depicts the trajectory of the piston and the trajectories of a molecule initially moving toward the piston (dashed lines) and for a molecule initially moving away from the piston (thinner dashed lines).

Let us focus on the work W done by the single molecule on the piston, in the time interval $\tau = 1$. The quantity e^W ($k_B T = 1$) is to be averaged over the possible initial states (x, v) of the molecule drawn from a Maxwell-Boltzmann distribution. Therefore

$$\langle e^W \rangle = \frac{\int_0^L dx \int_{-\infty}^{\infty} dv e^{-v^2/2} e^{w_\tau(x,v)}}{\int_0^L dx \int_{-\infty}^{\infty} dv e^{-v^2/2}} \quad (3)$$

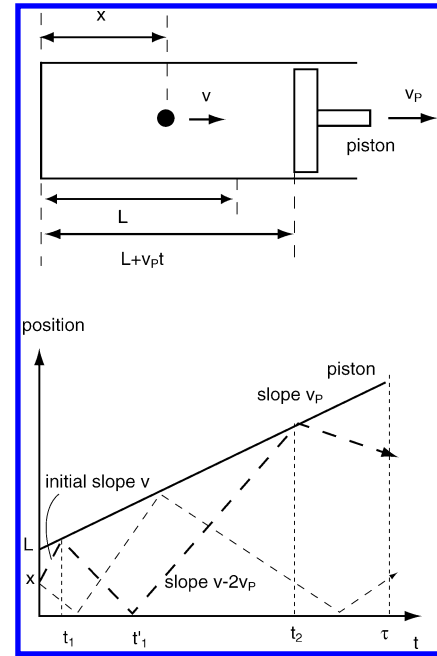


Figure 1. System and space-time diagram: (solid line) piston trajectory; (thick dashed line) molecule trajectory with positive initial velocity; (thin dashed line) molecule with negative initial velocity.

where $w_\tau(x, v)$ is the work done by the gas molecule given the initial coordinate (x, v) and time elapsed τ . To compute this function $w_\tau(x, v)$, we first need to work out the collision times between the molecule and the piston and the work done after n collisions.

Let us first assume a positive initial velocity, in which the molecule can strike the piston first before hitting the left end of the cylinder. The time taken for the first collision with the piston is $t_1 = (L - x)/(v - v_p)$. After the collision, the velocity of the molecule relative to the piston gets reversed and the speed of the molecule gets diminished to $v - 2v_p$ (assuming $v > 2v_p$). The time taken for the second collision with the piston is given by $t_2 = (3L - x)/(v - 3v_p)$. In general, for the n th collision

$$t_n^+ = \frac{(2n - 1)L - x}{v - (2n - 1)v_p} \quad (4)$$

Similarly, for a molecule with a negative initial velocity

$$t_n^- = \frac{(2n - 1)L + x}{v - (2n - 1)v_p} \quad (5)$$

These relations can be inverted to give conditions that should be satisfied by the speed of the molecule in order to result in exactly n collisions with the piston within the time interval $\tau = 1$. For positive initial velocities

$$(2n - 1)(L + v_p) - x < |v| < (2n + 1)(L + v_p) - x \quad (6)$$

For negative initial velocities

$$(2n - 1)(L + v_p) + x < |v| < (2n + 1)(L + v_p) + x \quad (7)$$

The work done by the piston on the molecule after one collision is the change in momentum of the molecule times the velocity of the piston

$$-w_1 = (-(v - 2v_p) - v)v_p = -2(v - v_p)v_p \quad (8)$$

In general, the work done after n collisions is

$$-w_n = -2v_p n + 2v_p^2 n^2 \quad (9)$$

Note that the work done can also be calculated from the change in kinetic energy after n collisions:

$$-w_n = 1/2(v - 2nv_p)^2 - v^2/2 = -2nv_p v + 2n^2 v_p^2 \quad (10)$$

The work done by the molecule on the piston is positive for an expanding volume.

We are now facing the laborious task of calculating the integral in the numerator of formula (3). It is cumbersome, because it must include the summation over all possible numbers of bounces of our molecule from the piston. Note that a large number of bounces correspond to a very large initial velocity of the molecule, as it has to have time to chase the piston for n bounces, even though it loses momentum and gets slower at every bounce. The actual calculation is described in Appendix A. Using the simplified result (30), the sought average is

$$\begin{aligned} \langle e^W \rangle &= \frac{\int_0^{L+v_p} dx \int_{-\infty}^{\infty} dv e^{-v^2/2}}{\int_0^L dx \int_{-\infty}^{\infty} dv e^{-v^2/2}} \\ &= \frac{L + v_p}{L} \end{aligned} \quad (11)$$

which can be recognized as the ratio of the partition functions at the final (after time $\tau = 1$) and initial volumes at the initial temperature $T = 1/k_B$, $Z(L + v_p \tau, T)/Z(L, T)$. This expression is also identical with that obtained from the Jarzynski identity.

3.2. Probability Distribution of the Work W . The prescription for evaluating the distribution is

$$P(W) = \frac{1}{\sqrt{2\pi L}} \int_0^L dx \int_{-\infty}^{\infty} dv e^{-v^2/2} \delta(W - w_\tau(x, v)) \quad (12)$$

The calculations are presented in detail in Appendix B. With the expression (16) for n , the number of bounces, one can get rid of the summation over this number and the distribution function simplifies to

$$P(W) = \delta(W)P_0 + \frac{e^{-1/2(nv_p + W/2nv_p)^2}}{\sqrt{2\pi n v_p}} f(W) \quad (13)$$

Here, P_0 is the probability to obtain vanishing work because the molecule is unable to chase the piston or hit it even once

$$P_0 = \frac{1}{\sqrt{2\pi L}} \int_0^L dx \int_{-(L+v_p)}^{(L+v_p)} dv e^{-(v-x)^2/2} \quad (14)$$

and the function $f(W)$, which we call the overlap factor, can be formulated as (see also Figure 2)

$$f(W) = \left\{ \begin{array}{ll} -(n-1)\left(\frac{v_p}{2L} + 1\right) + \frac{W}{4nv_p L} & \text{when } (n-1)(v_p + 2L) < \frac{W}{2nv_p} \leq (n-1)(v_p + 2L) + 2L \\ 1 & \text{when } (n-1)(v_p + 2L) + 2L < \frac{W}{2nv_p} \leq (n-1)(v_p + 2L) + 2L + 2v_p \\ (n+1)\left(\frac{v_p}{2L} + 1\right) - \frac{W}{4nv_p L} & \text{when } (n-1)(v_p + 2L) + 2L + 2v_p < \frac{W}{2nv_p} \leq (n+1)(v_p + 2L) \end{array} \right\} \quad (15)$$

Here, the integer n (which is the number of bounces by the molecule against the piston) is obtained in Appendix B and is given by the formula

$$n = \left[\left(1 + \sqrt{1 + \frac{2W}{v_p(2L + v_p)}} \right) / 2 \right] \quad (16)$$

where [...] means the integer part of For example, simple algebra indicates that as long as $W < 4v_p(2L + v_p)$, we have just one collision, $n = 1$. For the values of work W in the next interval, $4v_p(2L + v_p) < W < 12v_p(2L + v_p)$, we have $n = 2$, etc.

Thus, the probability distribution $P(W)$ consists of a δ function peak at $W = 0$ and a tail at positive W .

3.3. Limit of Large Volume and Fast-Moving Piston. As we said in the beginning, the most interesting case is when the piston moves fast, such that hardly any molecule can chase it and produce nonzero work. This means that the Jarzynski identity in this case relies exclusively on the far tail of the Maxwell distribution. Let us consider the probability distribution $P(W)$ in this limit, $v_p \gg 1$.

It is reasonable to assume simultaneously that the volume is large enough such that $L \gg v_p$. Since in more traditional units this condition reads $L \gg v_p \tau$, this means that the piston moves fast, but for a very short time.

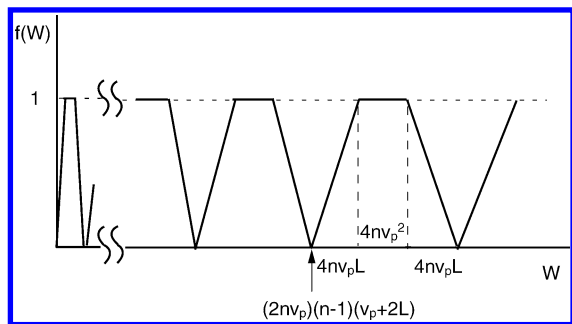


Figure 2. Structure of the overlap factor $f(W)$, which modulates the exponential in the distribution function. This factor becomes a rapidly oscillating function in the limit of small piston velocities.

In this case, the distribution is dominated by the single bounce; that is, $n = 1$. Assuming $n = 1$ and $v_p \ll L$, we have

$$f(W) \approx \begin{cases} \frac{W}{4v_p L} & \text{when } 0 < W < 4v_p L \\ 2 - \frac{W}{4v_p L} & \text{when } 4v_p L < W < 8v_p L \end{cases} \quad (17)$$

which yields the probability distribution expression

$$P(W) \approx \delta(W)P_0 + \frac{e^{-1/2(v_p+(W/2v_p))^2}}{\sqrt{2\pi}v_p} \frac{W}{4v_p L} \quad (18)$$

valid at $L \gg v_p \gg 1$ and $W < 4Lv_p$. For the larger W tail of the distribution $P(W)$, we have to include the second line of eq 17, and for even larger W also higher n values. Luckily, there is no need to do that, because the simple approximation (18) is good enough to capture the Jarzynski result. Although the Jarzynski identity involves $\langle e^W \rangle$, which includes integration over all values of W , the integral converges rapidly enough to yield the correct answer within the region of applicability of formula (18):

$$\begin{aligned} \langle e^W \rangle &= \int_{-\infty}^{\infty} P(W)e^W dW = P_0 + \\ &\quad \frac{1}{\sqrt{2\pi}v_p} \int_0^{\infty} e^{-1/(8v_p^2)(W-2v_p)^2} \frac{W}{4v_p L} dW \\ &= \int_0^L \frac{dx}{L} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dve^{-(1/2)(v-x)^2} + \\ &\quad \frac{1}{\sqrt{2\pi}v_p} \int_{-\infty}^{\infty} e^{-(1/8v_p^2)(W-2v_p)^2} \frac{2v_p^2}{4v_p L} dW \\ &= 1 + \frac{v_p}{L} \end{aligned}$$

Here, we made approximations in both the P_0 term, by extending the integral limits to $(-\infty, \infty)$, and in the tail term, by setting the integral lower limit to $-\infty$. This way, we do recover the formula (11).

Let us also calculate the probability of obtaining nonzero work values (one or more collisions) as well as the average work done, i.e., the zeroth (without the P_0 term) and first moments of the distribution. Using expression (18), we have

$$P_{W>0} = \int_0^{\infty} P(W) dW = \frac{e^{-v_p^2/2}}{4\sqrt{2\pi}Lv_p^2} \int_0^{\infty} We^{-(1/2)W-(1/8v_p^2)W^2} dW \quad (19)$$

$$\langle W \rangle = \int_0^{\infty} WP(W) dW = \frac{e^{-v_p^2/2}}{4\sqrt{2\pi}Lv_p^2} \int_0^{\infty} W^2 e^{-(1/2)W-(1/8v_p^2)W^2} dW \quad (20)$$

For large v_p , we neglect the term $W^2/(8v_p^2)$ in the exponents upon integration, yielding

$$P_{W>0} \approx \frac{1}{\sqrt{2\pi}Lv_p^2} e^{-v_p^2/2} \quad (21)$$

$$\langle W \rangle \approx \frac{1}{\sqrt{2\pi}Lv_p^2} e^{-v_p^2/2} (4) = 4P_{W>0} \quad (22)$$

To the same approximation, the probability to obtain zero work W is equal to

$$P_0 = 1 - \frac{1}{\sqrt{2\pi}Lv_p^2} e^{-v_p^2/2} \quad (23)$$

As one could have expected, these probabilities are governed by the tail of the Maxwell distribution.

3.4. Comparison with Simulations. Measurements were made in computer simulations and compared with the results obtained in the previous sections. The conditions for the “pulling” experiments were as follows: the “pulling” time was set to $\tau = 1$, the temperature was set to $k_B T = 1$ (which sets the width of the Gaussian distribution from which the initial velocities were selected), and the number of trials or iterations used per measured average was 100 000. The parameters that we varied were the piston velocity v_p and the initial piston length (or “volume”) L .

Figures 3 and 4 present the distribution of probabilities $P(W)dW$ for two different sets of piston velocities and piston lengths. In the first case, the piston velocity was set to $v_p = 0.01$ and in the second case was set to $v_p = 1$. The effect of the overlap factor is evident in the former case of a slower moving piston.

Figure 5 presents data for the average $\langle \exp(W/k_B T) \rangle$. The Jarzynski identity predicts that this average should be $(1 + v_p/L) = 2$.

Figure 6 presents data for the average work done. The expression corresponding to a free energy change at constant temperature T , namely $\ln(1 + v_p/L) = \ln\langle e^W \rangle = -\Delta F$, is plotted, as well as the expression for the average work done, (22), for large v_p ($v_p \gg 1$). As the velocity v_p increases, the average work done is seen to shift from one regime (in which $\langle W \rangle \approx -\Delta F$) to another (in which $\langle W \rangle < -\Delta F$). If we take $-\langle W \rangle - \Delta F = W_{\text{dis}}$ as some measure of “dissipation”, then it is also seen that this quantity increases as v_p increases, although the difference is not much more than $k_B T$.

In Figure 7 the expression for the probability of obtaining nonzero work values in the high-velocity limit is compared with the fraction of trials in which a collision occurred between molecule and piston. Due to the rarity of collisions (and dominance of single collisions) in the range of velocities tested ($v_p = 1, 1.5, 2, 2.5, 3, L = 1$), the fraction of trials with collisions is identical with the average number of collisions.

4. Discussion and Conclusion

Let us look closer at our main results obtained in section 3.3. One question to ask is this: how many times should one perform the experiment of moving the piston in order to get a

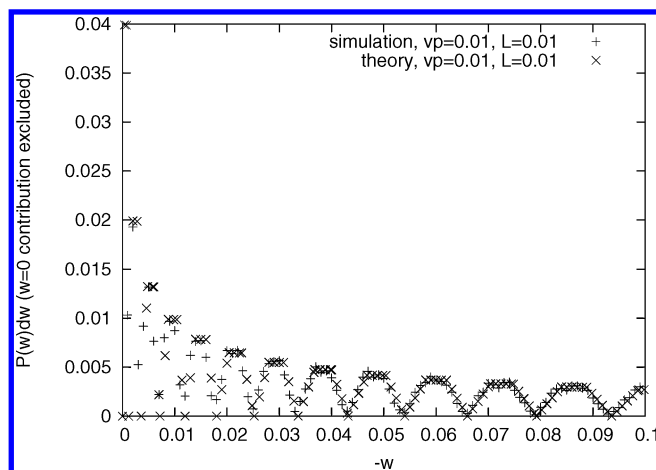


Figure 3. Simulation results (denoted by pluses, +) together with theoretical calculation (expression (13); denoted by crosses, x) for the work distribution. For each trial run, the cylinder volume was doubled ($v_p = 0.01$, $\tau = 1$, $L = 0.01$). The bin width used was $\Delta w = k_B T / 1000 = 1/1000$. The average number of collisions between molecule and piston was about 20.

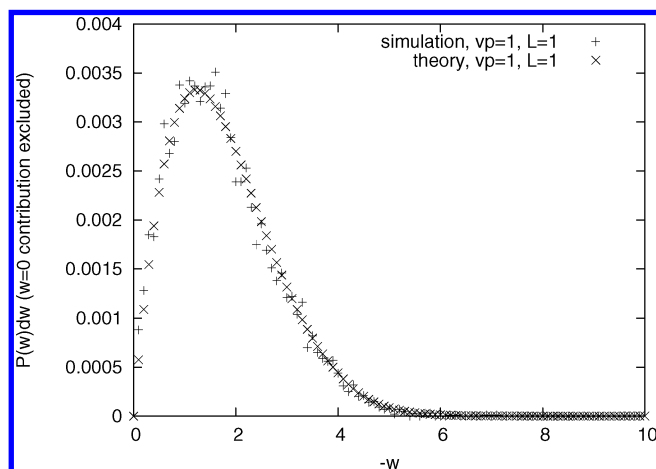


Figure 4. Simulation results (denoted by pluses, +) together with theoretical calculation (denoted by crosses, x) for the work distribution. For each trial run, the cylinder volume was doubled ($v_p = 1$, $\tau = 1$, $L = 1$). The bin width used was $\Delta w = k_B T / 10 = 1/10$. The average number of collisions between molecule and piston was low, about 0.08.

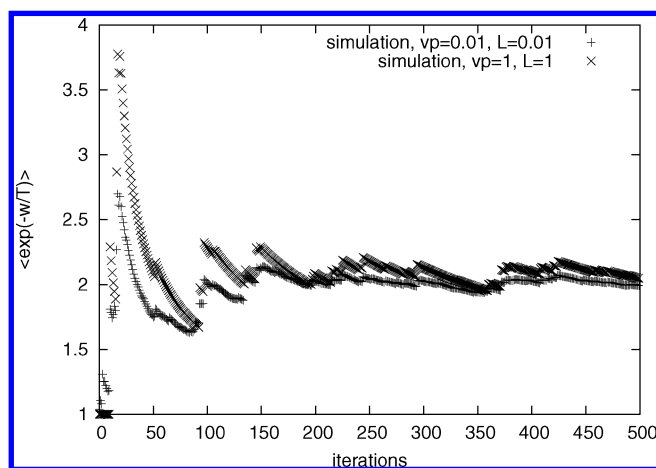


Figure 5. Evolution of the average of $\exp(-w/k_B T)$ with the number of trials.

reasonable estimate of the average $\langle e^W \rangle$? At the very least, to get the nonzero answer for the free energy difference from the Jarzynski formula (1), one has to get at least one case of nonzero work. For this, one has to perform about $1/P_{W>0}$ experiments,

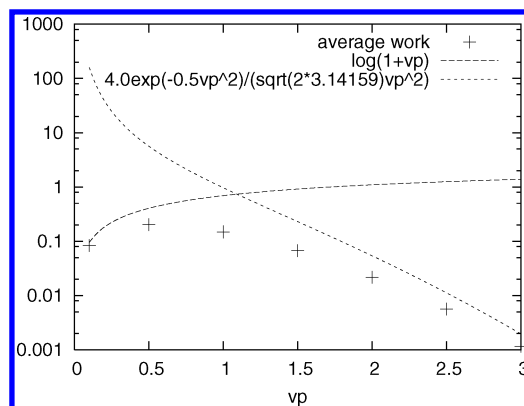


Figure 6. Plot of measurements of the work done (denoted by pluses, +) together with the expression $\ln(1 + v_p \tau / L)$ (i.e. “ $-\Delta F$ ”, with $\tau = 1$ and $L = 1$) and the expression for the average work done for large v_p (22).

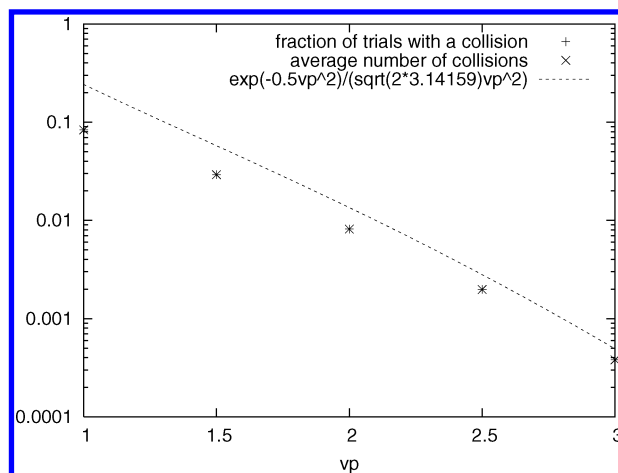


Figure 7. Plot of the expression (21) (denoted by the line), the fraction of trials with a collision (denoted by pluses, +) and the average number of collisions (denoted by crosses, x). The last two coincide.

which is already a very large number at $v_p \gg 1$. In fact, as our calculations show, to recover the Jarzynski identity, we have to continue integration into the region where W is as large as about $L v_p$. In practical terms, this means that we have to perform as many runs on the system as to get at least a few realizations with the work of this order. According to the formula (18), the corresponding probability is roughly proportional to e^{-2L^2} . In other words, this requires about e^{+2L^2} runs. Restoring the more traditional notations with $k_B T$ and τ , we estimate the necessary number of runs (or trials) as $\exp[mL^2/\tau^2 k_B T]$. Clearly, this is a very large number.

In practical terms, one may also want to know if the use of the Jarzynski identity is useful. At first glance, it seems extremely useful: one apparently does not have to equilibrate the system and by doing purely nonequilibrium measurements, one nevertheless recovers the equilibrium free energy. Our example suggests that the situation might be a little more tricky. Indeed, to do equilibrium measurements, one has to proceed very slowly, to keep the system close to equilibrium all the time; for this, τ has to be larger than the system relaxation time, which grows with the system size L (in our dimensionless variables, this corresponds to the limit $v_p \ll L \ll 1$). But, on the other hand, if one proceeds very rapidly, then one has to perform exponentially many experiments in order to catch the exponentially rare but decisively important fluctuations. This consideration suggests that there might be some optimal strategy. For the ideal gas model, such an optimal strategy is most likely the

(classical) slow “equilibrium” experiment, because the time for such an experiment grows only linearly with L , while the time for a “fast” experiment is exponential. For other systems, the optimal strategy might be intermediate between one very slow experiment and very many rapid ones. Unfortunately, it is clear that such an optimal strategy is highly sensitive to the particulars of the system in question. Our model, which is an ideal gas, is a system with a flat energy landscape. For other energy landscapes one may wonder about the trajectories visiting various valleys. Unfortunately, the knowledge of these valleys is exactly what one wants to learn from making measurements of equilibrium free energies. In any case, the insight we can gain from our primitive model is that rapid nonequilibrium measurements are not automatically advantageous.

To conclude, we have presented a very naive, simple model to look at the Jarzynski identity. We do recover the identity for our model, and we are able to demonstrate that its validity relies on the far tail of the Maxwell distribution, in the sense that the dominant contribution is provided by the very rapidly moving molecules. We are also able to estimate how many independent experimental runs are necessary to obtain the equilibrium free energy from the Jarzynski identity with a reasonable accuracy; the necessary number of trials appears to be exponential in the system size.

Acknowledgment. The present work was initiated by the discussion during the Conference on Statistical Physics of Macromolecules in Santa Fe, NM, in May of 2004, where A.Y.G. formulated the ideal gas model studied here. A.Y.G. acknowledges all participants of that discussion, particularly D. Nelson, who pointed to the possible role of the tails of the Maxwell distribution in the resolution of the paradox. Computations for the present work were performed using Minnesota Supercomputing Institute facilities. This work was supported in part by the MRSEC Program of the National Science Foundation under Award Number DMR-0212302. We are glad to present this paper to the journal honoring David Chandler and his penetrating insight into the underlying simplicity of complex physics.

Appendix

A. Computing the Numerator in Eq 3. Using the expression for the work done in n collisions (10) and in view of the inequalities (6) and (7) developed in section 3.1, we have

$$\begin{aligned}
 I &= \int_0^L dx \int_{-\infty}^{\infty} dv e^{-(1/2)v^2} e^{w_{T=1}(x,v)} \\
 &= \int_0^L dx \sum_{n=1}^{\infty} \int_{(2n-1)(L+v_p)-x}^{(2n+1)(L+v_p)-x} dv e^{-(1/2)v^2} e^{-(-2v_p n + 2v_p^2 n^2)} + \\
 &\quad \int_0^L dx \sum_{n=1}^{\infty} \int_{(2n-1)(L+v_p)+x}^{(2n+1)(L+v_p)+x} dv e^{-(1/2)v^2} e^{-(-2v_p n + 2v_p^2 n^2)} + \\
 &\quad \int_0^L dx \int_{-(L+v_p)-x}^{(L+v_p)-x} dv e^{-(1/2)v^2} e^0 \\
 &= \int_0^L dx \sum_{n=1}^{\infty} \left\{ \int_{(2n-1)(L+v_p)-x}^{(2n+1)(L+v_p)-x} dv e^{-(1/2)(v-2v_p n)^2} + \right. \\
 &\quad \left. \int_{(2n-1)(L+v_p)+x}^{(2n+1)(L+v_p)+x} dv e^{-(1/2)(v-2v_p n)^2} \right\} + \\
 &\quad \int_0^L dx \int_{-(L+v_p)-x}^{(L+v_p)-x} dv e^{-(1/2)v^2}
 \end{aligned}$$

Employing a change of variable, $v' = v - 2nv_p$

$$\begin{aligned}
 I &= \int_0^L dx \sum_{n=1}^{\infty} \left\{ \int_{(2n-1)L-x-v_p}^{(2n+1)L-x+v_p} dv' e^{-(1/2)v'^2} + \right. \\
 &\quad \left. \int_{(2n-1)L+x-v_p}^{(2n+1)L+x+v_p} dv' e^{-(1/2)v'^2} \right\} + \\
 &\quad \int_0^L dx \int_{-(L+x)-v_p}^{L-x+v_p} dv e^{-(1/2)v^2} \quad (24)
 \end{aligned}$$

If v_p is zero or absent, the separate integrals could be coalesced into a single integral of a Gaussian from $-\infty$ to ∞ and the result is trivial (identical with the denominator in the average). Therefore, let us separate the “excess” from the trivial result

$$\begin{aligned}
 I &= \int_0^L dx \int_{-\infty}^{\infty} dv e^{-(1/2)v^2} + \int_0^L dx \sum_{n=1}^{\infty} \left\{ \int_{(2n+1)L-x}^{(2n+1)L-x+v_p} dv + \int_{(2n-1)L-x-v_p}^{(2n-1)L-x} dv + \right. \\
 &\quad \left. \int_{(2n+1)L+x}^{(2n+1)L+x+v_p} dv + \int_{(2n-1)L+x-v_p}^{(2n-1)L+x} dv \right\} e^{-(1/2)v^2} + \\
 &\quad \int_0^L dx \left\{ \int_{L-x}^{L-x+v_p} dv + \int_{L+x}^{L+x+v_p} dv \right\} e^{-(1/2)v^2}
 \end{aligned}$$

The first, third, fifth, and sixth integrals after the summation symbol (those with upper limits “... + v_p ”) can be combined after making the change of variables, $x' = (2n+1)L - x$, $x' = (2n+1)L + x$, $x' = L - x$, $x' = L + x$, yielding

$$I_1 = \int_0^{\infty} dx' \int_{x'}^{x'+v_p} dv e^{-(1/2)v^2} \quad (25)$$

Combining the second and fourth integrals after the summation symbol (those with lower limits “... - v_p ”) in a similar away, after the change of variables $x' = (2n-1)L - x$, $x' = (2n-1)L + x$, the result is

$$I_2 = \int_0^{\infty} dx' \int_{x'-v_p}^{x'} dv e^{-(1/2)v^2} \quad (26)$$

Performing yet another change of variables, $v' = v - x'$

$$I_1 = \int_0^{\infty} dx' \int_0^{v_p} dv' e^{-(1/2)(v'+x')^2} \quad (27)$$

$$I_2 = \int_0^{\infty} dx' \int_{-v_p}^0 dv' e^{-(1/2)(v'+x')^2} \quad (28)$$

(Notice that the series of variable substitutions effectively exchanged the infinite limits associated with v with the finite limits associated with x .) After performing the change of variable for I_2 , $v' = -v''$, and combining the two integrals

$$\begin{aligned}
 I_1 + I_2 &= \int_0^{\infty} dx' \int_0^{v_p} dv' e^{-(1/2)(x'+v')^2} + \\
 &\quad \int_0^{\infty} dx' \int_0^{v_p} dv'' e^{-(1/2)(x'-v'')^2} \\
 &= \int_0^{v_p} dv' \int_{-\infty}^{\infty} dx' e^{-(1/2)(x'-v')^2}
 \end{aligned}$$

Exchanging the “roles” of x' and v' , i.e., letting $v = x'$ and $x = v'$

$$I_1 + I_2 = \int_0^{v_p} dx \int_{-\infty}^{\infty} dv e^{-(1/2)v^2} \quad (29)$$

Using this simplified result, the numerator in the average becomes

$$I = \int_0^L dx \int_{-\infty}^{\infty} dv e^{-(1/2)v^2} + \int_0^{v_p} dx \int_{-\infty}^{\infty} dv e^{-(1/2)v^2} \\ = \int_0^{L+v_p} dx \int_{-\infty}^{\infty} dv e^{-(1/2)v^2} \quad (30)$$

B. Computing the Probability Distribution $P(W)$, Eq 12.

The inequalities (6) and (7) developed in section 3.1 lead to the following partition of the integral:

$$P(W) = \frac{1}{\sqrt{2\pi L}} \int_0^L dx \sum_{n=1}^{\infty} \int_{(2n-1)(L+v_p)-x}^{(2n+1)(L+v_p)-x} dv e^{-v^2/2} \delta(W - (2vv_p n - 2v_p^2 n^2)) \\ + \frac{1}{\sqrt{2\pi L}} \int_0^L dx \sum_{n=1}^{\infty} \int_{(2n-1)(L+v_p)+x}^{(2n+1)(L+v_p)+x} dv e^{-v^2/2} \delta(W - (2vv_p n - 2v_p^2 n^2)) \\ + \frac{1}{\sqrt{2\pi L}} \int_0^L dx \int_{-(L+v_p)-x}^{(L+v_p)-x} dv e^{-v^2/2} \delta(W - 0)$$

Call the first term I_1 and the second term I_2 (the third term is “trivial”). Performing a change of variable to remove x from the limits, integrating over x , and taking advantage of the delta function results in

$$I_1 = \sum_{n=1}^{\infty} \frac{e^{-(1/2)(nv_p+(W/2nv_p))^2}}{\sqrt{2\pi nv_p}} \frac{1}{2L} \{\text{overlap between } [nv_p + (W/2nv_p), nv_p + (W/2nv_p) + L] \text{ and } [(2n-1)(L+v_p), (2n+1)(L+v_p)]\}$$

Similarly for I_2

$$I_2 = \sum_{n=1}^{\infty} \frac{e^{-(1/2)(nv_p+(W/2nv_p))^2}}{\sqrt{2\pi nv_p}} \times \frac{1}{2L} \{\text{overlap between } [nv_p + (W/2nv_p) - L, nv_p + (W/2nv_p)] \text{ and } [(2n-1)(L+v_p), (2n+1)(L+v_p)]\}$$

I_1 and I_2 can be combined as

$$I_1 + I_2 = \sum_{n=1}^{\infty} \frac{e^{-(1/2)(nv_p+(W/2nv_p))^2}}{\sqrt{2\pi nv_p}} \frac{1}{2L} \{\text{overlap between } [nv_p + (W/2nv_p) - L, nv_p + (W/2nv_p) + L] \text{ and } [(2n-1)(L+v_p), (2n+1)(L+v_p)]\} = \sum_{n=1}^{\infty} \frac{e^{-(1/2)(nv_p+(W/2nv_p))^2}}{\sqrt{2\pi nv_p}} f(n, W)$$

where the overlap factor f satisfies $0 \leq f \leq 1$, since the range of the smaller interval is at most $2L$. f is also zero for negative W , or positive work values $-W$ done by the piston.

The conditions that must be satisfied by W in order for the overlap associated with integer n to occur are

$$2nv_p(2(n-1)L + (n-1)v_p) < W < 2nv_p(2(n+1)L + (n+1)v_p) \quad (31)$$

Notice that the left boundary of the interval is a function of $n(n-1)$, while the right interval is a function of $n(n+1)$. Therefore, the right boundary can be transformed into the left boundary by making the replacement $n \rightarrow n-1$. This implies that the intervals (31) are contiguous and nonoverlapping and that at most one term in the summation in $P(W)$ survives. One can solve for the integer n by taking the integer part (or floor function) of a solution to a quadratic equation

$$W > 2nv_p(2(n+1)L + (n+1)v_p) \quad (32)$$

which results in the formula (16) in the main text.

References and Notes

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