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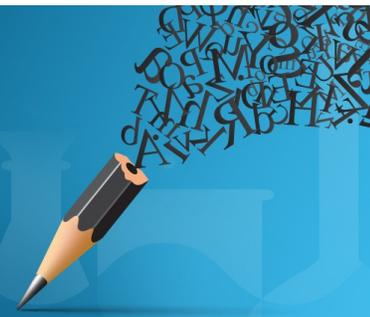


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Work from the Most Probable Macrostate, and Relation to the Adiabatic Piston Problem

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Abstract. A system's entropy is maximized not when it is localized in its most probable macrostate, but when it is in its most probable distribution of macrostates. This distribution includes all macrostates, including, albeit typically with much smaller probability than the most probable macrostate, those far removed from the most probable one. It is this distribution, and not the most probable macrostate alone, that characterizes true thermodynamic equilibrium. Thus, work, albeit typically only in small amounts, is extractable from a system localized in its most probable macrostate. We demonstrate these points via a simple system. We show that a small amount of work can be extracted from a box of gas in thermal equilibrium with a heat reservoir even if the gas is in its most probable macrostate with exactly half of the gas molecules in both the left and right halves of the box. We then qualitatively consider the relation to the adiabatic piston problem.

Keywords: equilibrium, macrostate, second law of thermodynamics, work, entropy, probability, binomial distribution, Gaussian distribution, adiabatic piston, diathermal piston

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I. INTRODUCTION

True thermodynamic equilibrium — maximum entropy, zero extractable work — is the most probable distribution of macrostates. This distribution includes all macrostates, including, albeit typically with much smaller probability than the most probable macrostate, those far removed from the most probable one. Thus, a system localized, or “frozen,” in its most probable macrostate is not in true thermodynamic equilibrium, and hence has a capacity, albeit typically only a small one, for increasing its entropy and for doing work.

The distinction between true thermodynamic equilibrium and the most probable macrostate is not always clearly made. Perhaps the most commonly stated viewpoint is that the most probable macrostate corresponds to true thermodynamic equilibrium, and that fluctuations to less probable macrostates correspond to spontaneous decreases in entropy, interpreted either as a violation of a classical formulation of the second law of thermodynamics that does not consider fluctuations, or consistently with a statistical-mechanical formulation thereof that encompasses fluctuations [1]. However, Guggenheim [2] and Pippard [3], for example, make this distinction very clearly. They carefully

explain how fluctuations away from the most probable macrostate increase — not decrease — the entropy, because these fluctuations delocalize a system in phase space to beyond the phase-space volume occupied by the most probable macrostate alone.

In Sec. II, we demonstrate these points via a simple system. We show that a small amount of work can be extracted from a box of gas in thermal equilibrium with a heat reservoir even if the gas is in its most probable macrostate with exactly half of the gas molecules in both the left and right halves of the box. Then, in Sec. III, we then qualitatively consider the relation of our discussions of Sec. II to the adiabatic piston problem.

In Secs. II and III, we assume that the number N of gas molecules is large. In the Appendix, modifications for small N , specifically, for $N = 2$, are discussed.

II. A SMALL AMOUNT OF WORK FROM THE MOST PROBABLE MACROSTATE

Consider a box containing N ideal gas molecules in thermal equilibrium with a heat reservoir at temperature T . (For simplicity, let N be even.) Let $N/2 + \Delta N$ be the number of molecules in the right half of the box and $N/2 - \Delta N$ the number in the left half at a given instant of time. The probability of a macrostate corresponding to a given ΔN is

$$\begin{aligned}
 P(\Delta N) &= 2^{-N} \frac{N!}{\left(\frac{N}{2} + \Delta N\right)! \left(\frac{N}{2} - \Delta N\right)!} \\
 &\doteq \frac{2^{-N} (2\pi N)^{1/2} \left(\frac{N}{e}\right)^N}{\left[2\pi \left(\frac{N}{2} + \Delta N\right)\right]^{1/2} \left(\frac{N/2 + \Delta N}{e}\right)^{\frac{N}{2} + \Delta N} \left[2\pi \left(\frac{N}{2} - \Delta N\right)\right]^{1/2} \left(\frac{N/2 - \Delta N}{e}\right)^{\frac{N}{2} - \Delta N}} \\
 &\doteq P(\Delta N = 0) e^{-2(\Delta N)^2/N}. \tag{1}
 \end{aligned}$$

In the second line of Eq. (1), we employed Stirling's approximation to second order, that is, including the factor $(2\pi N)^{1/2}$; and, in the third line of Eq. (1), we employed the Gaussian approximation to the binomial distribution [4]. Both of these approximations are already fairly accurate even for N as small as 10 (the former one is not far off even for $N = 2$), and both very rapidly approach perfect accuracy for large N . (The dot equal sign \doteq means very nearly equal to.) For the most probable macrostate, $\Delta N = 0$, Eq. (1)

reduces to

$$\begin{aligned}
P(\Delta N = 0) &= 2^{-N} \frac{N!}{\left[\left(\frac{N}{2}\right)!\right]^2} \\
&\doteq 2^{-N} \frac{(2\pi N)^{1/2} \left(\frac{N}{e}\right)^N}{\left\{ \left[2\pi \left(\frac{N}{2}\right)\right]^{1/2} \left(\frac{N}{e}\right)^{\frac{N}{2}} \right\}^2} = 2^{-N} \frac{(2\pi N)^{1/2} \left(\frac{N}{e}\right)^N}{\pi N \left(\frac{N}{2e}\right)^N} \\
&= 2^{-N} \left(\frac{2}{\pi N}\right)^{1/2} 2^N = \left(\frac{2}{\pi N}\right)^{1/2}. \tag{2}
\end{aligned}$$

Note that employing Stirling's approximation only to first order, that is, neglecting the factor $(2\pi N)^{1/2}$, incorrectly yields $P(\Delta N = 0) = 1$. Applying our result of Eq. (2) to the third line of Eq. (1) yields

$$P(\Delta N) = \left(\frac{2}{\pi N}\right)^{1/2} e^{-2(\Delta N)^2/N}. \tag{3}$$

We thus have the ratio

$$R_N \equiv \frac{P(\Delta N)}{P(\Delta N = 0)} \doteq e^{-2(\Delta N)^2/N}. \tag{4}$$

The entropy of the most probable macrostate is the highest entropy of any individual macrostate, but it is still not the maximum possible entropy that corresponds to true thermodynamic equilibrium. The maximum possible entropy obtains if the system is freely allowed to visit all microstates — and hence also all macrostates — in accordance with Eq. (1), including, albeit typically with much smaller probability than the most probable macrostate, macrostates that are far removed from the most probable one. It is this distribution, and not the most probable macrostate alone, that characterizes true thermodynamic equilibrium [2,3].

Now let a piston be inserted into our box, such that there are exactly $N/2$ gas molecules of either side of the piston. Let the length of our box be L . If the piston (whose width is, for simplicity, taken to be negligible compared with $L/2$) is centered at, say, ΔL to the right of the center of the box, that is, at $\frac{L}{2} + \Delta L$ from the left edge of the box, we have for the expectation value of the number of gas molecules in the left half of the

box, that is to the left of $L/2$,

$$\begin{aligned}
\langle N_{\text{left}} \rangle &= \frac{N}{2} - \langle \Delta N \rangle \\
&\doteq \frac{N}{2} \left[\frac{L/2}{(L/2) + \Delta L} \right] = \frac{N}{2} \left(\frac{L}{L + 2\Delta L} \right) \\
&= \frac{N}{2} \left(\frac{L + 2\Delta L}{L} \right)^{-1} = \frac{N}{2} \left(1 + \frac{2\Delta L}{L} \right)^{-1} \\
&\doteq \frac{N}{2} \left(1 - \frac{2\Delta L}{L} \right). \tag{5}
\end{aligned}$$

Hence,

$$\langle \Delta N \rangle \doteq N \frac{\Delta L}{L}. \tag{6}$$

$\langle \Delta N \rangle$ should not be confused with ΔN . ΔN obtains in the absence of a piston and has a unique value in accordance with Eqs. (1)–(4) and the associated discussions, while $\langle \Delta N \rangle$ is the expectation value of ΔN corresponding to our piston being centered at ΔL to the right of the center of the box, that is, at $\frac{L}{2} + \Delta L$ from its left edge. Since N is large, we can, with negligible error, consider R_N of Eq. (4) to be the same function of $\langle \Delta N \rangle$ as it really is of ΔN . Hence, we can apply Eq. (6) to Eq. (4) and obtain, as an alternative to our expression for R_N , the ratio R_L of the probability that the piston will be centered at ΔL to the right of the center of the box and at $\frac{L}{2} + \Delta L$ from the left edge thereof to the probability that it will be at the exact center of the box at $L/2$,

$$\begin{aligned}
R_N &\equiv \frac{P(\Delta N)}{P(\Delta N = 0)} \doteq e^{-2(\Delta N)^2/N} \doteq e^{-2\langle \Delta N \rangle^2/N} \\
&\doteq R_L \equiv \frac{P(\Delta L)}{P(\Delta L = 0)} \doteq e^{-2N(\frac{\Delta L}{L})^2}. \tag{7}
\end{aligned}$$

Of course, the result of Eq. (7) can also be derived directly via [5]

$$\begin{aligned}
R_L &= \left[\frac{(\frac{L}{2} + \Delta L)(\frac{L}{2} - \Delta L)}{(\frac{L}{2})^2} \right]^{N/2} = \left[\frac{(L + 2\Delta L)(L - 2\Delta L)}{L^2} \right]^{N/2} \\
&= \left[\frac{L^2 - 4(\Delta L)^2}{L^2} \right]^{N/2} = \left[1 - \frac{4(\Delta L)^2}{L^2} \right]^{N/2} \\
&\doteq e^{-2N(\frac{\Delta L}{L})^2}. \tag{8}
\end{aligned}$$

The Gaussian approximation in the last line of Eq. (8) is already fairly accurate even for N as small as 10, and very rapidly approaches perfect accuracy for large N . The direct derivation in accordance with Ref. [5] and Eq. (8) has the advantage of avoiding the approximation of employing *expectation values*, namely $\langle N_{\text{left}} \rangle$ and $\langle \Delta N \rangle$, that is required in the derivation of Eqs. (5)–(7).

Corresponding to the most probable macrostate $\Delta N = 0$ (ΔN being a discrete

random variable) in the absence of a piston, that in the presence of a piston, $\Delta L/L = 0$ ($\Delta L/L$ being a continuous random variable), should be taken of width $\delta l/L$ ($\delta l/2L$ on either side of $L/2$) so as to have the same probability, that is, the probability given by Eq. (2). The Gaussian probability density ρ for $\Delta L/L$ integrated to unity equals R_L times a normalization factor of $(2N/\pi)^{1/2}$ [4]. Thus we have

$$\rho \doteq \left(\frac{2N}{\pi}\right)^{1/2} e^{-2N\left(\frac{\Delta L}{L}\right)^2}, \quad (9)$$

which near the peak of the Gaussian simplifies to

$$\rho \doteq \left(\frac{2N}{\pi}\right)^{1/2} \left[1 - 2N \left(\frac{\Delta L}{L}\right)^2\right]. \quad (10)$$

Setting

$$\begin{aligned} \int_{-\frac{\delta l}{2L}}^{\frac{\delta l}{2L}} \rho d\left(\frac{\Delta L}{L}\right) &= 2 \int_0^{\frac{\delta l}{2L}} \rho d\left(\frac{\Delta L}{L}\right) \\ &\doteq 2 \left(\frac{2N}{\pi}\right)^{1/2} \int_0^{\frac{\delta l}{2L}} \left[1 - 2N \left(\frac{\Delta L}{L}\right)^2\right] d\left(\frac{\Delta L}{L}\right) \\ &= 2 \left(\frac{2N}{\pi}\right)^{1/2} \left[\frac{\delta l}{2L} - \frac{2N}{3} \left(\frac{\delta l}{2L}\right)^3\right] \\ &= 2 \left(\frac{2N}{\pi}\right)^{1/2} \frac{\delta l}{2L} \left[1 - \frac{2N}{3} \left(\frac{\delta l}{2L}\right)^2\right] \\ &= \left(\frac{2}{\pi N}\right)^{1/2} \end{aligned} \quad (11)$$

yields

$$\frac{\delta l}{L} \approx \frac{1}{N}. \quad (12)$$

Since the system must be in *some* macrostate with probability of unity after being released from constraint to the most probable macrostate, this release of constraint corresponds to an increase in entropy of

$$\Delta S = k_B \ln \frac{1}{P(\Delta N = 0)} \doteq k_B \ln \frac{1}{\left(\frac{2}{\pi N}\right)^{1/2}} = k_B \ln \left(\frac{\pi N}{2}\right)^{1/2} = \frac{1}{2} k_B \ln \frac{\pi N}{2}, \quad (13)$$

where k_B is Boltzmann's constant. Thus, ΔS is the negentropy of the system when constrained to be in its most probable macrostate. Since our system is in thermal equilibrium with a heat reservoir at temperature T , being released from this constraint yields

extractable work of

$$W = T\Delta S \doteq \frac{1}{2}k_B T \ln \frac{\pi N}{2}. \quad (14)$$

Our results of Eqs. (13) and (14) strictly obtain for the discrete random variable ΔN (without piston), but they also obtain for the continuous random variable $\Delta L/L$ (with piston) if macrostates, and in particular the most probable macrostate, of the latter are effectively discretized in accordance with Eqs. (9)–(12) and the associated discussions.

The work W is extractable as follows. Let the center of mass of a piston in our box be localized to within $\pm\delta l/2$ of the exact center of the box, that is, to within $L/2 \pm \delta l/2$, where $\delta l \approx L/N$ in accordance with Eq. (12). Thus, δl is much smaller than the fluctuations in the position of the piston resulting from typical, say, one-standard-deviation, fluctuations in the distribution of gas molecules within the box, the latter being $\approx L/N^{1/2}$ [5]. Thus, the piston initially divides the box into left and right halves. Let there be exactly $N/2$ gas molecules in each half of the box, on either side of the piston. Now, release the piston so that it can push on stops both to its left and to its right, thereby doing work. With the piston at the center of the box, at $L/2$, the gas pressure on either side of the piston is equal, and hence the pressure difference between its two sides is zero, according to thermodynamics, that is, on the average. Thus, according to thermodynamics, the piston can do strictly zero work. But, according to statistical mechanics, fluctuations occur about the average value, with the pressure difference sometimes slightly positive, pushing the piston to the right, and sometimes slightly negative, pushing it to the left. Thus, according to statistical mechanics, the piston can do positive work, albeit only a small amount of it. Once pushed to the right of the center of the box, further fluctuations pushing it even further to the right become ever less probable (and of course similarly once pushed to the left). Nevertheless, during the piston's delocalization from within δl to within a larger region $n\delta l = nL/N$, where $n > 1$, all of these pushes from fluctuations will do work on the piston, which in turn will transfer this work to the stops. Strictly, to extract all of the work W given by Eq. (14), $n\delta l$ must equal L less the width of the piston (which for simplicity we take to be negligible compared with $L/2$), but for, say, n as small as 10, very nearly all of W is extractable, because fluctuations in the position of the piston corresponding to $n > 10$ have negligible probability of occurrence [5].

Also, work $W' = k_B T \ln n$ will be obtained from the delocalization of the piston itself considered as a one-molecule ideal gas. But, in order to complete a cycle, work W' must then be expended to localize the piston to within $\delta l/2$ at the center of the box, that is, to within $L/2 \pm \delta l/2$, so W' contributes nothing to the our yield or cost.

Can we simply (re)localize our piston to within $L/2 \pm \delta l/2$, and then obtain the net work W as given by Eq. (14) again? If so, we could violate the second law of thermodynamics, even if only weakly. The important question is: In order to (re)localize our piston to within $L/2 \pm \delta l/2$, must we expend only work W' , or work $W + W'$? If the former, then we can violate the second law, albeit only weakly; if the latter, then we cannot.

Alas, at least *prima facie*, it seems that we cannot. For we have paid for the work W with the loss of the information that there are *exactly* $N/2$ molecules in each half of the

box, and with the loss of information associated with delocalization of the piston. When we try to (re)localize our piston to within $\pm\delta l/2$ of the center of the box, there could be a, say, two-standard-deviation magnitude fluctuation in the distribution of gas molecules into the left half of the box. Then our piston will be pushed preferentially to the right, and much more work will be done against the right stops than against the left stops. Thus, the “tightness” settings of the stops corresponding to there being *exactly* $N/2$ molecules in each half of the box are no longer the optimum settings for the extraction of work. We must then either determine the new initial ΔN and readjust the tightness settings of the stops accordingly, or (with the piston temporarily removed from the box) ensure that $\Delta N = 0$ again, that is, that there are again *exactly* $N/2$ gas molecules in each half of the box. And doing either is not free. Whether the cost is attributed to observation [6] or to erasure of memory [7], it is equal to the net work W as given by Eq. (14). Thus we just barely break even, and this is assuming perfect, reversible, operation. With any irreversibility, which obtains in any real system but which we did not consider, we do not just barely break even — we lose.

III. RELATION TO THE ADIABATIC PISTON PROBLEM

The piston considered in Sec. II is diathermal, that is, in an isothermal environment at temperature T . It is interesting, however, to consider the relationship of our discussions in Sec. II to the adiabatic piston problem [8]. For an adiabatic piston, the fluctuations in piston position are much larger, in fact M/m times larger, than in the diathermal case, where M is the mass of the piston and m is the mass of each gas molecule [8]. But they still obey a binomial (for all practical purposes, for $N \gtrsim 10$, Gaussian) distribution whose maximum is at the center of the box, that is, at $L/2$, albeit one whose standard deviation is M/m times larger than in the diathermal case [8]. In the adiabatic case, the pressure of the gas on either side of the piston remains *essentially* constant irrespective of piston position, but cannot remain *exactly* constant irrespective of piston position, because the binomial (or Gaussian) peak at $L/2$ implies that there must be, *on the average* (despite the large fluctuations about the average), *some* restoring force towards $L/2$, albeit one only m/M as strong as in the diathermal case.

Also, equality of pressures on either side of the piston irrespective of its position requires, in accordance with the ideal gas law, that the absolute temperatures of the gas on the left and right sides of the piston must be proportional to the respective volumes occupied thereby at any given instant of time [8]. But it is difficult to understand how this obtains physically. The gas on the side of the piston occupying the larger volume following the completion of a fluctuation away from the average must have done work in compressing the gas on the side occupying the smaller volume, so one would expect that the gas on the side occupying the larger volume must, at the completion of this fluctuation, be cooler than that on the side occupying the smaller volume. But then, of course, the gas pressures on both sides of the piston could not be equal — the pressure must then be larger on the side occupying the smaller volume, which would then tend to

return the piston towards $L/2$, albeit only m/M times as strongly as in the diathermal case.

As has been emphasized, our initial state, wherein the piston is localized to within $L/2 \pm \delta l/2$, is *not* the state of maximum entropy and zero extractable work that corresponds to true thermodynamic equilibrium. It is the most probable (discretized) macrostate, but as has been emphasized, the most probable macrostate alone is *not* the state of maximum entropy and zero extractable work — the distribution over *all* accessible macrostates is. The entropy increases once the piston is released and allowed to wander away from $L/2 \pm \delta l/2$, and hence information regarding its position is lost. Since the piston wanders much further, and hence suffers much greater delocalization, in the adiabatic case than in the diathermal case [8], this entropy increase is considerably larger in the former case than in the latter, and hence so would be the work required to (re)localize the piston to within $L/2 \pm \delta l/2$. Thus, an initial state wherein the piston is localized to within $L/2 \pm \delta l/2$ is much further removed from true thermodynamic equilibrium in the adiabatic case than in the diathermal case. Hence, the thermodynamic cost of initially preparing the system, that is, of initially localizing the piston to within $L/2 \pm \delta l/2$, is considerably larger in the adiabatic case than in the diathermal case, and this cost must be accounted for. It is not certain if the adiabatic piston problem is or is not thereby resolved without requiring a violation of the second law of thermodynamics. But, in any case, perhaps a formulation of the second law in terms of work [8], supplementing those in terms of entropy, may be helpful in the study, and possibly even in the resolution, of the adiabatic piston problem.

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APPENDIX: THE 2-MOLECULE SYSTEM

Up until now, we have assumed that N is large enough that the Gaussian approximations in Eqs. (1), (3), (4), (7), and (8) are valid. In this Appendix, we consider N so small that these Gaussian approximations are invalid, specifically, the smallest possible even N , namely, $N = 2$. While the $N = 2$ case reveals no new principles, it nevertheless displays some interesting features.

For $N = 2$, we have, without a piston in our box,

$$P(\Delta N = 0) = 1/2. \quad (15a)$$

$$P(\Delta N = \pm 1) = 1/4. \quad (15b)$$

With a piston therein, and with exactly $N/2 = 1$ molecule on either side of the piston, we have

$$\begin{aligned} R_L &= \frac{(\frac{L}{2} + \Delta L)(\frac{L}{2} - \Delta L)}{(\frac{L}{2})^2} = \frac{(L + 2\Delta L)(L - 2\Delta L)}{L^2} \\ &= \frac{L^2 - 4(\Delta L)^2}{L^2} = 1 - 4\left(\frac{\Delta L}{L}\right)^2. \end{aligned} \quad (16)$$

Thus normalization

$$\begin{aligned} \eta \int_{-1/2}^{1/2} R_L d\left(\frac{\Delta L}{L}\right) &= \eta \int_{-1/2}^{1/2} \left[1 - 4\left(\frac{\Delta L}{L}\right)^2\right] d\left(\frac{\Delta L}{L}\right) \\ &= 2\eta \int_0^{1/2} \left[1 - 4\left(\frac{\Delta L}{L}\right)^2\right] d\left(\frac{\Delta L}{L}\right) \\ &= \eta \times \frac{2}{3} = 1 \end{aligned} \quad (17)$$

yields a normalization factor of

$$\eta = \frac{3}{2} \quad (18)$$

and hence a probability density of

$$\rho = \frac{3}{2} \left[1 - 4\left(\frac{\Delta L}{L}\right)^2\right]. \quad (19)$$

Corresponding to a most probable macrostate with $P(\Delta N = 0) = 1/2$, in accordance

with Eq. (15a), we set [similarly to Eqs. (11) and (12)]

$$\begin{aligned} \frac{3}{2} \int_{-\frac{\delta l}{2L}}^{\frac{\delta l}{2L}} \left[1 - 4 \left(\frac{\Delta L}{L} \right)^2 \right] d \left(\frac{\Delta L}{L} \right) &= 3 \int_0^{\frac{\delta l}{2L}} \left[1 - 4 \left(\frac{\Delta L}{L} \right)^2 \right] d \left(\frac{\Delta L}{L} \right) \\ &= 3 \left[\frac{\delta l}{2L} - \frac{4}{3} \left(\frac{\delta l}{2L} \right)^3 \right] = \frac{3\delta l}{2L} \left[1 - \frac{4}{3} \left(\frac{\delta l}{2L} \right)^2 \right] \approx \frac{3\delta l}{2L} = \frac{1}{2}, \end{aligned} \quad (20)$$

whence

$$\frac{\delta l}{L} \approx \frac{1}{3}. \quad (21)$$

Note that, for the $N = 2$ case, diathermal and adiabatic fluctuations are of comparable magnitudes. Also note that, for the $N = 2$ case, the *relative* negentropy, that is, the negentropy per molecule, and also the extractable work per molecule, is very large for even for a diathermal system constrained to its most probable macrostate. The *absolute* negentropy and extractable work corresponding to a diathermal system being constrained to its most probable macrostate increases with increasing N , but only logarithmically [recall Eqs. (13) and (14)]. Thus, vastly larger *total* most-probable-macrostate negentropy and extractable work obtains if our diathermal N -gas-molecule system is divided into $N/2$ 2-molecule systems (for simplicity, let $N/2$ be even, which then of course automatically implies that N is also even).

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6. The older viewpoint — that work and hence negentropy must be expended to locate the particle — is discussed in, for example, Léon Brillouin, *Science and Information Theory*, 2nd edition, Academic, New York, 1962. A review of the older viewpoint is provided in, for example, W. Ehrenberg, “Maxwell’s Demon,” *Sci. Am.* **217** (5), pp. 103–110 (November, 1967). (Cited references are on p. 156.)

7. The newer viewpoint — that the only step in the process that necessarily entails an entropy cost is the erasure of memory — is discussed in C. H. Bennet, “The Thermodynamics of Computation — a Review,” *Int. J. Theor. Phys.* **21**, 905–940 (1982). (See especially Sec. 5.) A review of the newer viewpoint is provided in C. H. Bennet, “Demons, Engines, and the Second Law,” *Sci. Am.* **257** (5), pp. 108–116, (November, 1987). (Cited references are on pp. 150–151.)

8. See, for example, Bruno Crosignani and Paolo Di Porto, “Random Fluctuations of Diathermal and Adiabatic Pistons,” *Found. Phys.* **37**, 1707–1715 (2007); and also Bruno Crosignani and Paolo Di Porto, “On the validity of the second law of thermodynamics in the mesoscopic realm,” *Europhys. Lett.* **53**, 290–296 (2001). See also references cited in these two works. [We note that a further study related to the adiabatic piston problem appears in this volume. But this study concerns long-term restriction of accessibility to only a fraction of a system’s entire phase-space volume and the consequent slowness in attainment of accessibility to its entire phase-space volume and hence of true thermodynamic equilibrium, rather than, as the two aforementioned papers, fluctuations away from the most probable macrostate interpreted either as a violation of a classical formulation of the second law of thermodynamics that does not consider fluctuations, or consistently with a statistical-mechanical formulation thereof that encompasses fluctuations. (Various formulations of the second law are reviewed in Ref. [1].) See, in this volume, Eugenio DelRe, Paolo Di Porto, Stefano Di Sabatino, and Bruno Crosignani, “Reduced statistical fluctuations of the position of an object partitioning in two its environment,” (20 pages).]

9. See, for example, Peter Atkins and Julio de Paula, *Physical Chemistry*, 7th edition, Freeman, New York, 2002, Secs. 2.1–2.2 and 4.2c. See especially Secs. 2.2b–2.2c and the second paragraph of Sec. 4.2.c (unfortunately, these valuable discussions were omitted from the 8th and 9th editions). See also A. E. Allahverdyan and Th. M. Nieuwenhuizen, “A mathematical theorem as the basis for the second law: Thomson’s formulation applied to equilibrium,” *Physica A* **305**, 542–552 (2002); and A. John Mallinckrodt and Harvey S. Leff, “All about work,” *Am. J. Phys.* **60**, 356–364 (1992).