

Increase of Boltzmann entropy in a quantum forced harmonic oscillator

Michele Campisi*

Institut für Physik, Universität Augsburg, Universitätsstr. 1, D-86135, Augsburg, Germany

(Received 30 June 2008; published 24 November 2008)

Recently, a quantum-mechanical proof of the increase of Boltzmann entropy in quantum systems that are coupled to an external classical source of work has been given. Here we illustrate this result by applying it to a forced quantum harmonic oscillator. We show plots of the actual temporal evolution of work and entropy for various forcing protocols. We note that entropy and work can be partially or even fully returned to the source, although both work and entropy balances are non-negative at all times in accordance with the minimal work principle and the Clausius principle, respectively. A necessary condition for the increase of entropy is that the initial distribution is decreasing (e.g., canonical). We show evidence that for a nondecreasing distribution (e.g., microcanonical), the quantum expectation of entropy may decrease slightly. Interestingly, the classical expectation of entropy cannot decrease, irrespective of the initial distribution, in the forced harmonic oscillator.

DOI: [10.1103/PhysRevE.78.051123](https://doi.org/10.1103/PhysRevE.78.051123)

PACS number(s): 05.30.-d, 05.70.Ln

I. INTRODUCTION

Recently, it has become clear that the formulation of the second law of thermodynamics in terms of the *minimal work principle* holds as a quantum-mechanical theorem [1–4]. That is, the unitary law of quantum-mechanical evolution implies that the work W done by a classical external source on an isolated quantum system is larger than or equal to the value \tilde{W} corresponding to the quasistatic limit. This is summarized as

$$W \geq \tilde{W}, \quad (1)$$

where

$$W \doteq \text{Tr} \hat{H}(t_f) \hat{\rho}(t_f) - \text{Tr} \hat{H}(t_i) \hat{\rho}(t_i) \quad (2)$$

and $\hat{\rho}$ is the density matrix. The result in (1) is of great theoretical and practical relevance as it shows in a clear way how thermodynamic laws already exist at the microscopic quantum level. When the system is initially in a canonical equilibrium, Eq. (1) can be derived from the Jarzynski equality [5,6], but Eq. (1) holds in general for any initial equilibrium characterized by decreasing probabilities. Recently, it has been proven that, under the same assumptions also the Clausius formulation of the second law holds as a theorem in quantum mechanics [3,7]. The approach, presented originally by Tasaki and later rediscovered in [7], is very novel if compared to the traditional approaches, and it is strictly related to the approach of [1–4], summarized in Eq. (1). The main feature of the new approach is that it employs Boltzmann entropy, which is a function of the energy of the system and of the external parameters, instead of H entropy, Gibbs entropy, von Neumann entropy, or Tolman entropy, which instead are functionals of the system probability distribution (or density matrix). When studying the Boltzmann entropy, the Clausius principle follows directly as a consequence of the unitary and time-reversal symmetric quantum or classical evolution (without any assumption that would break the

time-reversal invariance) in the same way as Eq. (1) does [7].

It must be stressed that there are many different formulations of the second law of thermodynamics, which are not all equivalent [8]. Oftentimes the second law is understood as a condition on the monotonic increase of entropy. The Boltzmann entropy approach that we study here instead is based on the very first historical formulation of the second law of thermodynamics in terms of entropy, namely the Clausius principle, which states [8]:

“For every non-quasi-static process in a thermally isolated system that begins and ends in an equilibrium state, the entropy of the final state is greater than or equal to that of the initial state, and for every quasistatic process in a thermally isolated system, the entropy of the final state is equal to that of the initial state.”

Note that this formulation does not imply that the entropy is a monotonically increasing function of time: all it says is that the final entropy is larger than the initial.

From a mechanical point of view, (non-)quasi-static processes are modeled as (non)adiabatic changes of an external parameter, on which the Hamiltonian depends parametrically. Thus, the idea behind the present approach is that of studying the average change of Boltzmann entropy due to the action of an external source of work that makes the Hamiltonian time-dependent. Toda *et al.* [9] note that during the nonadiabatic transformation, the distribution of energies inevitably drifts and diffuses due to the finite transition probabilities between different states (see also [10]). They suggest that this mechanism is at the origin of the second law. The work of Refs. [3,7] proves formally that the drift and diffusion of energy are responsible for the increase of Boltzmann entropy. The proof of this result is almost identical to the proof of the minimal work principle (1) given in [1,3,4]. A different proof, valid only for high-dimensional Hamiltonian classical chaos, has been given by Sasa and Komatsu [11].

Here we study the Boltzmann entropy increase for an exactly solvable model, namely the forced harmonic oscillator. This has recently attracted the attention of Talkner *et al.*, who have reported on the statistics of work performed on the

*Michele.Campisi@physik.uni-augsburg.de

system [12]. Such a system can now be studied experimentally by means of multisegmented optical ion traps [13].

The paper is organized as follows. Section II is devoted to a review of the quantum-mechanical proof of entropy principle as given in [7]. In Sec. III, we apply it to the forced harmonic oscillator. A discussion of the results is presented in Sec. IV. In the Appendix, we offer a derivation of the time-dependent quantum transition probabilities of the forced harmonic oscillator based on Wigner functions.

II. QUANTUM-MECHANICAL PROOF OF THE CLAUSIUS PRINCIPLE

Consider an isolated, nondegenerate, time-dependent quantum system. Let

$$\hat{H}(t) = \sum_{k=0}^K \varepsilon_k(t) |k, t\rangle \langle k, t| \quad (3)$$

be the time-dependent Hamiltonian, where $|k, t\rangle$ are the instantaneous eigenvectors and $\varepsilon_k(t)$ are the corresponding instantaneous eigenvalues. These are assumed to be nondegenerate at all times and to not cross each other.

Let the system be initially (that is at time t_i) in an equilibrium state described by a density matrix $\hat{\rho}(t_i) = \sum_{k=0}^K p_k |k, t_i\rangle \langle k, t_i|$, which is diagonal over the Hamiltonian basis $\{|k, t_i\rangle\}$. Let the density-matrix eigenvalues be ordered in a decreasing fashion,

$$p_m \leq p_n \text{ if } m > n. \quad (4)$$

This is an important assumption that is used explicitly in the proof. As time passes, transitions will occur between the quantum states according to the transition probabilities

$$|a_{kn}(t_i, t_f)|^2 = |\langle n, t_f | \hat{U}(t_i, t_f) | k, t_i \rangle|^2, \quad (5)$$

where $\hat{U}(t_i, t_f)$ is the unitary time evolution operator. As a consequence, the density matrix evolves to some $\hat{\rho}(t_f)$. The minimal work principle of Eq. (1) has been proven under these assumption with work defined as $W = \text{Tr}[\hat{\rho}(t_f) \hat{H}(t_f) - \hat{\rho}(t_i) \hat{H}(t_i)]$ [1,3,4]. Here instead we are interested in the change in the expectation value of Boltzmann entropy.

In classical statistical mechanics, we have two possible definitions for Boltzmann entropy, which are sometimes referred to as ‘‘surface’’ and ‘‘volume’’ entropies [14,15]. The former is the logarithm of the instantaneous density of states $\Omega(E, t)$, whereas the latter is the logarithm of the volume of phase space enclosed by the instantaneous constant energy hypersurface $\Phi(E, t)$. The two are known to be equivalent in the case of large systems with short-range interactions, but when small systems are taken into account the equivalence breaks [16] and the proper definition is the ‘‘volume entropy’’ [7,14–25],

$$S^{\text{cl}}(E, t) = \ln \Phi(E, t), \quad (6)$$

$$\Phi(E, t) \doteq \int_{H(\mathbf{q}, \mathbf{p}; t) \leq E} \frac{d^{3N} \mathbf{q} d^{3N} \mathbf{p}}{h^{3N}}. \quad (7)$$

Here we are interested in constructing the quantum counterpart of Eq. (6). Thus we proceed with its quantization. This is accomplished by means of the semiclassical approximation. In one dimension (1D), the volume integral $\Phi(E, t)$ is the *reduced action* [26], which, according to the Bohr-Sommerfeld quantization rule [27], is quantized as

$$\Phi = \oint \frac{pdq}{h} = n + \frac{1}{2}. \quad (8)$$

The operator that takes on these values over the Hamiltonian eigenstates is evidently the following:

$$\hat{N}(t) + \hat{I}/2, \quad (9)$$

where $\hat{N}(t)$ is the *quantum number operator* defined as

$$\hat{N}(t) \doteq \sum_{k=0}^K k |k, t\rangle \langle k, t| \quad (10)$$

and \hat{I} is the identity operator. Thus the quantum version of Boltzmann entropy is simply

$$\hat{S}(t) \doteq \ln[\hat{N}(t) + \hat{I}/2]. \quad (11)$$

The same formula applies to multidimensional systems by noting that the integral Φ of Eq. (6) counts the number of quantum states with energy not above a certain energy $E = \varepsilon_n$ [28]. Assuming nondegeneracy, such a number is $n + \frac{1}{2}$, where we set the convention that the ground state counts as half a state [41].

The definition in Eq. (10) is the generalization of the harmonic-oscillator number operator $a^\dagger a$ to any possibly time-dependent and multidimensional quantum system with nondegenerate energy eigenvalues.

The change of entropy between t_i and some later time t_f reads

$$S_f - S_i = \text{Tr}[\hat{\rho}(t_f) \hat{S}(t_f) - \hat{\rho}(t_i) \hat{S}(t_i)]. \quad (12)$$

The proof that this entropy change is non-negative can be summarized as follows (see [7] for a detailed discussion). Let us denote the probability that the system is found in state n at time t_f by p'_n , where evidently $p'_n = \sum_{k=0}^K p_k |a_{kn}(t_i, t_f)|^2$. Simple calculations lead to

$$S_f - S_i = \sum_{n=0}^K (p'_n - p_n) \ln(n + 1/2). \quad (13)$$

Using the ‘‘summation by parts’’ rule [29], Eq. (13) becomes

$$S_f - S_i = \sum_{m=0}^K \ln \frac{m + \frac{3}{2}}{m + \frac{1}{2}} \sum_{n=0}^m (p_n - p'_n). \quad (14)$$

Using the property of the coefficients $|a_{kn}|^2$ of forming a doubly stochastic matrix [i.e., $\sum_{k=0}^K |a_{kn}(t_i, t_f)|^2 = \sum_{n=0}^K |a_{kn}(t_i, t_f)|^2 = 1$ and $|a_{kn}(t_i, t_f)|^2 \geq 0$], and the ordering of probabilities (4), it can be shown [4,7] that $\sum_{n=0}^m (p_n - p'_n)$

≥ 0 , which, by noting that $\ln \frac{m+3/2}{m+1/2} > 0$ in Eq. (14), implies

$$S_f \geq S_i. \quad (15)$$

A. Remarks

Like Eq. (1), Eq. (15) holds as a consequence of the laws of quantum mechanics for every time-dependent nondegenerate quantum-mechanical system that is in an equilibrium state described by decreasing probabilities at time t_i . As such, it is an exact *nonequilibrium* result. In case the perturbation is adiabatic, the quantum adiabatic theorem would ensure that no transition will occur between states with different quantum number [30] so that $p'_n = p_n$ and consequently $S_f = S_i$. Note that, like the Clausius principle, Eq. (15) in no way implies that the expectation value of the entropy is monotonically increasing. Equation (15) says *only* that after time t_i , the expectation value of the entropy operator will never be less than the initial value. This does not rule out the possibility that for two times $t_1 > t_2 > t_i$ one might have $S_1 < S_2$. The \geq sign in Eq. (15) does not stem from a breakdown of the time-reversal symmetry of the dynamics but rather from the fact that the initial state is of a special form: the density matrix is diagonal and its eigenvalues are ordered in a decreasing fashion. In accordance with the *minus first law* [31], the asymmetry of thermodynamic laws is entailed in the asymmetric character of the concept of equilibrium.

B. The classical limit

The classical limit is obtained from the quantum treatment by letting the phase-space cell size vanish. In this limit, the discrete quantity $n + \frac{1}{2}$ becomes the continuous quantity Φ , and the probability p_n becomes the probability density function $P(\Phi)$ of having one member of the ensemble being on an orbit that encloses a volume Φ . Accordingly, all sums over n will be replaced with integrals over $d\Phi$. The coefficients $|a_{kn}|^2$ become the ‘‘classical transition probability’’ $A(\Phi, \Theta; t_i, t_f)$ that a representative point which is on an orbit that encloses a volume Φ at time t_i will be found on an orbit that at time t_f encloses a volume Θ [42]. Accordingly, the distribution at a certain time t_f relates to the initial distribution $P_{t_i}(\Phi)$ through [7] $P_{t_f}(\Theta) = \int d\Phi A(\Phi, \Theta; t_i, t_f) P_{t_i}(\Phi)$. In the classical limit, the quantum-mechanical requirement of nondegeneracy (only one state per energy eigenvalue) becomes the requirement of ergodicity (only one trajectory per energy level) [43], and the requirement in Eq. (4) becomes the requirement that $P_{t_i}(\Phi)$ be monotonically decreasing. Then one obtains [7] [compare with Eq. (13)]

$$S_f^{\text{cl}} - S_i^{\text{cl}} = \int_0^\infty d\Phi [P_{t_f}(\Phi) - P_{t_i}(\Phi)] \ln \Phi \geq 0. \quad (16)$$

III. APPLICATION: FORCED HARMONIC OSCILLATOR

Time-dependent harmonic oscillators have attracted much attention recently in the field of quantum thermodynamics of small systems [12,32,33]. They are particularly important be-

cause they can be solved exactly [34] and are relevant in many applications, such as, for example, optical ion traps [35], which constitute a promising technological asset for the implementation of quantum computers [13]. In this section, we will study the change of expectation of Boltzmann entropy for the driven harmonic oscillator. We first treat the classical and quantum cases in general, and then we apply them to specific forcing protocols.

A. Classical case

The Hamiltonian reads

$$H(x, p, t) = \frac{p^2}{2m} + \frac{m}{2} \omega^2 \left(x - \frac{f(t)}{m\omega^2} \right)^2. \quad (17)$$

For simplicity, we set $m=1$, $\omega=1$, $t_i=0$, $f(0)=0$. The Hamilton equations can be solved with the aid of Laplace transforms. The solution reads

$$\begin{pmatrix} x(t) \\ p(t) \end{pmatrix} = \begin{pmatrix} \cos t & \sin t \\ -\sin t & \cos t \end{pmatrix} \begin{pmatrix} x_0 \\ p_0 \end{pmatrix} + \begin{pmatrix} S(t) \\ C(t) \end{pmatrix}, \quad (18)$$

where

$$S(t) = \int_0^t dt' f(t') \sin(t-t'), \quad (19)$$

$$C(t) = \int_0^t dt' f(t') \cos(t-t'). \quad (20)$$

Let us now calculate the energy E at time t of a representative point that is initially at (x_0, p_0) . It is $E(t) = \frac{p(t)^2}{2} + \frac{[x(t)-f(t)]^2}{2}$. After some algebra, one gets

$$E(t) = E_0 + W(t) + 2\sqrt{E_0 W(t)} \cos[t - \varphi - \theta(t)], \quad (21)$$

where E_0 is the initial energy $E_0 = \frac{p_0^2 + x_0^2}{2}$, φ is the initial phase $\varphi = \arctan \frac{p_0}{x_0}$, and $W(t)$ and $\theta(t)$ are defined as

$$W(t) = \frac{C(t)^2}{2} + \frac{[S(t) - f(t)]^2}{2}, \quad (22)$$

$$\theta(t) = \arctan \frac{S(t) - f(t)}{C(t)}. \quad (23)$$

Starting at time $t_i=0$ with a microcanonical ensemble of energy E_0 , and letting the ensemble evolve to time t , Eq. (21) allows us to calculate the average energy of the evolved ensemble, which in general is no longer δ -distributed in the energy space. Figure 1 shows the evolved distribution. As will become clearer later, such distribution is merely the classical transition probability $A(\Phi, \Theta, 0, t)$. In order to calculate the average energy, it is sufficient to average Eq. (21) over the initial phase φ . One immediately gets

$$\langle E \rangle_{E_0, t} = E_0 + W(t), \quad (24)$$

where $\langle \cdot \rangle_{E_0, t}$ denotes the average over the distribution that results from the evolution (at time t) of the initial microca-

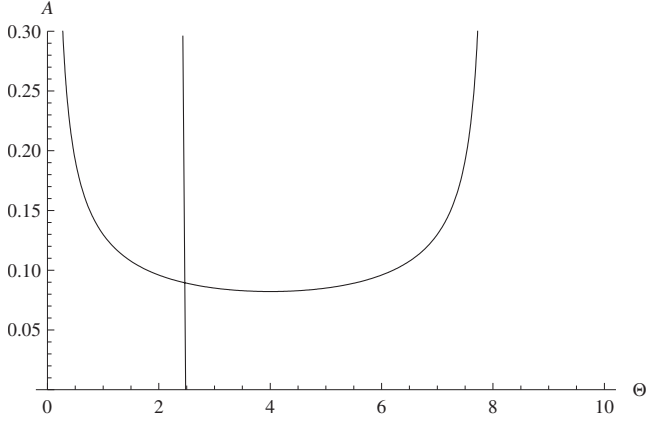


FIG. 1. Classical transition probability, Eq. (31), for $\Phi=2.5$ and $W=1.5$. The initial microcanonical distribution evolves to a U-shaped distribution.

nonical distribution of energy E_0 . Equation (24) tells us that $W(t)$ represents the work done on the ensemble at time t .

By squaring Eq. (21) and averaging over φ , one gets $\langle E(t)^2 \rangle_{E_0}$. Then one easily finds

$$\Delta E_{E_0,t} = \langle E^2(t) - \langle E \rangle_{E_0,t}^2 \rangle_{E_0,t} = 2E_0W(t). \quad (25)$$

Let us now turn our attention to the enclosed volume variable Φ and its connection to the energy. Let us pick a representative point \tilde{x}, \tilde{p} in phase space at a certain time t , and draw in phase space the circular orbit $H(x, p, t) = H(\tilde{x}, \tilde{p}, t)$. Let \tilde{r} be the radius of such an orbit. Then $\frac{\tilde{r}^2}{2}$ will be the energy E of the system and the enclosed volume Φ will be given by $\frac{2\pi}{h}E = \frac{E}{h}$. Let us then choose the units in such a way that $\hbar=1$. Then, in this specific problem, and with units adopted, *energy and enclosed volume coincide*. Thus we can write the enclosed volume at time t , Θ , in terms of the volume enclosed at time $t=0$, Φ , as

$$\Theta = \Phi + W(t) + 2\sqrt{\Phi W(t)} \cos[t - \varphi - \theta(t)]. \quad (26)$$

The average enclosed volume and its square deviation read

$$\langle \Theta \rangle_{\Phi,t} = \Phi + W(t), \quad (27)$$

$$\langle \Delta \Theta^2 \rangle_{\Phi,t} = 2\Phi W(t), \quad (28)$$

where Φ and Θ are the initial and final enclosed volume, respectively. The final entropy is given by the average over φ of the logarithm of Eq. (26),

$$\langle \ln \Theta \rangle_{\Phi,t} = \int_0^{2\pi} \frac{d\varphi}{2\pi} \ln[\Phi + W(t) + 2\sqrt{\Phi W(t)} \cos \varphi].$$

This integral is known [36] and gives

$$\langle \ln \Theta \rangle_{\Phi,t} = \ln[\max(\Phi, W(t))]. \quad (29)$$

Note that trivially one has

$$\langle \ln \Theta \rangle_{\Phi,t} \geq \ln \Phi. \quad (30)$$

That is, the Clausius formulation is satisfied *classically* in this example even for an initial microcanonical distribution. This means that the condition of decreasing probability (4) is

sufficient but not necessary for the *classical* validity of the Clausius principle. According to Eq. (22), W is definite positive, $W \geq 0$. Since the enclosed volume is an adiabatic invariant, then, for an adiabatic protocol, the final enclosed volume, i.e., the final energy, is equal to the initial one. So the quasistatic work is zero, $\tilde{W}=0$. Therefore, the minimal work principle $W \geq \tilde{W}$ is also satisfied here, regardless of whether the initial ensemble is distributed according to a decreasing probability or not.

The classical transition probability $A(\Phi, \Theta; 0, t)$ of ending up enclosing a volume Θ from a point that initially encloses a volume Φ can be easily calculated as $A(\Phi, \Theta; 0, t) = 1/(\pi |\frac{d\Theta}{d\varphi}|)$. Using Eq. (26), we get

$$A(\Phi, \Theta; 0, t) = \frac{1}{\pi \sqrt{4\Phi W(t) - [\Theta - \Phi - W(t)]^2}}. \quad (31)$$

One can check that $A(\Phi, \Theta; 0, t)$ is doubly stochastic. The average of any function of Θ is conveniently expressed in terms of A as follows:

$$\begin{aligned} \langle f(\Theta) \rangle_{\Phi,t} &= \int_0^{2\pi} \frac{d\varphi}{2\pi} f[\Phi + W(t) + 2\sqrt{\Phi W(t)} \cos \varphi] \\ &= \int d\Theta A(\Phi, \Theta; 0, t) f(\Theta). \end{aligned} \quad (32)$$

1. Canonical initial condition

The classical canonical distribution reads

$$P_0(\Phi) d\Phi = \beta e^{-\beta\Phi} d\Phi. \quad (33)$$

The initial and final classical entropies are

$$S_0^{\text{cl}} = \beta \int_0^\infty e^{-\beta\Phi} \ln \Phi d\Phi, \quad (34)$$

$$S_t^{\text{cl}} = \beta \int_0^\infty e^{-\beta\Phi} \ln[\max(\Phi, W(t))] d\Phi. \quad (35)$$

Simple calculations lead to

$$S_t^{\text{cl}} - S_0^{\text{cl}} = -\beta W(t) \int_0^1 e^{-\beta W(t)x} \ln x dx, \quad (36)$$

which is clearly positive since $W(t)$ is positive.

B. Quantum case

The quantum transition probabilities $|a_{nm}|^2$ are expressed in terms of Charlier polynomials $C(m, n|W)$ [37],

$$C(m, n|W) = \sum_l^{\max(m,n)} \frac{(-1)^l m! n!}{l!(m-l)!(n-l)! W^l}, \quad (37)$$

$$|a_{nm}(t, 0)|^2 = \frac{e^{-W(t)} W^{m+n}(t)}{m! n!} [C(m, n|W(t))]^2, \quad (38)$$

where W is given by the classical formula (22). The quantum transition probabilities have been derived by Husimi [37] by

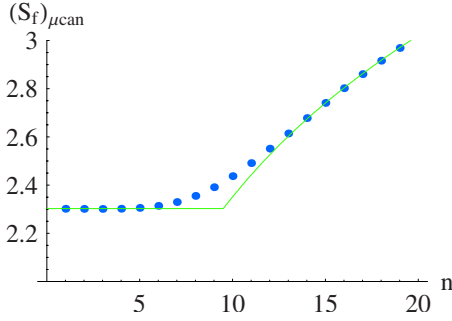


FIG. 2. (Color online) Quantum entropy as a function of the initial quantum number n for $W=10$. Solid line: classical case, Eq. (29). Dots: quantum case, Eq. (41); the sum has been truncated at $m=1000$. The quantum phenomena smooth out the sharp angle in the classical graph.

solving the Schrödinger equation. An alternative derivation, based on path-integral methods, has been given by Feynman [34]. In order to highlight the relations between classical and quantum transition probabilities, we offer yet another derivation based on Wigner phase-space functions in the Appendix.

The average quantum number and its square deviation have been given by Husimi [37]. Their expressions are analogous to the classical formulas [compare with Eqs. (27) and (28)]

$$\langle m \rangle_{n,t} = n + W(t), \tag{39}$$

$$\langle \Delta m^2 \rangle_{n,t} = 2(n + 1/2)W(t), \tag{40}$$

where the symbol $\langle \cdot \rangle_{n,t}$ denotes average over the distribution $\hat{\rho}_t^{(n)}$, resulting from the temporal evolution of the initial microcanonical distribution $\hat{\rho}_0^{(n)} = |n, 0\rangle\langle n, 0|$. Equation (39) says that $W(t)$ is the quantum-mechanical work done on the initial microcanonical ensemble. Note that it is exactly the same as the classical work. Also W is determined once and for all by the forcing function $f(t)$ and it does not depend on the initial state of the system. This implies that the average work is always the same for any possible initial classical or quantum ensemble. It is important to stress that the quantum transition probability depends on time through W . Thus also the entropy depends on time through W , which is a fundamental quantity in this problem.

The microcanonical quantum entropy reads

$$\langle \ln(m + 1/2) \rangle_{n,t} = \sum_m |a_{nm}(t)|^2 \ln(m + 1/2). \tag{41}$$

Unlike the average quantum number and square deviation, this does not correspond exactly to the classical expression. Figure 2 shows the quantum and classical average microcanonical expectation of entropy. Unlike work, entropy does depend on the initial quantum number n , so different entropy changes characterize different initial ensembles. Note how the quantum effects smooth out the sharp angle that appears in the classical case in Fig. 2. A close inspection of Eq. (41) shows that the Clausius principle is not satisfied in general for the microcanonical initial condition in the quantum case, that is,

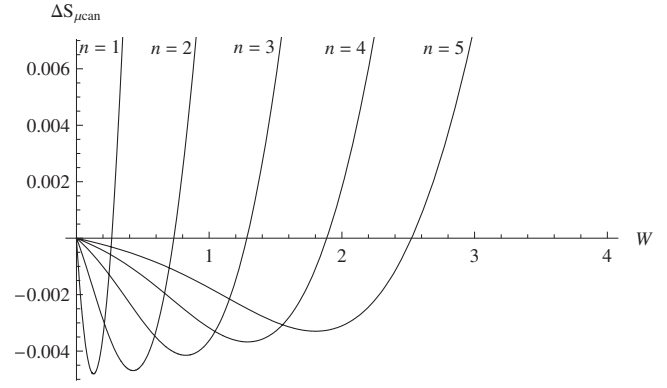


FIG. 3. Quantum entropy change for an initial microcanonical condition with $n=1, 2, 3, 4, 5$, as a function of work W .

$$\langle \ln(m + 1/2) \rangle_{n,t} \neq \ln(n + 1/2). \tag{42}$$

This is in agreement with the discussion of possible violations of the second law given in Ref. [29]. Note that the minimal work principle, instead, is satisfied for the microcanonical initial condition because, from Eq. (39), $W \geq 0$.

Figure 3 shows the dependence of the quantum expectation of entropy on the work W for a microcanonical initial condition. Note that for small W , the entropy change is slightly negative.

1. Canonical initial condition

Let the initial density matrix be canonical,

$$\hat{\rho}_0 = (1 - e^{-\beta}) \sum_n e^{-\beta n} |n, 0\rangle\langle n, 0|. \tag{43}$$

We have

$$S_t - S_0 = (1 - e^{-\beta}) \sum_n e^{-\beta n} [\langle \ln(m + 1/2) \rangle_{n,t} - \ln(n + 1/2)]. \tag{44}$$

Since p_n is decreasing in this case, this entropy change is non-negative.

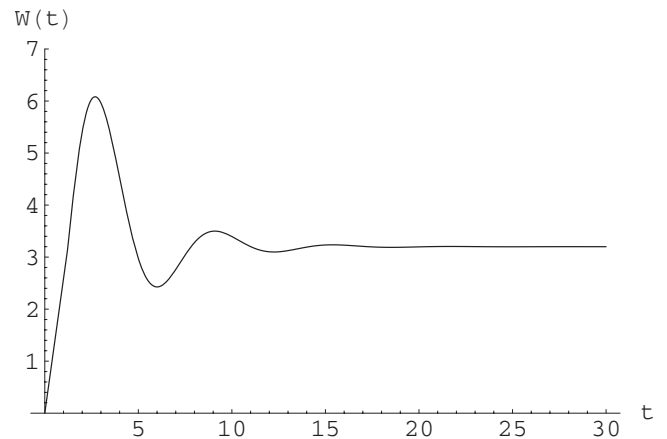


FIG. 4. Work as a function of time for the exponential driving protocol in Eq. (45) with $L=8$, $\tau=3$. This is the same in the quantum and classical cases.

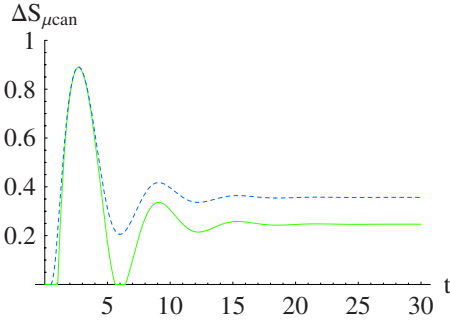


FIG. 5. (Color online) Entropy change as a function of time for the exponential driving protocol in Eq. (45) with $L=8$, $\tau=3$, and the initial microcanonical distribution of energy $E=n+1/2$ with $n=2$. Solid green line, classical case, Eq. (29). Blue dashed line, quantum case, Eq. (41); the summation is truncated at $m=100$.

C. Examples of driving protocols

Let us now study the actual change in expectation value of the entropy for certain specific shapes of $f(t)$.

1. Exponential driving

Let

$$f(t) = L[1 - \exp(-t/\tau)]. \tag{45}$$

Using Eqs. (19), (20), and (22) with Eq. (45), we get

$$W(t) = \frac{L^2(1 + e^{-2t/\tau} - 2e^{-t/\tau} \cos t)}{2(1 + \tau^2)}. \tag{46}$$

The shape of $W(t)$ is depicted in Fig. 4. Note the oscillations, which are a consequence of the fact that the oscillator returns some of the work to the external source of work. Nonetheless, the balance is always positive in accordance with the minimal work principle. Figure 5 shows the corresponding entropy change resulting from a microcanonical initial condition. Note how the quantum curve smooths out the sharp angle in the classical curve. The final quantum entropy is in

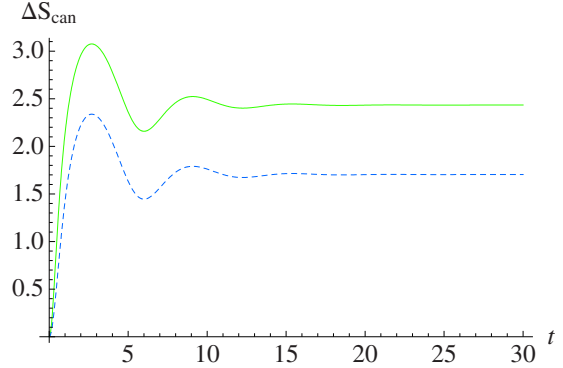


FIG. 6. (Color online) Entropy change as a function of time for the exponential driving protocol in Eq. (45) with $L=8$, $\tau=3$, and the initial canonical distribution of inverse temperature $\beta=2$. The canonical distribution is truncated at $n=20$. Solid green line, classical case, Eq. (29). Blue dashed line, quantum case, Eq. (41); the summation is truncated at $m=100$.

general larger than the corresponding classical one. Also note that $W(t)$ [Eq. (46)] is bounded from above. Therefore, if the initial energy is larger than the maximum of $W(t)$, the classical change in expectation of entropy is null, even if the protocol is not adiabatic. This is quite an interesting result. Figure 6 shows the entropy change for the canonical initial condition. Note that the classical entropy is larger than the quantum one in this case. Again, note the oscillations due to the fact that the oscillator returns some entropy to the external source. This is not in contradiction with the Clausius principle, which does not pose any condition on the monotonicity of entropy as a function of time.

2. Sinusoidal driving

Let

$$f(t) = L \sin \Omega t. \tag{47}$$

From Eqs. (19), (20), and (22), we obtain

$$W(t) = \frac{L^2 \Omega^2 \{\cos^2 t - 2 \cos t \cos(\Omega t) + \cos^2(\Omega t) + [\sin t - \Omega \sin(\Omega t)]^2\}}{2(-1 + \Omega^2)^2}. \tag{48}$$

Figure 7 shows the profile of W for $\Omega=2$. Note that if Ω is not a rational number, then W is not periodic. Figure 8 shows the entropy change resulting from a microcanonical initial condition. Note that the classical entropy change is non-negative, whereas the quantum entropy change is slightly negative for certain t 's. Figure 9 shows the entropy change resulting from a canonical initial distribution. Note that, in agreement with the theory exposed in Sec. II, the classical and quantum entropy changes are both non-negative.

Note that since the time dependence of entropy passes through W , for a periodic W we also have a periodic S . So at

times multiples of the period, the work W is zero; accordingly the quantum transition probability becomes a Kronecker δ (the classical transition probability becomes a Dirac δ), and the entropy goes back to its original value. So the system can actually go back to its original state, even if the driving is not adiabatic. This reflects the fact that no time-reversal symmetry breaking is involved here, and that the inequality $S_f \geq S_i$ is an exact and purely mechanical inequality induced by the unitary quantum (or classical) evolution.

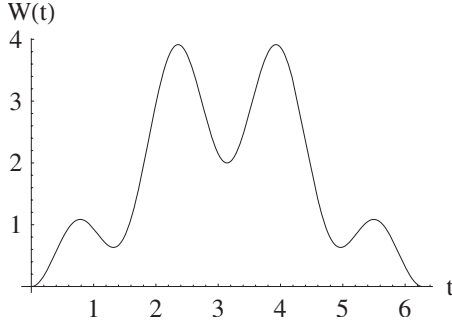


FIG. 7. Work as a function of time for the sinusoidal driving protocol in Eq. (47) with $L=3/2$, $\Omega=2$.

3. On/off switching protocol

Let us conclude this section by studying a switching protocol in which the external source is turned on and off in a finite time. Let us consider the following driving protocol:

$$f(t) = \begin{cases} L \sin \Omega t & 0 \leq t \leq \pi/\Omega \\ 0 & \text{otherwise.} \end{cases} \quad (49)$$

Let us focus on the time $T=\pi/\Omega$ at which the driving is turned off. We shall refer to T as the switching time. From Eq. (48), we get

$$W(T) = \frac{L^2 \pi^2 T^2 (1 + \cos T)}{(\pi^2 - T^2)^2}. \quad (50)$$

Figure 10 shows the quantum and classical entropy change resulting from the force (49) as a function of switching time $T=\pi/\Omega$ for the microcanonical initial condition. Note that, as expected, the change in entropy goes to zero in the adiabatic limit $T \rightarrow \infty$. For T larger than a certain threshold value, the classical entropy change is exactly null. Correspondingly, the quantum entropy change becomes approximately null and oscillates around zero, thus getting positive and negative values. Note also, in analogy with the previous discussion concerning the exponential driving, that the function $W(T)$ is bounded from above $W(T) \leq cL^2$. Thus, for a given initial energy Φ and amplitude L , if L is not suffi-

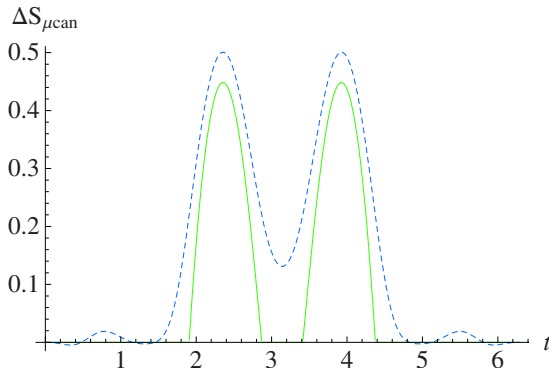


FIG. 8. (Color online) Entropy change as a function of time for the sinusoidal driving protocol in Eq. (47) with $L=3/2$, $\Omega=2$, and the initial microcanonical distribution of energy $E=n+1/2$ with $n=2$. Solid green line, classical case, Eq. (29). Blue dashed line, quantum case, Eq. (41); the summation is truncated at $m=100$.

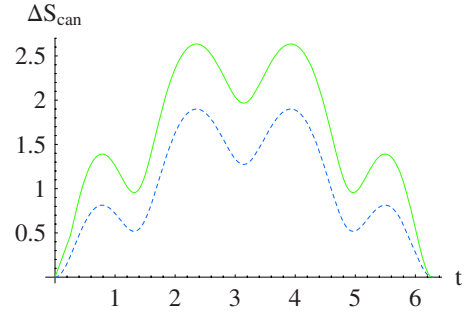


FIG. 9. (Color online) Entropy change as a function of time for the sinusoidal driving protocol in Eq. (47) with $L=3/2$, $\Omega=2$, and the initial canonical distribution of inverse temperature $\beta=2$. The canonical distribution is truncated at $n=20$. Solid green line, classical case, Eq. (29). Blue dashed line, quantum case, Eq. (41); the summation is truncated at $m=100$.

ciently large, the change in classical entropy remains zero for all values of switching time T . In fact, one has $L \leq \sqrt{\Phi/c} \Rightarrow W(T) \leq \Phi \Rightarrow \langle \ln \Theta \rangle_{\Phi} = \ln \Phi, \forall T$.

Figure 11 shows the quantum and classical entropy change for the canonical initial condition. Evidently, the change in entropy goes to zero as the switching time increases (adiabatic limit). Note also the oscillatory behavior of the entropy change as a function of T . Interestingly enough, the change in entropy vanishes for $T=3\pi, 5\pi, 7\pi$. This is because the work is also zero for those values [see Eq. (50)].

Note that, in accordance with Eqs. (15) and (16), the entropy change is *non-negative* for the canonical initial condition (see Figs. 6, 9, and 11).

IV. DISCUSSION

We have reviewed here the quantum-mechanical proof of the Clausius principle based on Boltzmann entropy, and we have applied it to a specific model, namely the driven harmonic oscillator.

One interesting feature that we have noticed is that the

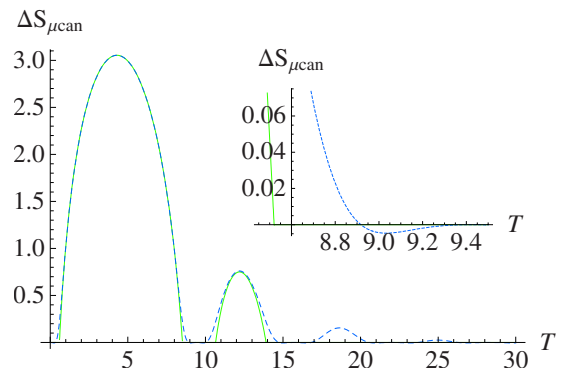


FIG. 10. (Color online) Entropy change for the force in Eq. (47) with $L=6$, $n=2$, as a function of switching time T , for the initial microcanonical condition. Solid line: classical case, Eq. (29), with $\Phi=n+1/2=5/2$. Dashed line: quantum case, Eq. (41); the summation is truncated at $m=1000$.

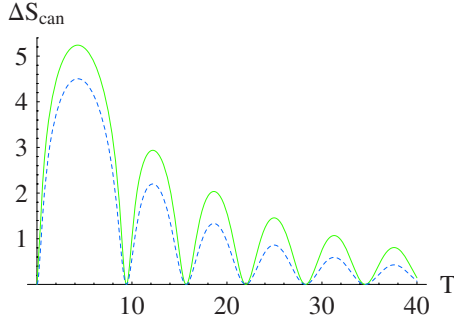


FIG. 11. (Color online) Entropy change for the force in Eq. (47) with $L=6$, $\beta=2$, as a function of switching time T , for the initial canonical distribution. The canonical distribution is truncated at $n=100$. Solid line: classical case, Eq. (29), with $\Phi=n+1/2=5/2$. Dashed line: quantum case, Eq. (41); the summation is truncated at $m=1000$.

Clausius principle is satisfied *classically* in this example even in the microcanonical ensemble, thus showing that the requirement of decreasing probabilities is sufficient but not necessary in the classical case. This is in agreement with the work of [11], where a general proof of the increase of the classical Boltzmann entropy has been given for high-dimensional classical chaos and initial microcanonical distribution. The same work also reports numerical evidence of an increase of entropy for time-dependent low dimensional classical Fermi-Pasta-Ulam chains initially at a microcanonical condition. Thus we expect this to be quite a general condition that applies to systems with an energy spectrum that has a lower bound but no upper bound. Instead, the quantum entropy change may be negative when starting from a microcanonical condition. As can be seen from the graphs, the quantum entropy change may become slightly negative, thus the Clausius principle is satisfied quantum mechanically only approximately, when starting from the microcanonical ensemble.

On the other hand, the Clausius principle is always satisfied when starting from the canonical ensemble, or any other ensemble characterized by a decreasing distribution.

The example of the driven harmonic oscillator has also shown how the Boltzmann entropy and the work, when considered as functions of time, *are not monotonic increasing*. Although the total balances of work and entropy stay non-negative in accordance with the minimal work principle and the Clausius principle, the system may return some amount (or even all) of the work and entropy to the external source. A similar nonmonotonicity was found in a related study on forced oscillators [33].

Interestingly, while the quantum work coincides with the classical work in the driven harmonic oscillator, the classical and quantum entropy changes do not (Fig. 2). In particular, the change in entropy may turn out to be null even in cases in which the work is not null for the initial microcanonical condition. Thus, interestingly, it is possible to implement isentropic driving protocols that are neither quasistatic nor isenergetic.

Another interesting feature of the driven harmonic oscillator is that when the driving force is sinusoidal with a rational ratio between the driving force frequency and the oscil-

lator frequency, both work and entropy are periodic. In fact, the system returns periodically to its original state, and accordingly the entropy change and work return to zero periodically. Such behavior of entropy and work is not in contrast with the second law as formulated by Clausius and Thomson. Furthermore, it provides an example of a process that is at the same time *non-quasi-static and reversible*. This helps to clarify the fact, already pointed out in [8], that reversibility and quasistaticity are quite distinct concepts.

The results presented here concerning the increase of entropy in a quantum forced harmonic oscillator can be tested experimentally by means of multisegmented optical ion traps of the type described in [13].

ACKNOWLEDGMENTS

Support award from the Texas Section of the American Physical Society is gratefully acknowledged.

APPENDIX A: CALCULATION OF QUANTUM TRANSITION PROBABILITIES WITH WIGNER FUNCTIONS

In order to appreciate the connection between the classical transition probabilities $A(\Theta, \Phi, t_i, t_f)$ and the quantum transition probability, we calculate the latter using the Wigner functions of the system’s eigenstates. For the eigenstates of the simple harmonic oscillator $H(p, x)=p^2/2+x^2/2$, the Wigner functions read [35]

$$W_{|m\rangle}(x, p) = \frac{(-1)^m}{\pi} \exp\{-[p^2 + x^2]\} L_m\{2[p^2 + x^2]\}, \tag{A1}$$

where L_m denote the Laguerre polynomials. Since the Hamilton function of the driven harmonic oscillator reads $H(p, x, t)=p^2/2+[x-f(t)]^2/2$, the Wigner function associated with the instantaneous eigenvector $|m, t\rangle$ can be derived from $W_{|m\rangle}$ by means of a translation along the x axis,

$$W_{|m, t\rangle}(x, p, t) = \frac{(-1)^m}{\pi} \exp(-\{p^2 + [x - f(t)]^2\}) \times L_m(2\{p^2 + [x - f(t)]^2\}). \tag{A2}$$

Now, from Eq. (5) we have

$$|a_{km}(0, t)|^2 = |\langle m, t | \psi_k(t) \rangle|^2, \tag{A3}$$

where $|\psi_k(t)\rangle \doteq \hat{U}(0, t)|k, 0\rangle$. Using the properties of Wigner functions [35] (and recalling that we have set $\hbar=1$), we can rewrite Eq. (A3) as

$$|a_{km}(0, t)|^2 = 2\pi \int dp dx W_{|m, t\rangle}(x, p, t) W_{|\psi_k(t)\rangle}(x, p, t), \tag{A4}$$

where $W_{|\psi_k(t)\rangle}(x, p, t)$ is the Wigner function associated with the state $|\psi_k(t)\rangle$. The function $W_{|\psi_k(t)\rangle}(x, p)$ can be easily calculated by evolving the function $W_{|k, 0\rangle}(x, p)$ according to the *classical* evolution in phase space. This is because the evo-

lution of Wigner functions is dictated by the classical Liouville equation in the case of quadratic potentials [35]. Thus

$$W_{|\psi_k(t)\rangle}(x,p,t) = W_{|m\rangle}(x_0(x,p,t),p_0(x,p,t)), \quad (\text{A5})$$

where $(x_0(x,p,t),p_0(x,p,t))$ is the point in phase space at time $t=0$ that evolves to (x,p) in the time t . In the case of the driven harmonic oscillator, by inverting Eq. (18) we have

$$\begin{pmatrix} x_0 \\ p_0 \end{pmatrix} = \begin{pmatrix} \cos t & -\sin t \\ \sin t & \cos t \end{pmatrix} \begin{pmatrix} x - S(t) \\ p - C(t) \end{pmatrix}. \quad (\text{A6})$$

Therefore,

$$|a_{km}(0,t)|^2 = 2 \frac{(-1)^{m+k}}{\pi} \int dp dx e^{-2\eta(x-f_t,p)} L_m(4\eta(x-f_t,p)) \times e^{-2\eta(x-S_t,p-C_t)} L_k(4\eta(x-S_t,p-C_t)), \quad (\text{A7})$$

where $\eta(y,q) \doteq \frac{y^2+q^2}{2}$, and f_t, C_t, S_t are short-hand notations for $f(t), C(t), S(t)$. Applying the change of variables $x' = x - S_t, p' = p - C_t$,

$$|a_{km}(0,t)|^2 = 2 \frac{(-1)^{m+k}}{\pi} \int dp' dx' e^{-2\eta(x'+S_t-f_t,p'+C_t)} \times L_m(4\eta(x'+S_t-f_t,p'+C_t)) \times e^{-2\eta(x',p')} L_k(4\eta(x',p')). \quad (\text{A8})$$

Let us pass to the ‘‘enclosed volume’’-angle variables Φ, φ (that is, the action-angle variables), defined from $x' = \sqrt{2\Phi} \cos \varphi, p' = \sqrt{2\Phi} \sin \varphi$. Simple calculations lead to

$$|a_{km}(0,t)|^2 = 2 \frac{(-1)^{m+k}}{\pi} \int_0^\infty d\Phi e^{-2\Phi} L_k(4\Phi) \times \int_0^{2\pi} d\varphi e^{-2[\Phi+W(t)+2\sqrt{\Phi W(t)} \sin \varphi]} \times L_m(4[\Phi+W(t)+2\sqrt{\Phi W(t)} \sin \varphi]). \quad (\text{A9})$$

Now, using Eq. (32) and defining

$$u_m(x) = 2(-1)^m e^{-2x} L_m(4x), \quad (\text{A10})$$

we get

$$|a_{km}(0,t)|^2 = \int_0^\infty d\Phi \int_0^\infty d\Theta u_k(\Phi) A(\Phi, \Theta; 0, t) u_m(\Theta). \quad (\text{A11})$$

Thus the quantum transition probabilities are the coefficients of the double expansion of the classical transition probabilities over the Laguerre basis $\{u_m(\Phi)u_k(\Theta)\}$. In order to prove

that the expression in Eq. (A11) is equal to the expression in Eq. (38), we calculate the double generating function of both and show that they are equal. The double generating function is defined as

$$g(\alpha, \beta; W) \doteq \sum_{n,m=0}^\infty \alpha^n \beta^m |a_{mn}(W)|^2, \quad (\text{A12})$$

where for simplicity we omitted the dependence on time of a_{mn} and we made the dependence on W explicit. Using the Laguerre polynomials generating function,

$$\sum_{k=0}^\infty \alpha^k L_k(W) = \frac{e^{-[\alpha/(1-\alpha)]W}}{1-\alpha}, \quad (\text{A13})$$

one finds from Eq. (A9)

$$g(\alpha, \beta; W) = \frac{e^{[(\alpha-1)(\beta-1)/(\alpha\beta-1)]W}}{1-\alpha\beta}. \quad (\text{A14})$$

The calculation involves the use of the following integrals [36]: $\int_0^{2\pi} d\varphi e^{a \cos \varphi} = 2\pi I_0(a)$ and $\int_0^\infty dx e^{bx} I_0(\sqrt{x}) = -\frac{e^{-1/4b}}{b}$, where $I_0(x)$ is the Bessel I function of order 0.

On the other hand, the generating function associated with the expression in Eq. (38) can be obtained by expressing the Charlier polynomials in terms of the associated Laguerre polynomials $L_n^{(s)}$ as [38]

$$C(n, m|W) = (-W)^{-n} n! L_n^{(m-n)}(W). \quad (\text{A15})$$

In terms of associated Laguerre polynomials, then, Eq. (38) becomes

$$|a_{mn}(W)|^2 = e^{-W} (-1)^{m+n} L_n^{(m-n)}(W) L_m^{(n-m)}(W). \quad (\text{A16})$$

Using the double generating function of the associated Laguerre polynomials [39]

$$\sum_{n,m=0}^\infty \alpha^n \beta^m L_m^{(n-m)}(W) L_n^{(m-n)}(W) = \frac{e^{-[(2\alpha\beta+\alpha+\beta)/(1-\alpha\beta)]W}}{1-\alpha\beta}, \quad (\text{A17})$$

and accounting for the sign change of α and β stemming from the term $(-1)^{m+n}$ in Eq. (A16), one immediately recovers Eq. (A14). We deduce that

$$|a_{mn}(0,t)|^2 = \int_0^\infty d\Phi \int_0^\infty d\Theta u_m(\Phi) A(\Phi, \Theta; 0, t) u_n(\Theta) = \frac{e^{-W(t)} W^{m+n}(t)}{m!n!} [C(m, n|W(t))]^2, \quad (\text{A18})$$

thus recovering the known result.

- [1] I. M. Bassett, *Phys. Rev. A* **18**, 2356 (1978).
- [2] A. Lenard, *J. Stat. Phys.* **19**, 575 (1978).
- [3] H. Tasaki, arXiv:cond-mat/0009206.
- [4] A. E. Allahverdyan and T. M. Nieuwenhuizen, *Phys. Rev. E* **71**, 046107 (2005).
- [5] C. Jarzynski, *Phys. Rev. Lett.* **78**, 2690 (1997).
- [6] P. Talkner, E. Lutz, and P. Hänggi, *Phys. Rev. E* **75**, 050102(R) (2007).
- [7] M. Campisi, *Stud. Hist. Philos. Mod. Phys.* **39**, 181 (2008).
- [8] J. Uffink, *Stud. Hist. Philos. Mod. Phys.* **32**, 305 (2001).
- [9] M. Toda, R. Kubo, and N. Saitô, *Statistical Physics* (Springer-Verlag, Berlin, 1983), Vol. 1.
- [10] C. Jarzynski, *Phys. Rev. A* **46**, 7498 (1992).
- [11] S. Sasa and T. S. Komatsu, *Prog. Theor. Phys.* **103**, 1 (2000).
- [12] P. Talkner, P. S. Burada, and P. Hänggi, *Phys. Rev. E* **78**, 011115 (2008).
- [13] S. A. Schultz, U. Poschinger, F. Ziesel, and F. Schmidt-Kaler, *New J. Phys.* **10**, 045007 (2008); G. Huber, F. Schmidt-Kaler, S. Deffner, and E. Lutz, *Phys. Rev. Lett.* **101**, 070403 (2008).
- [14] M. Campisi, *Stud. Hist. Philos. Mod. Phys.* **36**, 275 (2005).
- [15] A. Adib, *J. Stat. Phys.* **117**, 581 (2004).
- [16] G. B. Bağcı and M. Campisi (unpublished).
- [17] A. E. Allahverdyan and D. B. Saakian, *Europhys. Lett.* **81**, 30003 (2008).
- [18] V. L. Berdichevsky, *Thermodynamics of Chaos and Order* (Addison-Wesley, Longman, Essex, 1997).
- [19] E. M. Pearson, T. Halicioglu, and W. A. Tiller, *Phys. Rev. A* **32**, 3030 (1985).
- [20] J. Dunkel and S. Hilbert, *Physica A* **370**, 390 (2006).
- [21] P. Talkner, P. Hänggi, and M. Morillo, *Phys. Rev. E* **77**, 051131 (2008).
- [22] P. Hertz, *Ann. Phys.* **33**, (Leipzig), 225 (1910).
- [23] A. Schlüter, *Z. Naturforsch. A* **3a**, 350 (1948).
- [24] A. Münster, *Statistical Thermodynamics* (Springer-Verlag, Berlin, 1969), Vol. 1.
- [25] R. Becker, *Theory of Heat*, 2nd ed. (Springer-Verlag, Berlin, 1969), Vol. 1.
- [26] L. Landau and E. Lifshitz, *Mechanics*, 2nd ed. (Pergamon, Oxford, 1969).
- [27] L. Landau and E. Lifshitz, *Quantum Mechanics, Non-relativistic Theory*, 3rd ed. (Pergamon, Oxford, 1977).
- [28] L. Landau and E. Lifshitz, *Statistical Physics*, 2nd ed. (Pergamon, Oxford, 1969).
- [29] A. E. Allahverdyan and T. M. Nieuwenhuizen, *Physica A* **305**, 542 (2002).
- [30] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1962).
- [31] H. R. Brown and J. Uffink, *Stud. Hist. Philos. Mod. Phys.* **32**, 525 (2001).
- [32] S. Deffner and E. Lutz, *Phys. Rev. E* **77**, 021128 (2008).
- [33] T. M. Nieuwenhuizen and A. E. Allahverdyan, *Phys. Rev. E* **66**, 036102 (2002).
- [34] R. Feynman and A. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
- [35] W. P. Schleich, *Quantum Optics in Phase Space* (Wiley-VCH, Berlin, 2001).
- [36] I. Gradshteyn and I. Ryzhik, *Table of Integrals, Series and Products* (Elsevier/Academic, Amsterdam, 2007).
- [37] K. Husimi, *Prog. Theor. Phys.* **9**, 381 (1953).
- [38] P.-A. Lee, *J. Phys. A* **30**, L183 (1997).
- [39] A. Messina and E. Paladino, *J. Phys. A* **29**, L263 (1996).
- [40] M. Campisi, Ph.D. thesis, University of North Texas (2008).
- [41] The choice of adding the term $1/2$ is dictated by the Bohr-Sommerfeld rule in 1D, but remains perhaps arbitrary in the more general multidimensional case. Tasaki, for example, sets such an additive term to zero [3]. Anyway, the value of the constant that is added to the number operator does not affect the proof of the entropy increase.
- [42] The quantity A is the same object studied in [10] and denoted therein as ζ . Liouville's theorem implies that the "classical transition probability" $A(\Phi, \Theta; t_i, t_f)$ is doubly stochastic, i.e., $\int A(\Phi, \Theta; t_i, t_f) d\Phi = \int A(\Phi, \Theta; t_i, t_f) d\Theta = 1$ [40].
- [43] This is necessary for the classical validity of Thomson formulation too. See A. E. Allahverdyan and T. M. Nieuwenhuizen, *Phys. Rev. E* **75**, 051124 (2007).