Minimal-work principle and its limits for classical systems

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The minimal-work principle asserts that work done on a thermally isolated equilibrium system is minimal for the slowest (adiabatic) realization of a given process. This principle, one of the formulations of the second law, is operationally well defined for any finite (few particle) Hamiltonian system. Within classical Hamiltonian mechanics, we show that the principle is valid for a system of which the observable of work is an ergodic function. For nonergodic systems the principle may or may not hold, depending on additional conditions. Examples displaying the limits of the principle are presented and their direct experimental realizations are discussed.

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Thermodynamics originated in the 19th century as a science of macroscopic machines, constructed for transferring, applying, or transmitting energy [1]. The main results of this science are summarized in several formulations of the second law [1]. The last 50 years witnessed progressive miniaturization of the components employed in the construction of devices and machines [2]. This will open the way to new technologies in various fields.

For microscopic machines and devices, we need to understand how the second law applies to small systems. There are two aspects of this program: (i) Emergence of the second law, where one studies fluctuations of work or entropy, knowing that on the average they satisfy the second law. Important contributions to this topic were made by Smoluchowski and others, nearly 100 years ago [3]. Recently, activity in this field has been revived in the context of fluctuation theorems [4]. (ii) Limits of the second law, where the very formulation is studied from first principles [18]. Here we continue on that and study (the limits of) the minimal-work principle based on classical mechanics. This formulation of the second law is operationally well defined for finite systems, and it relates the energy cost of an operation to its speed. The principle was deduced from experience and postulated in thermodynamics, where it is equivalent to other formulations of the second law. Its derivation in statistical physics was formulated several times on various levels of generality [5–7]. Almost all these studies concentrate on macroscopic systems and confirm the validity of the principle. In Ref. [7] the principle was derived for finite quantum systems and limits, related to energy level crossing, were indicated. However, the reduction level of quantum mechanics is not always needed; e.g., certain aspects of nanoscience are adequately understood already with classical ideas [2]. In addition, it is not easy to design experiments in the quantum domain that would check the validity of formulations of the second law. Thus it is necessary to understand the principle in classical mechanics and this is our present purpose. Our results will apply to small systems, possibly having one degree of freedom.

Consider a classical system with a Hamiltonian $H(q,p,R_t)$, where $q=(q_1,\dots,q_N)$ and $p=(p_1,\dots,p_N)$ are, respectively, canonical coordinates and momenta. The interaction with external sources of work is realized via a time-dependent parameter R_t. We denote $z\equiv(q,p)$, $dz\equiv dq\,dp$ and $H_k=H(z,R_k)$ with $k=i,\ f$, for the initial and final values, respectively.

The system starts its evolution from an equilibrium Gibbs state at temperature $T=1/\beta>0$: $\mathcal{P}_i(z)=e^{-\beta H_i(z)}/\mathcal{Z}_i$, where $\mathcal{Z}_i=\int dz\, e^{-\beta H_i(z)}$. The work done on the system is the average energy difference [1]

$$W=\int dz[\mathcal{P}_f(z)H_f(z)-\mathcal{P}_i(z)H_i(z)] \tag{1}$$

$$=\int_{t_i}^{t_f} ds\dot{R}_s\mathcal{P}(z,s)\partial_R H(z,R_s), \tag{2}$$

where $\mathcal{P}_f(z)$ is the final distribution and where the equivalence between Eqs. (1) and (2) is established with help of the Liouville equation for $\mathcal{P}$ and the standard boundary condition $\mathcal{P}(z)=0$ for $z\to\pm\infty$ [1]. Equation (2) justifies calling $w(z,R)\equiv\partial_R H(z,R)$ the "observable of work." Note that in the quantum situation, no observable of work can be properly identified [19].

Let the trajectory of R_t be fixed: $R_t=r(t/\tau_R)$, where τ_R is the characteristic time and where r is a smooth function defined on a finite interval. We assume that for given trajectory r, the system has an internal characteristic time τ_S (a more precise definition of τ_S is discussed below). In the adiabatic limit $\tau_R\gg\tau_S$, R_t changes very slowly, producing an amount of work $\widetilde{W}$. Let W be the work done for a finite τ_R for the same trajectory $r(\overline{t})$ and the same start and end points, $R_k=r(\overline{t_k})$ $(k=i,f)$. *The minimal-work principle* claims that

$$\Delta W\equiv W-\widetilde{W}\geqslant 0. \tag{3}$$

This is an optimality statement: the smallest amount of work to be put into the system ($W>0$) is the adiabatic one, and the largest amount of work to be extracted from the system ($W<0$) is again the adiabatic one. The most common argument on the validity of the principle is the known inequality $W\geqslant F_f-F_i$ [4], where $F_{f,i}=-T\ln\int dz\, e^{-H_{f,i}(z)/T}$ are free energies at initial temperature T. If now $\widetilde{W}=F_f-F_i$, the principle is proven. The problem is that in general—e.g., for finite systems—$\widetilde{W}$ is not equal to $F_f - F_i$; see [7,8] and also below. Our derivation of the adiabatic principle (3) consists of three steps and assumes that $w(z,R)$ is an ergodic observable of the dynamics with R=const. This puts restrictions on $R_t = r(t/\tau_R)$, which need not be met.

(i) The initial distribution $\mathcal{P}_i(z)$ is generated by sampling microcanonical distribution $\mathcal{M}$ with initial energy probability $P_i(E)$: $\mathcal{P}_i(z) = \int dE P_i(E)\mathcal{M}(z,E,R_i)$,

$$\mathcal{M}(z,E,R_i) = \frac{1}{\omega_i(E)}\delta[E - H(z,R_i)], \tag{4}$$

$$\omega_i(E) \equiv \int dz\,\delta[E - H_i(z)], \quad P_i(E) = \frac{\omega_i(E)}{\mathcal{Z}_i}e^{-\beta E}. \tag{5}$$

The Hamilton equations of motion imply $\frac{d}{dt}H(z_t,R_t) = \dot{R}_t\partial_R H(z_t,R_t)$. Assuming the adiabatic limit $\tau_S \ll \tau_R$, we have for the energy change on times $\tau_S \ll \tau \ll \tau_R$

$$\Delta_\tau E \equiv \frac{1}{\tau}[H(z_{t+\tau},R_{t+\tau}) - H(z_t,R_t)] = \int_t^{t+\tau}\frac{ds}{\tau}\frac{dH}{ds}(z_s,R_s)$$

$$= \frac{\dot{R}_t}{\tau}\int_t^{t+\tau} ds\frac{\partial H}{\partial R}(z_s,R_t) + o\left(\frac{\tau}{\tau_R}\right). \tag{6}$$

The last integral refers to the R=const dynamics with $R_t = R$. Now recall the Liouville theorem $dz = dz_t$ and energy conservation $H(z_{t+\tau}) = H(z_t) = E_t$, so for any w

$$\int dz\, w(z)\mathcal{M}(z,E_t) = \frac{1}{\tau}\int_t^{t+\tau} ds \int dz\, w(z)\mathcal{M}(z,E_t) \tag{7}$$

$$= \int dz_t\mathcal{M}(z_t,E_t)\frac{1}{\tau}\int_t^{t+\tau} ds\, w(z[s;z_t]), \tag{8}$$

where $z[s;z_t] = \Phi_{s-t}\,z_t$, and where Φ_s with $\Phi_0 = 1$ is the flow generated by the Hamiltonian $H(z)$. If $w(z) = \partial_R H(z,R)$ is an *ergodic observable* of the R=const dynamics, then for $\tau \gg \tau_S$ the time average in Eq. (8) depends on the initial condition z_t only via its energy $H(z_t)$[10,11]; the latter condition frequently serves as a definition of τ_S.[1] Thus the integration over z_t in Eq. (8) drops out, and we get from Eq. (7) that the time average in Eq. (6) is equal to the microcanonical average at the energy E_t: $\Delta_\tau E = \dot{R}_t \int dz\, \partial_R H(z,R_t)\mathcal{M}(z,E_t,R_t)$. This implies adiabatic invariance of the phase-space volume Ω enclosed by the energy shell E:

$$\Delta_\tau\Omega(E,R) = 0, \quad \Omega(E,R) \equiv \int dz\,\theta(E - H(z,R)). \tag{9}$$

In the adiabatic limit of ergodic systems, phase-space points located initially at the energy shell E_i appear on the energy shell E_f, which is found from $\Omega(E_i,R_i) = \Omega(E_f,R_f)$. Note that only the end points of R_t matter for the energy changes in the adiabatic limit. Since $\partial_E\Omega(E,R) \equiv \omega(E,R) \geq 0$, we can define for fixed R_f and R_i two monotonous functions: $E_f = \phi_f(E_i)$ and its inverse $E_i = \phi_i(E_f)$. Note that $\phi_f'(E) = \omega_i(E) \times [\omega_f(\phi_f(E))]^{-1} \geq 0$. Adiabatic invariance of Ω for ergodic systems is well known [9] and motivated the microcanonical definition of entropy as ln Ω rather than ln ω [10]

(ii) Let $P(E|E')$ be the conditional probability of having energies E and E' at $t = t_f$ and $t = t_i$, respectively:

$$P(E|E')P_i(E') = \int dz\, dz'\,\delta[E - H_f(z)] \times \delta[E' - H_i(z')]\mathcal{P}(z|z')\mathcal{P}_i(z'), \tag{10}$$

where $\mathcal{P}(z|z')$ is the conditional phase-space probability,

$$\mathcal{P}(z|z') = \mathcal{U}\delta[p - p']\delta[q - q'], \quad \mathcal{U} \equiv \overleftarrow{e}^{\int_{t_i}^{t_f} ds\mathcal{L}(s)}, \tag{11}$$

and where $\mathcal{L}(t) = \partial_q H(t)\partial_p - \partial_p H(t)\partial_q$ is the Liouville operator, with $\overleftarrow{e}$ being the chronological exponent. We see that $\int dz'\mathcal{P}(z|z') = 1$, since $\mathcal{U} - 1$ is a sum of differential operators. This implies together with Eqs. (5) and (10)

$$P(E|E') = \int dz\, dz'\,\delta[E - H_f(z)]\frac{\delta[E' - H_i(z')]}{\omega_i(E')}\mathcal{P}(z|z'),$$

$$\int dE'\,\omega_i(E')P(E|E') = \omega_f(E), \tag{12}$$

in addition to the normalization $\int dE\, P(E|E') = 1$. For the adiabatic situation we get from the invariance of Ω

$$\widetilde{P}(E|E') = \delta[E - \phi_f(E')]. \tag{13}$$

Out of the adiabatic limit, $P(E|E')$ is not a δ function, since now different phase-space points located in the energy shell E_i end up at different energies E_f. The phase-space volume is still conserved due to Liouville's theorem, but it does not impose a fixed final energy.

(iii) Now recall Eq. (1) and write ΔW as

$$\Delta W = \int dz H_f(z)[\mathcal{P}_f(z) - \widetilde{\mathcal{P}}_f(z)]$$

$$= \int E\, dE \int dE' P_i(E')[P(E|E') - \widetilde{P}(E|E')]. \tag{14}$$

Integrating by parts we get $\Delta W = \int dE g_E$, where

$$g_E = \int^E du \int dE' P_i(E')[\widetilde{P}(u|E') - P(u|E')].$$

We shall show that $g_E \geq 0$ for any conditional probability $P(E|E')$ in Eq. (14) which satisfies Eq. (12). This will prove the principle. Denoting $c_E(E') \equiv \int^E du\, P(u|E')$, using Eq. (13), and employing $\theta[E - \phi_f(E')] = \theta[\phi_i(E) - E']$, we get

[1] τ_S does in general depend on the trajectory r and the range of energies involved.

$$g_E = \int^{\phi_i(E)} dE' P_i(E') - \int dE' P_i(E') c_E(E')$$
$$= \int^{\phi_i(E)} dE' P_i(E')[1 - c_E(E')] - \int_{\phi_i(E)} dE' P_i(E') c_E(E').$$

We now employ Eq. (5) and then Eq. (12) to obtain

$$\mathcal{Z}_i g_E \geq e^{-\beta\phi_i(E)} \int^{\phi_i(E)} dE' \omega_i(E')[1 - c_E(E')] - e^{-\beta\phi_i(E)} \int_{\phi_i(E)} dE' \omega_i(E') c_E(E') = e^{-\beta\phi_i(E)} \left[\int^{\phi_i(E)} dE' \omega_i(E') - \int^{E} dE' \omega_f(E') \right]. \quad (15)$$

Recalling that $\omega(E)=\Omega'(E)$ and that $\Omega(E_{\min})=0$ for the lowest energy $E_{\min}$, we get (15)=0—i.e., $g_E \geq 0$. Thus the principle is proven from Eq. (14). Note that (i) the same proof applies for $P_i(E)/\omega_i(E)$ being a decaying function of E and (ii) whenever the proof applies, the adiabatic work depends only on the end points of R_t.

For *nonergodic systems*, where under driving the system can move from one ergodic component (of the R=const dynamics) to another, the above proof of the principle is endangered, since in general Ω in Eq. (9) is not conserved. Indeed, the argument expressed by Eqs. (7) and (8) may not apply, since now the time average in Eq. (8) depends on the ergodic component to which the initial condition z_t belongs, and it cannot be substituted by the microcanonical average over the full phase space. However, $\partial_R H(z,R)$ may be ergodic, even though the system is not [11]. Consider the *symmetric* double well $H=\frac{1}{2}p^2 - R_t q^2 + g q^4$, with $g>0$. For $E<0$, there are two ergodic components related by the inversion $q \to -q$, but $\partial_R H = -q^2$ is degenerate with respect to them. Though the R_t= const motion on the separatrix $E=0$ has an infinite period (due to unstable fixed point $q=0$), when the initial distribution is microcanonical, the fraction of particles trapped by the separatrix is negligible [12], so that for the ensemble τ_S is finite. Thus $\Omega(E,R)$ [with the integration in Eq. (9) over the whole phase space] is conserved [12] and the proof of the principle applies.

Limits of the principle. The principle was derived assuming that the frozen-parameter dynamics supports the microcanonical distribution. This need not be always the case. Consider the basic model of the parametric oscillator: $H=\frac{1}{2}p^2+\frac{1}{2}R_t q^2$. If R_t is always positive, the phase-space volume is conserved and the above construction applies. But what if R_t touches zero? This is another nonergodic example, since for $R_t=0$ the frozen-parameter phase space consists of two ergodic components with, respectively, $p>0$ and $p<0$. Though $\partial_R H = \frac{1}{2}q^2$ is degenerate with respect to them, the microcanonical distribution does not exist for $R_t=0$. Write the solution of the equations of motion $\ddot{q}+R_t q=0$ as

$$p(t) = \theta_{pp} p_i + \theta_{pq} q_i, \quad q(t) = \theta_{qq} q_i + \theta_{qp} p_i, \quad (16)$$

where $\theta_{kl}=\theta_{kl}(t)$. With Gibbsian initial distribution $\mathcal{P}_i(p,q) \propto \exp\left[-\frac{p^2}{2T} - \frac{R_i q^2}{2T}\right]$, the work reads from Eq. (1)

$$\frac{W}{T} = -1 + \frac{1}{2}\theta_{pp}^2 + \frac{\theta_{pq}^2}{2R_i} + \frac{1}{2}R_f\left(\theta_{qp}^2 + \frac{\theta_{qq}^2}{R_i}\right). \quad (17)$$

Next we consider an exactly solvable situation $R_t = t^2/\tau_R^2$ (see below for generalizations). The equation of motion is solved by substitution $q(t)=\sqrt{t}x(t)$:

$$q(t) = c_1\sqrt{|t|}J_{-1/4}\left(\frac{t^2}{2\tau_R}\right) + c_2 \frac{t}{\sqrt{|t|}} J_{1/4}\left(\frac{t^2}{2\tau_R}\right), \quad (18)$$

where $J_{\pm 1/4}$ are the Bessel functions and c_1 and c_2 are to be found from initial conditions. $q(t)$ is written in a way that applies to $t<0$ as well: noting $J_\mu(x\to 0^+) = \frac{x^\mu}{2^\mu \Gamma(\mu+1)}$ [13], we get $q(t) \approx \tilde{c}_1 + \tilde{c}_2 t$ for $t\to 0$. Since R_t should change between fixed R_i and R_f, we scale the initial and final times as $t_i = -\tau_R\sqrt{R_i}$ and $t_f = \tau_R\sqrt{R_f}$. In the slow limit $\tau_R \gg 1$ we need $J_\mu(x) = \sqrt{\frac{2}{\pi x}}\cos\left(x - \frac{\pi\mu}{2} - \frac{\pi}{4}\right) + O(x^{-3/2})$ [13]. Equations (16) and (18) then imply

$$\theta_{qq,pp} = R_i^{\pm 1/4} R_f^{\mp 1/4}(\mp \sin u + \sqrt{2}\cos v), \quad (19)$$

$$\theta_{qp,pq} = R_i^{\mp 1/4} R_f^{\mp 1/4}(\cos u \pm \sqrt{2}\sin v), \quad (20)$$

where $u = \frac{1}{2}\tau_R(\sqrt{R_i} - \sqrt{R_f})$ and $v = \frac{1}{2}\tau_R(\sqrt{R_i} + \sqrt{R_f})$. Inserting Eqs. (19) and (20) into Eq. (17) we get for the adiabatic work

$$\tilde{W} = T(3\sqrt{R_f/R_i} - 1). \quad (21)$$

Note that if R_t is always positive, the conservation of the phase-space volume $\Omega \propto E(t) R_t^{-1/2}$ gives $\tilde{W} = \langle E_f - E_i \rangle = (\sqrt{R_f/R_i} - 1)\langle E_i \rangle = T(\sqrt{R_f/R_i} - 1)$. Thus Ω is not conserved if $R_t=0$ at one instant. Note that the adiabatic limit still exists, since for a large τ_R, W converges to $\tilde{W}$; see Fig. 1. Equation (21) shows that the minimal-work principle does not hold. Indeed, for a sudden variation the Hamiltonian changes, while the state of the ensemble does not. This brings

$$W_s = \int dz\, \mathcal{P}_i(z)[H_f(z) - H_i(z)] = T\left(\frac{R_f}{2R_i} - \frac{1}{2}\right). \quad (22)$$

W_s is sometimes smaller than Eq. (21)—e.g., take $R_i = R_f$; see also Fig. 1. A qualitative picture behind this is that for $R_t=0$ the particle runs to infinity, and to confine it back (for $R_f>0$), the work to be spent is larger for the slow case, since for a quick process the particle does not have time to move very far; see Eq. (22). Figure 1 illustrates that for an extended setup $R_t = -b + t^2/\tau_R^2$, $b \geq 0$, the principle is satisfied if R_t decays monotonically: $t_i < t_f \leq 0$. It is violated if the change of R_t is nonmonotonic: $t_i < 0 < t_f$. The work does not saturate for $\tau_R \to \infty$ if R_t becomes strictly negative. These limits obviously exist for uncoupled particles. We expect that they extend to coupled particles put in a (de)confining potential.

Note that whenever the principle gets limited via the above scenario, the slowest process is irreversible. Recall

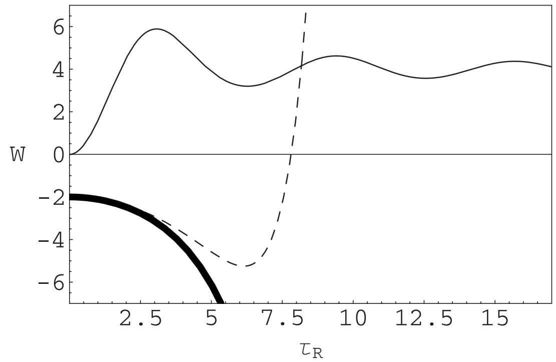

FIG. 1. Work W versus the time scale τ_R for an ensemble of harmonic oscillators with $R_t = -b + t^2/\tau_R^2$ at initial temperature $T=2$. Solid line: $b=0$, $t_f = -t_f = \tau_R$; the adiabatic work is $\widetilde{W}=4$, as given by Eq. (21). Dashed line: $b=0.5$, $t_i = -\tau_R$, and $t_f = \tau_R\sqrt{0.1}$. Bold line: $b=0.5$, $t_i = -\tau_R$, and $t_f = 0$. For the last two cases the adiabatic work (the limit $\tau_R \to \infty$) is, respectively, plus and minus infinity. The minimal-work principle $W(\tau_R) \geq W(\infty)$, for all τ_R, is seen to hold in the third case, but not in the first and second cases.

that a process is reversible if after supplementing it with its mirror reflection (the same process moved backwards with the same speed), the work done for the total cyclic process is zero [1]. As seen from Eq. (21), the work (equal to $2T$) does not vanish for the cyclic adiabatic process with R_t touching zero. Thus the process is irreversible. This fact contrasts the quantum limits of the minimal work principle found in [7]. Those limits are related to energy level crossing, where the adiabatic work is reversible [7].

Compare the minimal-work principle with Thomson's formulation of the second law: no work is extracted, $W>0$, from an equilibrium system via any cyclic Hamiltonian process $H_i = H_f$. This follows *only* from the equilibrium character of the initial distribution and the Hamiltonian structure of the dynamics; see [4,16] and our discussion after Eq. (3). In contrast, the minimal- work principle requires the ergodicity feature and becomes limited without it. We thus face a dynamical nonequivalence between these two formulations of the second law.[2]

Here is an experimentally realizable example that can demonstrate the above limits. The simplest LC circuit consists of capacitance C and inductance L (the resistance is either small or compensated) [14]. The Hamiltonian is $H = \frac{\Phi^2}{2L} + \frac{Q^2}{2C}$, where Q (coordinate) is the charge and where $\Phi = L\frac{dQ}{dt}$ (momentum) is the magnetic flux. The parametric oscillator with $R_t \to 0$ corresponds to a time-dependent C (or L), becoming very large at some time. R_t becoming negative at some time can be achieved via a *negative capacitance* $C_a < 0$ given by a special active circuit [14]. If such a capacitance is sequentially added to a positive capacitance C_n, then the resulting inverse capacitance $C^{-1} = C_a^{-1} + C_n^{-1}$ can be made zero and then negative by tuning C_n. The same effect is obtained via a negative inductance [15] added in parallel to a normal one. As the negative inductance and capacitance emulators are widely applied in compensation of parasitic processes and for improving the radiation pattern in antennas [14,15], they can serve to test our predictions.

In conclusion, we studied the second law in its minimal-work formulation for classical Hamiltonian systems. It was shown to hold under the assumption that the observable of work (i.e., the derivative of the Hamiltonian with respect to the driven parameter) is an ergodic function. The result applies to small systems. There are, however, numerous examples of nonergodicity both for finite and macroscopic systems. For such systems we explored several possibilities met in the single degree of freedom situation. The minimal-work principle applies if the observable of work is degenerate over ergodic components and if the microcanonic equilibrium exists for all values of the driven parameters. If the latter condition is not met, the principle can be violated. The simplest example of the latter is provided by a parametrically driven harmonic oscillator whose frequency passes through zero. As we saw, this situation can be realized experimentally in LC electrical circuits. Multidimensional systems provide more complex examples of nonergodicity. The understanding of the second law for such systems still deserves to be deepened, in view of the importance of nonergodicity in processes of measurement and information storage [17]. In a broader perspective, generic finite-particle Hamiltonian systems are known to be non-ergodic [20]. As the number of particles increases, and certain additional conditions are satisfied [21], the ergodicity is recovered for an observable that can be represented as a sum of single-particle contributions [21]. In view of our results, this fact may explain the applicability of the minimum work principle to some macroscopic systems. The situation is less clear for more general observables, those which cannot be represented as a sum of single-particle contributions. There are even statements in literature that at least for some systems a complete ergodicity is not recovered even in the thermodynamic limit [22].

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[2] Note that Ref. [6] claims that the two formulations of the second law are always equivalent. In view of the presented arguments we do not agree with this.

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