Illustration of the Jarzynski nonequilibrium work relation for an ideal gas

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The Jarzynski relation is a recently discovered result relating the average exponential of the work done under nonequilibrium conditions to an equilibrium free energy difference. We illustrate this remarkable relation by considering the expansion and compression of a classical ideal gas particle inside a cavity with a moving piston in one dimension. Using a simple relationship between the distributions of the nonequilibrium work done in the two (forward and reverse) processes, we verify the Jarzynski relation and discuss the practical realization of the Jarzynski equality for the model.

I. INTRODUCTION

Most relations in thermodynamics are valid under equilibrium or near-equilibrium conditions. For example, consider a system in contact with a heat bath at temperature $T$. If under some (infinitesimal) process an energy $Q$ is exchanged with the bath, the first law of thermodynamics tells us that

$$ Q = \Delta U + W, $$

where $\Delta U$ is the change in the internal energy of the system and $W$ is the work done by the system. The statement (1) is of course an expression of the conservation of energy, which is valid not just in equilibrium or whether the process is reversible or irreversible. If we assume that the process takes place very slowly (quasistatic, reversible), the second law of thermodynamics further relates the entropy change $\Delta S$ to the energy $Q$ via the relation $Q = T\Delta S$. With this replacement, the relationship (1) may be recast as

$$ W = \Delta U - T\Delta S = \Delta F $$

relating the work done on the system $-W$ to the change in the Helmholtz free energy $\Delta F$.

If the process is not quasistatic, we have from the second law of thermodynamics, $\langle Q \rangle \leq T\Delta S$, and the equality (2) converts into an inequality

$$ -\langle W \rangle \geq \Delta F $$

where the $\langle \cdots \rangle$ denotes an average over an ensemble of measurements of $W$ (or $Q$), where each measurement is taken as the system undergoes the same variation in external parameters starting from an equilibrium state. (For the system of a gas under a piston and the process consisting of movement of the piston, this means that for each measurement the piston moves along the same trajectory, with the gas in thermal equilibrium at the start of every trajectory. The external parameter in this case is the volume of the enclosure, which is the same at the start of every trajectory and the same at the end of every trajectory.)

Many macroscopic physical quantities measured in experiments where the system is driven away from equilibrium satisfy inequalities such as (3). However, in 1997, Jarzynski announced to the scientific community the following equality that now bears his name

$$ \langle e^{W/k_BT} \rangle = e^{-\Delta F/k_BT} $$

where the angle brackets have the same meaning as in the previous paragraph. This remarkable formula tells us that we can extract equilibrium information $\langle \Delta F \rangle$ from the ensemble of nonequilibrium (finite-time) measurements. By application of the mathematical identity $(e^x)^n \geq e^{nx}$, the Jarzynski relation (4) yields the inequality in (3).

For our purposes, the Jarzynski relation is valid when at the start of every measurement the system is at thermal equilibrium with a heat bath, and that during the finite-time switching of the external parameters, no energy is exchanged with the heat bath (i.e. the process is adiabatic). The free energies $F_1$ and $F_0$ that comprise the difference $\Delta F = F_1 - F_0$ refer to states of the system in equilibrium at the external parameters corresponding to the start and end of the switching process. More detailed and general conditions for the validity of (4) can be found in [1, 2] and references therein.

The utility of the Jarzynski relation lies in its potential to give a good estimate of the free energy change, $\Delta F$, given a finite number of measurements of the work within a finite amount of time. (e.g. compared with the use of (3)) In fact, the Jarzynski relation has been used to measure free energy differences in experiments involving single molecule systems such as the pulling of RNA or protein [3, 4].

Nevertheless, it should be pointed out that there exists considerable recent debate in the literature concerning when precisely the Jarzynski relation is valid and whether it is applicable in practice, even for an ideal gas [5, 6, 7, 8, 9]. In reference [10], Lua and Grosseberg discussed the practical applicability of the Jarzynski relation in the context of an ideal gas particle expanding under a piston and moving in one dimension. (See figure 1.) The Jarzynski equality for $N$ independent particles is given by the Jarzynski equality for 1 particle raised to the power $N$. In that work, the Jarzynski relation was verified with an explicit calculation. The work distribution function was also derived and given explicitly. Finally, the limit of a fast moving piston was examined, leading to the conclusion that it might be difficult to realize the
Jarzynski equality in practice for the case of an expansion with the fast moving piston, as was also pointed out in [12].

Our goal in this article is to illustrate the Jarzynski relation and gain some insight into how it works by considering the same ideal gas model discussed in [11]. Our results and conclusions for the case of an expanding cavity are the same as in that work. However, in the present work we also examine the ‘reverse’ case in which the piston compresses the cavity. Furthermore, we verify the Jarzynski relation in an indirect but simpler fashion.

The plan of the rest of the article is as follows. In section [11] we give explicit expressions for the probability distribution functions of the work done by the gas particle (or piston) for the case when the piston expands the cavity (arbitrarily called the ‘forward’ process, with distribution denoted by $P_F(W)$, where the argument $W$ is the magnitude of the work done by the gas) and for the case when the piston compresses the cavity (called the ‘reverse’ process, with distribution denoted by $P_R(W)$, where $W$ is the work done by the piston). These probability distributions appear when calculating the average defined above, e.g., \( \langle e^{W/k_BT} \rangle_F = \int_0^\infty P_F(W)e^{W/k_BT}dW \). We assume that the piston moves with the same constant speed during the expansion and compression. In an attempt to make the main presentation short and simple, we shall also relegate cumbersome derivations to the Appendix. In section [11] we show that the forward and reverse distributions, $P_F(W)$ and $P_R(W)$, satisfy a simple relation, which we then use to derive the Jarzynski relation. In this section we discuss the practical evaluation of the free energy difference from the exponential average in the Jarzynski relation for the forward and reverse processes.

II. PROBABILITY DISTRIBUTION OF THE WORK

Referring to figure [11] the initial state of the particle \((x, v)\) consists of a position \(x\) drawn with uniform probability within the initial length of the cavity, and a velocity \(v\) drawn from a Maxwell-Boltzmann distribution (i.e. a Gaussian distribution, \(e^{-v^2/2}\)). To simplify the writing and without loss of generality, we use units such that \(k_BT = 1\), the mass of the particle \(m = 1\), and that the piston displaces by an amount \(\Delta L\) during time \(\tau = 1\).

For the forward process in which the cavity expands from ‘volume’ \(L\) to a final volume of \(L + \Delta L\), the prescription for evaluating the distribution is

$$P_F(W) = \frac{1}{\sqrt{2\pi L}} \int_0^L dx \int_{-\infty}^\infty dv e^{-v^2/2} \delta (W - w_r(x, v)) ,$$

(5)

where \(w_r(x, v)\) is the work done by the particle given the initial coordinate \((x, v)\). The \(\delta\) function picks out the initial states which lead to an amount of work \(W\). The calculation is presented in detail in Appendix A. The final result is

$$P_F(W) = \delta(W) P_0 + \frac{e^{-\frac{1}{2}(n\Delta L + \frac{W}{k_BT})^2}}{\sqrt{2\pi n\Delta L}} f(W) .$$

(6)

Here, \(P_0\) is the probability to obtain vanishing work because the particle is unable to chase the piston or hit it even once,

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

(7)

The integer \(n\) (which is the number of bounces by the particle against the piston) is obtained in Appendix A and is given by the formula

$$n = \left( 1 + \sqrt{1 + \frac{2W}{\Delta L(2L + \Delta L)}} \right)^2 / 2 ,$$

(8)

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

Finally, the function \(f(W)\), which we call the overlap factor, varies between 0 and 1 and is illustrated in figure [10]. An explicit expression is given by (A10) in Appendix A.

Similarly, for the reverse process in which the cavity contracts from ‘volume’ \(L + \Delta L\) to a final volume of \(L\), the prescription for evaluating the distribution is

$$P_R(W) = \frac{1}{\sqrt{2\pi(L + \Delta L)}} \int_0^{L+\Delta L} dx \times$$

$$\times \int_{-\infty}^{\infty} dv e^{-v^2/2} \delta (W - w_r(x, v)) ,$$

(9)

where \(w'_r(x, v)\) is the work done by the piston given the initial coordinate of the particle \((x, v)\). The final result is

$$P_R(W) = \delta(W) P'_0 + \frac{e^{-\frac{1}{2}(n\Delta L - \frac{W}{k_BT})^2}}{\sqrt{2\pi n\Delta L}} Lf(W) / (L + \Delta L) .$$

(10)

Here, \(P'_0\) is given by

$$P'_0 = \frac{1}{\sqrt{2\pi(L + \Delta L)}} \int_0^{L+\Delta L} dx \int_L^{L+\Delta L} dv e^{-(v-x)^2/2} ,$$

(11)

The integer \(n\) and the function \(f(W)\) are the same as in the forward case.

Thus, the probability distributions [6] and [10] consist of a \(\delta\) function peak at \(W = 0\) and a tail or hump at positive \(W\) (see figure [9] for the case of a fast moving piston). The forward distribution is examined in Appendix C in the limit of a fast moving piston and in Appendix D in the limit of a slow moving piston.
III. VERIFICATION OF THE JARZYNSKI RELATION

We now show that our model satisfies the Jarzynski relation \([4] \). Taking the ratio of expressions \([6] \) and \([10] \), we obtain

\[
P_F(W) = e^{-W - \Delta F}, \tag{12}
\]

where \(\Delta F = -\ln \left( \frac{L + \Delta L}{L} \right) \) is the difference between the free energies at volumes \(L + \Delta L\) and \(L\), in equilibrium at the same temperature. (Relation \([12] \) is reminiscent of another remarkable result called the fluctuation theorem or Crooks relation, which relates the distribution of entropy productions of a driven system that is initially in equilibrium to the entropy production of the same system driven in reverse \([2, 3, 4, 5, 6] \). The simple proof below was also inspired by the first two of these references.)

The exponential average of the work is readily evaluated from \([12] \) and the normalization of the probability distributions. For the forward process,

\[
\langle e^W \rangle_F = \int_0^\infty P_F(W)e^W dW
\]

\[
= e^{-\Delta F} \int_0^\infty P_R(W)dW
\]

\[
= e^{-\Delta F} \tag{13}
\]

Similarly, for the reverse process

\[
\langle e^{-W} \rangle_R = \int_0^\infty P_R(W)e^{-W} dW
\]

\[
= e^{\Delta F} \int_0^\infty P_F(W)dW
\]

\[
= e^{\Delta F} \tag{14}
\]

The Jarzynski relation is also verified explicitly in appendices \([3, 4, 5, 6, 10] \) in the opposite limits of a fast moving piston and a slow moving piston.

IV. REALIZING THE JARZYNSKI EQUALITY IN PRACTICE

In this section we examine how well the average of the left-hand-side of the Jarzynski relation \([4] \) can reproduce the equality with the right-hand-side, based on a finite-number of measurements of the work. This issue is of immense practical interest in experiments involving the manipulation of nanoscale objects and biological molecules.

From the definition of the exponential average, \(\langle e^W \rangle_F = \int_0^\infty P_F(W)e^W dW\), one can already see the potential problem. In an expansion, when the piston moves very fast, only the very fast (and very rare) particles can hit the piston to produce non-zero work. But these fast particles can give a significant contribution to the average because of the factor \(e^W\). Many measurements or repetitions of the expansion are necessary to sample an adequate number of particles that move fast enough in order to assess this contribution accurately.

To be more precise, and to see a clear difference between the forward and reverse processes, we consider the case when the piston moves very fast, such that a typical particle moves very little during the expansion or compression of the cavity. This is equivalent to the conditions \(L \gg c \tau\) and \(\Delta L \gg c \tau\), where \(c = \sqrt{k_B T/m}\) is roughly the speed of sound in the gas. In our simplified units, this translates to \(L, \Delta L \gg 1\).

First, let us rewrite \([12] \) as

\[
P_F(W)e^W = P_R(W)e^{-\Delta F} \tag{15}
\]

we see that the contribution of the expanding or forward work measurements to the average, \(e^{-\Delta F}\), is given by the reverse work distribution, \(P_R(W)\). This indicates that measurements of \(P_F(W)\) can give an accurate result for the average if \(P_F(W)\) is significant at values of \(W\) where \(P_R(W)\) is significant; that is, if there is a reasonable overlap between the forward and reverse work distributions \([16] \).

Now let us determine the probability of obtaining zero work for the forward and reverse processes. For the forward process, the probability \(P_F(0)\) is clearly close to 1. From the relation \([12] \), the probability of obtaining zero work for the reverse process is given by

\[
P_R(0) \approx \frac{L}{L + \Delta L} \tag{16}
\]

Clearly, in the limit of a fast moving piston, this probability is given by the fraction of the cavity volume that is not swept or visited by the piston.

As to the probability of obtaining non-zero work, in the forward process this clearly vanishes (the area under the lower curve in figure \([3] \) in the limit of a fast moving piston. In contrast, the probability of obtaining non-zero work in the reverse process is finite (the area under the taller curve in figure \([3] \). This probability is given by the fraction of the cavity volume that is swept by the piston, \(\Delta L/(L + \Delta L)\).

Now we can address the issue presented at the start of this section. In the forward process, rare events (non-zero work values) contribute a finite fraction to the average, given by the area under the ‘reverse’ curve of figure \([3] \). This means that many measurements are necessary (given roughly by the inverse probability of obtaining non-zero work values \([3, 4, 5, 6] \)) in order to faithfully produce the equality in the Jarzynski relation \([4] \). In contrast, for the reverse process, the dominant contribution is given by the zero work values, which have finite probability. Therefore a smaller number of measurements in the reverse process can reproduce the equality in \([4] \) quite well, as was indeed revealed in computer simulations.
V. CONCLUSION

We obtained explicit expressions for the distribution of the work done in the forward and reverse processes, $P_F(W)$ and $P_R(W)$, for a simple ideal gas model. By noting a simple relationship between the two distributions (equation 12) we illustrated the validity of the Jarzynski relation (equation 4) for the model. We also conclude that in the forward or expanding case, the evaluation of the average exponential of the nonequilibrium work from a finite number of trials or measurements can give a poor result for the free energy difference when the piston moves sufficiently fast (indicating that repeated, rapid nonequilibrium measurements may not be automatically advantageous 10). This is in sharp contrast to the average that can be obtained from the complementary or reverse process. In general an optimal result may be obtained by a suitable combination of the measurements in the forward and reverse processes 17.

Acknowledgments

I thank my research adviser, Alexander Yu. Grosberg, for introducing me to the Jarzynski relation and its application to the ideal gas model discussed here, which pointed to the role of the far tails of the Maxwell distribution in resolving a paradox involving a very fast moving piston. I also appreciate his comments on this manuscript.

APPENDIX A: CALCULATION OF $P_F(W)$

In this section, we first derive an expression for $P_F(W)$, based on the work in 10. Again, we take reduced units such that $k_B T = 1$, the particle mass $m = 1$, and the piston moves with speed $\Delta L/\tau$ during a time interval $\tau = 1$.

Let us first assume a positive initial velocity (refer to figure 1), in which the particle can strike the piston first before hitting the left end of the cavity. The time taken for the first collision with the piston is $t_1 = \frac{L-x}{v-\Delta L}$. After the collision, the velocity of the particle relative to the piston gets reversed and the speed of the particle gets diminished to $v - 2\Delta L$ (assuming $v > 2\Delta L$). The time taken for the second collision with the piston is given by $t_2 = \frac{3L-x}{v-3\Delta L}$. In general, for the $n^\text{th}$ collision

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

Similarly, for a particle with a negative initial velocity,

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

These relations can be inverted to give conditions that should be satisfied by the speed of the particle in order to result in exactly $n$ collisions with the piston within a time interval $\tau = 1$. For positive initial velocities, (2n-1)(L+\Delta L) - x < |v| < (2n+1)(L+\Delta L) - x \quad (A3)

For negative initial velocities,

(2n-1)(L+\Delta L) + x < |v| < (2n+1)(L+\Delta L) + x \quad (A4)

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

$$-w_1 = -(v - 2\Delta L - v)\Delta L = -2(v - \Delta L)\Delta L \quad (A5)$$

In general, the work done after $n$ collisions is

$$-w_n = -2v\Delta Ln + 2\Delta L^2n^2 \quad (A6)$$

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

$$-w_n = \frac{1}{2}(v-2n\Delta L)^2 - v^2/2 = -2n\Delta Lv + 2n^2\Delta L^2 \quad (A7)$$

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

The inequalities (A3) and (A4) lead to the following partition of the integral in (5),

$$P_F(W) = \frac{1}{\sqrt{2\pi L}} \int_0^L dx \sum_{n=1}^{\infty} \int_{(2n-1)(L+\Delta L) - x}^{(2n+1)(L+\Delta L) - x} dv e^{-v^2/2} \times \delta (W - (2v\Delta Ln - 2\Delta L^2n^2)) +

\frac{1}{\sqrt{2\pi L}} \int_0^L dx \sum_{n=1}^{\infty} \int_{(2n-1)(L+\Delta L) + x}^{(2n+1)(L+\Delta L) + x} dv e^{-v^2/2} \times \delta (W - (2v\Delta Ln - 2\Delta L^2n^2)) +

\frac{1}{\sqrt{2\pi L}} \int_0^L dx \int_{-(L+\Delta L) - x}^{(L+\Delta L) - 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 re-
move \( x \) from the limits, integrating over \( x \) and taking advantage of the delta function results in

\[
I_1 = \sum_{n=1}^{\infty} e^{-\frac{1}{2} \left( n\Delta L + \frac{W}{2\pi n\Delta L} \right)^2} \times \\
\quad \times \frac{1}{2L} \times \text{overlap between} \\
\quad \left[ n\Delta L + \frac{W}{2n\Delta L}, n\Delta L + \frac{W}{2n\Delta L} + L \right] \\
\quad \text{and} \quad [(2n-1)(L + \Delta L), (2n+1)(L + \Delta L)]
\]

and similarly for \( I_2 \),

\[
I_2 = \sum_{n=1}^{\infty} e^{-\frac{1}{2} \left( n\Delta L + \frac{W}{2\pi n\Delta L} \right)^2} \times \\
\quad \times \frac{1}{2L} \times \text{overlap between} \\
\quad \left[ n\Delta L + \frac{W}{2n\Delta L} - L, n\Delta L + \frac{W}{2n\Delta L} \right] \\
\quad \text{and} \quad [(2n-1)(L + \Delta L), (2n+1)(L + \Delta L)]
\]

(For two intervals \([a, b]\) and \([c, d]\) where \(a < b\) and \(c < d\), the expression \{overlap between \([a, b]\) and \([c, d]\) \} equals 0 when \(b < c\), equals \(b - c\) when \(a < c < b < d\), etc.) \(I_1\) and \(I_2\) can be combined as follows,

\[
I_1 + I_2 = \sum_{n=1}^{\infty} e^{-\frac{1}{2} \left( n\Delta L + \frac{W}{2\pi n\Delta L} \right)^2} \times \\
\quad \times \frac{1}{2L} \times \text{overlap between} \\
\quad \left[ n\Delta L + \frac{W}{2n\Delta L} - L, n\Delta L + \frac{W}{2n\Delta L} + L \right] \\
\quad \text{and} \quad [(2n-1)(L + \Delta L), (2n+1)(L + \Delta L)]
\]

\[
= \sum_{n=1}^{\infty} e^{-\frac{1}{2} \left( n\Delta L + \frac{W}{2\pi n\Delta L} \right)^2} \times f(n, W)
\]

where the overlap factor \(f(n, W)\) 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

\[
2n\Delta L (2(n-1)L + (n-1)\Delta L) < W < 2n\Delta L (2(n+1)L + (n+1)\Delta L)
\]  

(A8)

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 \([A8]\) are contiguous and nonoverlapping and that at most one term in the summation in \(P_F(W)\) survives. One can solve for the integer \(n\) by taking the integer part (or floor function) of

\[
f(W) = \begin{cases} 
-(n-1) \left( \frac{\Delta L}{2L} + 1 \right) + \frac{W}{2\pi n\Delta L} & \text{when } (n-1)(\Delta L + 2L) + 2L < \frac{W}{2\pi n\Delta L} \leq (n-1)(\Delta L + 2L) + 2L \\
1 & \text{when } (n-1)(\Delta L + 2L) + 2L < \frac{W}{2\pi n\Delta L} \leq (n-1)(\Delta L + 2L) + 2L \\
(n+1) \left( \frac{\Delta L}{2L} + 1 \right) - \frac{W}{2\pi n\Delta L} & \text{when } (n-1)(\Delta L + 2L) + 2L < \frac{W}{2\pi n\Delta L} \leq (n+1)(\Delta L + 2L)
\end{cases}
\]

(A10)

**APPENDIX B: OBTAINING \(P_R(W)\) FROM \(P_F(W)\)**

To obtain \(P_R(W)\) from \(P_F(W)\), make the following series of replacements \(W \rightarrow -W, \Delta L \rightarrow -\Delta L, L \rightarrow L + \Delta L\). The result is

\[
P_R(W) = \sum_{n=1}^{\infty} e^{-\frac{1}{2} \left( n\Delta L + \frac{W}{2\pi n\Delta L} \right)^2} \times \\
\quad \times \frac{1}{2L} \times \text{overlap between} \\
\quad \left[ n\Delta L + \frac{W}{2n\Delta L} - L, n\Delta L + \frac{W}{2n\Delta L} \right] \\
\quad \text{and} \quad [(2n-1)(L + \Delta L), (2n+1)(L + \Delta L)]
\]

where the overlap factor \(f(n, W)\) 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

\[
2n\Delta L (2(n-1)L + (n-1)\Delta L) < W < 2n\Delta L (2(n+1)L + (n+1)\Delta L)
\]  

(A8)
\[ P_n(W) = P_0 \delta(W) + \frac{e^{-\frac{1}{2}(n\Delta L + \frac{W}{2n\Delta L})^2}}{\sqrt{2\pi n\Delta L}} \times 2(L + \Delta L) \times \left\{ \text{overlap between } [-n\Delta L + \frac{W}{2n\Delta L} - (L + \Delta L), -n\Delta L + \frac{W}{2n\Delta L} + L + \Delta L] \text{ and } [(2n - 1)(L), (2n + 1)(L))] \right\} \]

where
\[ P_0' = \frac{1}{\sqrt{2\pi(L + \Delta L)}} \int_0^{L+\Delta L} dx \int_{-L}^L dv e^{-(v-x)^2/2} \] (B1)

and
\[ n = \left[ 1 + \sqrt{1 + \frac{2W}{\Delta L(2L + \Delta L)}} \right] / 2 \] (B2)

Notice that \( n \) on the forward and reverse cases are identical.

\[ \left\{ \text{overlap between } [-n\Delta L + \frac{W}{2n\Delta L} - (L + \Delta L), -n\Delta L + \frac{W}{2n\Delta L} + L + \Delta L] \text{ and } [(2n - 1)(L), (2n + 1)(L))] \right\} = \left\{ \text{overlap between } [n\Delta L + \frac{W}{2n\Delta L} - L - 2\Delta L, n\Delta L + \frac{W}{2n\Delta L} + L] \text{ and } [(2n - 1)(L + \Delta L), (2n + 1)(L + \Delta L) - 2\Delta L] \right\} \] (B4)

Comparing this expression for the overlap in the reverse case with that of the forward case, one sees that they are identical apart from the shift of \(-2L\) in the left boundary of the first interval and a shift of \(-2\Delta L\) on the right boundary of the second interval. Because the difference of the lengths of the two intervals is \(2\Delta L\), the overlaps are identical.

**APPENDIX C: LIMIT OF A FAST MOVING PISTON**

In this section, we obtain the form of the forward distribution \( P(W) \) when the piston takes a very short time \( \tau \) to undergo the displacement \( \Delta L \), such that a typical particle moves very little during the expansion. That is, we assume that \( \Delta L \gg c\tau \) and \( L \gg c\tau \), where \( c = \sqrt{k_B T/m} \). The formulas in this section are similar to that in [10].

In this limit, the distribution is dominated by a single bounce, \( n = 1 \), and values \( W < 4(\Delta L)L \), giving
\[ P(W) \simeq \delta(W)P_0 + \frac{e^{-\frac{1}{2}(\Delta L + \frac{W}{2\Delta L})^2}}{\sqrt{2\pi \Delta L}} \frac{W}{4(\Delta L)L} \] (C1)

This form of the distribution suffices to produce the Jarzynski equality:
\[ \langle e^W \rangle = \int_0^\infty P(W)e^W dW = P_0 + \frac{1}{\sqrt{2\pi \Delta L}} \int_0^\infty e^{-\frac{1}{2}(W - 2\Delta L)^2} \times \frac{W}{4\Delta LL} \frac{W}{4(\Delta L)L} dW \]

\[ = \int_0^L dx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty e^{\frac{-1}{2}(v-x)^2} + \frac{1}{\sqrt{2\pi \Delta L}} \int_{-\infty}^\infty e^{-\frac{1}{2}(W - 2\Delta L)^2} \times \frac{2\Delta L^2}{4(\Delta L)L} dW \]

\[ = 1 + \frac{\Delta L}{L} \Delta F = e^{-\Delta F}. \]

Where \( \Delta F = -\ln(1 + \Delta L/L) \). 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 \(-\infty\).

Let us also calculate the probability of obtaining non-
zero work values. Using expression (C1), we have
\[
P_{W>0} = \int_{0^+}^{\infty} P(W)\,dW
= \frac{e^{-\Delta L^2/2}}{4\sqrt{2\pi L(\Delta L)^2}} \int_0^\infty W \times
\times e^{-\frac{1}{2}W-\frac{\alpha W^2}{\pi\Delta L}} \,dW
\tag{C2}
\]

For large \(\Delta L\), we neglect the term \(W^2/(8\Delta L^2)\) in the exponent upon integration, yielding
\[
P_{W>0} \approx \frac{1}{\sqrt{2\pi L(\Delta L)^2}} e^{-\Delta L^2/2} \tag{C3}
\]

This quantity represents the area under the smaller curve in figure 8.

**APPENDIX D: LIMIT OF A SLOW MOVING PISTON**

In this section, we obtain the form of the forward distribution (6) when the piston takes a very long time \(\tau\) to undergo the displacement \(\Delta L\), such that a typical particle bounces off the piston many times. This means that \(\Delta L \ll \tau\) and \(L \ll \tau\), where \(\tau = \sqrt{k_B T/m}\).

Defining \(\Delta L/L = \alpha\), we have \(P_0 \approx 0\) and \(n\) is very large with \(n\Delta L \approx \frac{W}{2(1+\alpha)^2}\). Thus,
\[
P(W) \approx \frac{\alpha(2+\alpha)/\pi}{\alpha\sqrt{W}} \exp\left(-\frac{(1+\alpha)^2}{\alpha(2+\alpha)}W\right) \cdot f(W).
\tag{D1}
\]

The factor \(f(W)\) behaves like a rapidly oscillating function in this limit (albeit the period increases as \(n\) increases). We shall replace \(f(W)\) by its average value, given by the ratio of the area of a trapezoid in figure 2 to the length of the base of the trapezoid, \(\frac{1+\alpha}{2+\alpha}\), when we evaluate the integrals below.

One can derive the \(W\) dependence of this distribution using adiabatic invariants, except without the factor \(f(W)\), as follows.

In [2], Jarzynski considers as an example a single particle bouncing around inside a three-dimensional cavity with hard walls, where the shape of the cavity is a function of a control parameter \(\lambda\). In it, he mentions the quantity \(H_\lambda^{3/2}V_\lambda\) as an adiabatic invariant (i.e. a constant when the control parameter is varied very slowly), where \(H_\lambda\) is the particle energy and \(V_\lambda\) is the volume of the cavity. These give the work performed on the particle with initial energy \(E_0\): \(W_\infty = H_1 - E_0 = [(V_0/V_1)^{2/3} - 1]E_0\), and the work distribution when \(\lambda\) is switched infinitely slowly from 0 to 1:
\[
\lim_{t_\alpha \to \infty} \rho(W, t_\alpha) = \left(\frac{4\beta^3W}{\pi r^3}\right)^{1/2} \exp\left(-\frac{\beta W}{r}\right) \theta(W) \tag{D2}
\]

where \(r = (V_0/V_1)^{2/3} - 1\), \(\beta = 1/k_B T\), and \(V_0 > V_1\) (the cavity is being compressed).

We would like to employ the same idea here for the one-dimensional particle.

In one dimension, we take \(H_\lambda^{1/2}L_\lambda\) as the invariant. This quantity is just the action or phase space area [8], \(\# p\, dq/2\pi\), where \(p\) and \(q\) are momentum and position coordinates, respectively.

The work done by the particle as the piston extends from \(L\) to \((1+\alpha)L\), when the initial energy is \(E_0\), is then
\[
W = \left(1 - \frac{1}{(1+\alpha)^2}\right)E_0 \tag{D3}
\]

The initial energy \(E_0\) is boltzmann distributed. Multiplying the boltzmann factor by the density of states for a particle in one-dimension, \(dp/dE \sim 1/\sqrt{E}\), produces the following expression (apart from normalization factors):
\[
\lim_{t_\alpha \to \infty} \rho(W, t_\alpha) \sim \frac{1}{\sqrt{W}} \exp\left(-\frac{\beta W (1+\alpha)^2}{\alpha(2+\alpha)}\right) \tag{D4}
\]

which has the same functional dependence on \(W\) as (D1) when \(\beta = 1\), apart from the overlap factor \(f(W)\).

With the distribution (D1), the Jarzynski relation is verified explicitly as follows. Using the integral
\[
\int_0^\infty t^n e^{-st} \,dt = \frac{\Gamma(n+1)}{s^{n+1}} \tag{D5}
\]

one obtains
\[
\langle e^W \rangle = \int_0^\infty P(W)e^W \,dW
= \frac{\sqrt{\alpha(2+\alpha)/\pi}}{\alpha} \times \frac{1+\alpha}{2+\alpha} \times \frac{\Gamma(1/2)}{\sqrt{|\alpha(2+\alpha)|^{1/2}}} \tag{D6}
\]

\[
= 1 + \alpha = e^{-\Delta F} \tag{D7}
\]

where \(\Delta F = -\ln (1+\alpha) = -\ln (1 + \Delta L/L)\).

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FIG. 2: The structure of the overlap factor $f(W)$ that modulates the exponential in the distribution function. This factor becomes a rapidly oscillating function in the limit of small piston velocities (i.e. a quasistatic process).

FIG. 3: Probability distribution for the non-zero work values in the forward and reverse processes, when the piston moves fast.