

Carnot's cycle for small systems: Irreversibility and cost of operations

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In the thermodynamic limit, the existence of a maximal efficiency of energy conversion attainable by a Carnot cycle consisting of quasistatic isothermal and adiabatic processes precludes the existence of a perpetual machine of the second kind, whose cycles yield positive work in an isothermal environment. We employ the recently developed framework of the energetics of stochastic processes (called “stochastic energetics”) to reanalyze the Carnot cycle in detail, taking account of fluctuations, without taking the thermodynamic limit. We find that in this nonmacroscopic situation both processes of connection to and disconnection from heat baths and adiabatic processes that cause distortion of the energy distribution are sources of inevitable irreversibility within the cycle. Also, the so-called null-recurrence property of the cumulative efficiency of energy conversion over many cycles and the irreversible property of isolated, purely mechanical processes under external “macroscopic” operations are discussed in relation to the impossibility of a perpetual machine, or Maxwell’s demon. This analysis may serve as the basis for the design and analysis of mesoscopic energy converters in the near future.

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I. INTRODUCTION

A. Background

The principles of thermodynamics were established in the last century as the universal laws characterizing the thermal and mechanical behavior of macroscopic systems. The fact that we cannot control all the details of energy transfer leads to the concept of *heat* as a form of energy flow, and the *Carnot cycle* has played a crucial role in the course of investigation leading to the introduction of entropy as a state variable in addition to energy [1]. On the other hand, Brownian motion and the stochastic dynamics of mesoscopic systems in general have also been studied for many years, and projection methods have allowed for the derivation of Langevin dynamics from microscopic Hamiltonian mechanics. In a properly defined Langevin equation, the influence of the unpredictable microscopic dynamics, which essentially represent the heat, is taken into account by Markovian random forces obeying the fluctuation-dissipation relationship. In this manner, such an equation describes the canonical equilibrium distribution of the variables in question [2].

Very recently, the concept of heat on mesoscopic scales has been unambiguously defined in terms of Langevin dynamics [3]. We refer to the formalism providing this definition as *stochastic energetics*. The essential point of the thinking behind this formalism is that the heat transferred to the system is nothing but the microscopic work done by both the

frictional forces *and* the random force in the Langevin equation. The theoretical framework resulting from this realization widens the scope of application of Langevin dynamics to the extent that it can be used to describe not merely equilibrium states of system in contact with heat baths, but also general thermodynamic *processes* connecting different equilibrium states. As a result, we can derive the first and the second laws of thermodynamics [3,4] from stochastic energetics. This formalism, together with projection methods, bridges a long-standing gap between microscopic Hamiltonian mechanics and macroscopic thermodynamics. In this paper we apply the method of stochastic energetics to the investigation of the Carnot cycle in the context of small systems. To make this paper self-contained, we briefly summarize the framework of stochastic energetics in Sec. II.

Stochastic energetics has also been applied to the study of thermodynamic processes under nonequilibrium conditions, such as processes including two heat baths [3] and processes in the presence of steadily driving forces [5]. In particular, the ratchet model of Feynman *et al.* [6] has been analyzed. Regarding this model, doubt has been cast by Parrondo and Espanol [7], and later by Sekimoto [3] independently, on the attainability of reversible energy conversion with the “Carnot efficiency” $1 - T_L/T_H$, where T_L and T_H are the temperatures of the cool and hot heat baths. Analysis using stochastic energetics has shown explicitly that the efficiency of Feynman’s ratchet is much less than the Carnot efficiency mentioned above [3].

B. Problems

With the descriptive power of stochastic energetics in hand, we wish to reconsider the Carnot cycle. We consider

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the Carnot cycle as an *object* of analysis within the theoretical framework of stochastic energetics. Note that, since we can derive the laws of thermodynamics directly using stochastic energetics based on the Langevin description, the Carnot cycle in our study is *not* a source of theoretical results from which one derives the laws of thermodynamics, as was its historical role. (Of course both the Langevin description and thermodynamics have a microscopic basis in mechanics.)

We now describe our viewpoint in more detail. Usually the Carnot heat engine is considered in an ideally macroscopic context, working in the thermodynamic limit. There, the small relative fluctuations of the variables, typically on the order of the inverse square root of the system size, are neglected. Also, the cost involved in the operations of attaching/detaching the system under study to/from heat baths is neglected, since this is not an extensive quantity. It is important to note that the second law of thermodynamics, which is consistent with such a macroscopic Carnot engine, can exclude *only marginally* the existence of a perpetual machine of the second kind whose cycles yield positive work in an isothermal environment. Thus we may gain a deeper insight into the nature of statistical thermodynamics and mechanics if we can formulate a method to take account of the finiteness of the system under study as well as the cost involved in operations of changing its interaction with heat baths, in particular considering reversibility and the second law of thermodynamics.

The approach of the present work is to construct the simplest model of the Carnot heat engine with a finite number of degrees of freedom (actually only three), including the apparatus connecting/disconnecting it with heat baths, and to determine the effect of the finiteness of the system and the change resulting from operations of the type mentioned above. As the system of study (or the “working material”) we choose a single harmonic oscillator. We show that there is an inevitable source of dissipation due to the *intrinsically* irreversible nature of the operations of connecting and disconnecting it with heat baths, and that, with the exception of such loss, our model can attain the Carnot maximal efficiency defined as a properly defined average over infinitely many cycles, each of which is performed infinitely slowly. At the same time this study reveals several basic problems that should be further scrutinized in the future: one concerns the smooth connection between the adiabatic process and the isothermal processes, and the other concerns the irreversibility of adiabatic processes. In the last section we discuss these problems as well as the problem of energy conversion with no help from external operations.

In the remaining part of this section we give a qualitative description of the aspects of the Carnot cycle that we study in detail in the later sections.

1. The operations of connection to and disconnection from the heat bath

We ask first how we can describe *mechanically* the connection and disconnection of the system to/from the heat baths. In an idealized picture, this description essentially consists of the switching on and off of the interaction between the system and each heat bath. In Sec. III we describe explicitly a model that realizes these operations. We repre-

sent the influence of the heat baths by a frictional force and the random force of a Langevin equation, and we control the strength of the coupling between the system and the heat baths by controlling the values of the corresponding interaction potentials. We call these interaction potentials “couplers.” (In an actual mechanical system, the control of such a coupler could be exercised by a system of clutches.)

One could also imagine such control exercised through change of the friction constants that appear in the Langevin equation. Because of the absence of a definition of the required work to change these friction constants, however, this idea is not pursued in the present paper.

2. The reversible and irreversible work of operating the couplers

The operation of the couplers can, *in principle*, never be carried out quasistatically, but, at the same time, the accompanying irreversible work can be made arbitrarily small. The former part of this assertion is based on the following argument: When the interaction between the system and a heat bath is strong, the energy transfer between them occurs with a short relaxation time. However, if we gradually weaken this interaction, this relaxation time increases more and more until it diverges when the system is completely detached from the heat bath. As long as the time scale of the operation (i.e., the switching off) is finite, this operation can never remain “slow” in comparison to the diverging relaxation time. Thus the switching-off process is by no means quasistatic, or quasiequilibrium. (This is analogous to the nonadiabaticity encountered in chemical reactions; the Born-Oppenheimer approximation is inevitably invalid when the distance between nuclei is neither sufficiently large nor sufficiently small.) Inevitable irreversibility can also exist in the process of strengthening the interaction between the system and the heat bath. Such extreme strengthening of the interaction leads to the freezing of some degree(s) of freedom involved in the interaction, and the mean first-passage time associated with these degrees of freedom may become larger than the time scale of the operation (i.e., the strengthening). In such a situation also, the operation can never be carried out quasistatically. Unlike the switching-off process, however, the indefinite strengthening of the interaction is not necessarily a part of the Carnot cycle. Despite this fact, we consider the latter process in the sections that follow, because this allows us to minimize the calculations needed to reach a general conclusion.

We should, however, note that the inevitably irreversible nature of the operations described above does not necessarily imply an associated large amount of irreversible work. In Sec. IV we analyze the work involved in operating the coupler and show that the amount of irreversible work resulting from these inevitably irreversible operations can be made arbitrarily small in the limit that the time scale of the operation becomes large. We also show that the reversible part of the work associated with these operations remains finite in this limit, but that it cancels out within a cycle.

3. The condition for reversible contact between the system and a heat bath

Temporarily putting aside the concept of irreversibility in the sense described in Sec. I B 2 above, we can scrutinize the

remaining part of the cycle and ask if and how the Carnot maximum efficiency can be attained. With regard to a macroscopic Carnot cycle, according to textbook descriptions, in order to realize a reversible cycle, “the temperature of the system should be the same as that of the heat bath with which the system is to make contact after an adiabatic process.” Strictly speaking, however, the energy, rather than the temperature, takes a definite value in a thermally isolated system, and the above statement needs to be refined in terms of the language of probability. We argue in Sec. V that reversible contact requires the probability distribution of the energy of the system just before interaction with a heat bath to be identical to the canonical distribution at the temperature of the heat bath. This condition can be satisfied if the system consists of harmonic oscillators, like the model described below. Generally, however, this is not the case, and in the general situation an irreversible process takes place when a system contacts a heat bath, even though there occurs no net irreversible energy transfer between the two (Sec. VII A). In Sec. VIA we summarize the necessary conditions for the Carnot cycle to realize the maximal efficiency $1 - T_H/T_L$ without assuming the thermodynamic limit. We show at the same time that this actually is the case for the model described in Sec. III.

4. Statistics of the efficiency of a finite number of cycles

The efficiency of the energy conversion of an *individual* cycle is statistically distributed, because the energy possessed by the system is different each time the system is disconnected from a heat bath. This fact reflects the indeterminate nature of the details of the microscopic states of the system and of the heat bath upon disconnection. As a consequence, if we define the cumulative “bonus” work as the difference between the cumulative work obtained over n cycles and what we would expect from the Carnot maximal efficiency, this bonus work takes the form of a discrete random walk as a function of n . We show in Sec. VIB and Appendix B that the so-called null-recurrence property of a one-dimensional random walk ensures that, although if we actually carry out a sequence of these cycles the cumulative bonus work we obtain will with probability 1 first become positive after a finite number of repetitions n^* , the statistical average of n^* is infinite.

5. Irreversibility of adiabatic processes

The Carnot cycle includes an adiabatic process that is purely mechanical. We are interested in determining what work can be obtained through the cycle including nonquasistatic adiabatic processes. If the efficiency in this case is increased in comparison to the quasistatic case, the existence of a perpetual machine of the second kind is inspired, because our Carnot cycle can attain the maximal (reversible limit) efficiency under certain conditions specified in Sec. VIA. In Sec. VII B we show that, in relation to the impossibility of a perpetual machine, there emerges the concept of the irreversibility of purely mechanical processes (with no assumption of the thermodynamic limit or mixing properties necessary) under the influence of “macroscopic” operations by an external agent. Here, designation of an operation as “macroscopic” implies that (i) we are ignorant of the initial

phase point on a given energy surface, and (ii) we are interested only in the statistical average over such an initial ensemble at a given energy.

II. BRIEF SUMMARY OF STOCHASTIC ENERGETICS

We consider a Langevin equation that represents a system in contact with a heat bath at temperature T ,

$$\frac{dx}{dt} = \frac{p}{m}, \quad (1)$$

$$\frac{dp}{dt} = -\gamma \frac{p}{m} - \frac{\partial U(x,a)}{\partial x} + \xi(t).$$

Here we denote by x and p the dynamical variable of the system and its conjugate momentum, while m represents the mass, γ the friction constant, and U the potential energy for x . We assume that U may depend on, in addition to x , the variable (or variables) a , which is controlled by an external agent (or agents). The function $\xi(t)$ represents, as usual, Gaussian white noise obeying the relations (hereafter we adopt units in which $k_B = 1$)

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t) \xi(t') \rangle = 2\gamma T \delta(t - t'). \quad (2)$$

The second relation (Einstein's relation) insures a canonical distribution of x and p at temperature T if the parameter a is held fixed for an infinitely long time.

Multiplication of each term in the second equation in (1) by the displacement dx yields the equation [8]

$$\frac{d}{dt} \left(\frac{p^2}{2m} \right) dt = \left(-\gamma \frac{p}{m} + \xi(t) \right) dx - \frac{\partial U(x,a)}{\partial x} dx, \quad (3)$$

where we have used the first equation of Eq. (1) and also the identity $(dp/dt)dx = (dp/dt)(p/m)dt$. We note that $-[-\gamma(dx/dt) + \xi(t)]$ is the *reaction* force exerted by the system against the heat bath, since the frictional force $-\gamma(dx/dt)$ and the random force $\xi(t)$ are both due to the heat bath. We identify the work done by the reaction force as the *heat* transferred from the system to the heat bath, which we denote by $(-dQ)$ [3]:

$$-dQ \equiv - \left(-\gamma \frac{dx}{dt} + \xi(t) \right) dx. \quad (4)$$

(The minus sign in front of dQ is included to conform to the convention of thermodynamics textbooks.) The key point of introducing the concept of heat is that, although the heat bath is idealized and not affected by the system's dynamics, it can still be subject to a reaction force exerted by the system. Adding the total differential dU to both sides of Eq. (3), we obtain the general expression for the *energy balance* as

$$d \left(\frac{p^2}{2m} + U \right) = \frac{\partial U}{\partial a} da + dQ. \quad (5)$$

Now, because the left-hand side (LHS) is the total increase of the energy, and dQ is the energy input to the system as heat, the first term on the RHS of Eq. (5) must be identified

as the *work* done by the external system, dW , on the system through the change of variable a ,

$$dW \equiv \frac{\partial U}{\partial a} da. \quad (6)$$

We conclude that the law of energy balance expressed as

$$dE = dW + dQ, \quad E \equiv \frac{p^2}{2m} + U \quad (7)$$

is satisfied for any *single* realization of the stochastic process described by Eq. (1).

For a quasistatic process, in which $|da/dt|$ is arbitrarily small, the work is reversible and is equal to the change in the Helmholtz free energy $F(T, a)$ with probability 1. That is, in an ensemble of infinitely many realizations of such a process, the probability distribution of the work becomes a point distribution concentrated at the value of $F(T, a)$:

$$dW = dF(T, a) \quad (\text{for a quasistatic process with } T \text{ fixed}), \quad (8)$$

with

$$F(T, a) \equiv -T \ln \left[\int \int e^{-E/T} dx dp \right]. \quad (9)$$

The derivation of Eq. (8) is as follows. We first note that, for a to change by any small but finite amount da , it takes a time $|da|/|da/dt|$, which is indefinitely large in the quasistatic limit. During this time interval the state point (x, p) comes arbitrarily close to almost all possible values, and its empirical distribution becomes asymptotically equal to the canonical distribution, $P_{\text{eq}}(x; T, a) = \exp\{[F(T, a) - E]/T\}$. (The exception here is the case in which the interval $[a, a + da]$ includes a point at which the equilibration time diverges. See Sec. IB 2 and Sec. I B and § IV below.) We can then evaluate $(\partial U/\partial a)da$ using its average with respect to P_{eq} in the quasistatic limit. Using the identity

$$\int dx \frac{\partial U(x, a)}{\partial a} P_{\text{eq}}(x; T, a) = \frac{\partial F(T, a)}{\partial a} \quad (T \text{ fixed}), \quad (10)$$

we reach the result Eq. (8).

In fact Eq. (8) is a stronger statement than the usual second law of thermodynamics for extensive systems. Note that for a thermodynamic system constituted by an ensemble of a large number of independent stochastic systems obeying Eq. (1), the first law of thermodynamics is obtained from Eq. (7),

$$\langle dE \rangle = \langle dW \rangle + \langle dQ \rangle, \quad (11)$$

and the second law of thermodynamics for quasistatic processes is obtained from Eq. (8) [4,9],

$$\langle dW \rangle = dF(T, a) \quad (\text{for a quasistatic process with } T \text{ fixed}). \quad (12)$$

These relations are concerned with only the ensemble averages denoted by $\langle \cdot \rangle$. It has also been shown [4] that, for a finite rate of change of $a(t)$, the Clausius inequality

$$\langle dW \rangle \geq dF(T, a) \quad (13)$$

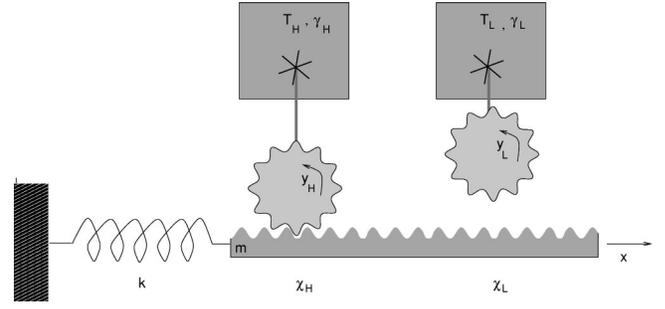


FIG. 1. Schematic view of a Carnot heat engine. The spring and the shaded linear ‘‘gear’’ represent the harmonic oscillator as the system. The left end of the spring (the black box) is fixed. Heat baths of temperatures T_H and T_L (the square shaded boxes) exert forces on the vanes (the star-shaped symbols inside the heat baths) whose angles of rotation are denoted by γ_H and γ_L , respectively. These vanes are tightly connected to the circular gears. These circular gears can interact with the system in a manner that depends on the control parameters χ_H and χ_L of the couplers.

holds, and an explicit formula for the *irreversible* work $\langle dW \rangle - dF(T, a)$ has been obtained up to the second order in da/dt .

III. MODEL

Figure 1 schematizes the idea of our model. We employ a single harmonic oscillator with mass m and spring constant k (>0) as the system under study, which we call simply the ‘‘system.’’ We denote by x and p the position and momentum of the system. Increasing (decreasing) the value of k corresponds to compressing (decompressing) the ideal gas. Below, we consider k to be a quantity that can be controlled, as the volume of a gas system is controlled in macroscopic Carnot cycles.

In order to allow independent and variable interaction with each heat bath, we represent each such interaction in the form of a mechanical force, which subsumes the corresponding frictional and Gaussian random forces. Such mechanical forces should be related in some way to the degrees of freedom that directly interact with the heat baths, which we denote by y_H and y_L . For simplicity, we do this by writing the mechanical forces as interaction forces, $-\partial\phi_H/\partial x$ and $-\partial\phi_L/\partial x$. As interaction potentials, we choose functions $\phi_H(x - y_H, \chi_H)$ and $\phi_L(x - y_L, \chi_L)$, where χ_H and χ_L are the control parameters. We call ϕ_H and ϕ_L the couplers, because their values directly indicate the strength of the coupling between the system and the corresponding heat bath. We use expressions like ‘‘control the coupler(s)’’ in reference to changes made in the values of these control parameters. We assume that the functions ϕ_α ($\alpha = H, L$) are 2π -periodic functions of $x - y_\alpha$. (For details, see Sec. IV and Fig. 3 below.) The degrees of freedom y_H and y_L are subject to the frictional forces $-\gamma_H(dy_H/dt)$ and $-\gamma_L(dy_L/dt)$ and the random forces $\xi_H(t)$ and $\xi_L(t)$ exerted by the heat baths at temperatures T_H and T_L , respectively, as well as the interaction forces from the system, $-\partial\phi_H/\partial y_H$ and $-\partial\phi_L/\partial y_L$. Here, γ_H and γ_L are the friction constants, and $\xi_H(t)$ and $\xi_L(t)$ are the white Gaussian random forces satisfying $\langle \xi_H(t)\xi_H(t') \rangle = 2\gamma_H T_H \delta(t - t')$, $\langle \xi_L(t)\xi_L(t') \rangle = 2\gamma_L T_L \delta(t - t')$, and $\langle \xi_H(t)\xi_L(t') \rangle = 0$. The equations of motion for x , p , y_H , and y_L are given as follows:

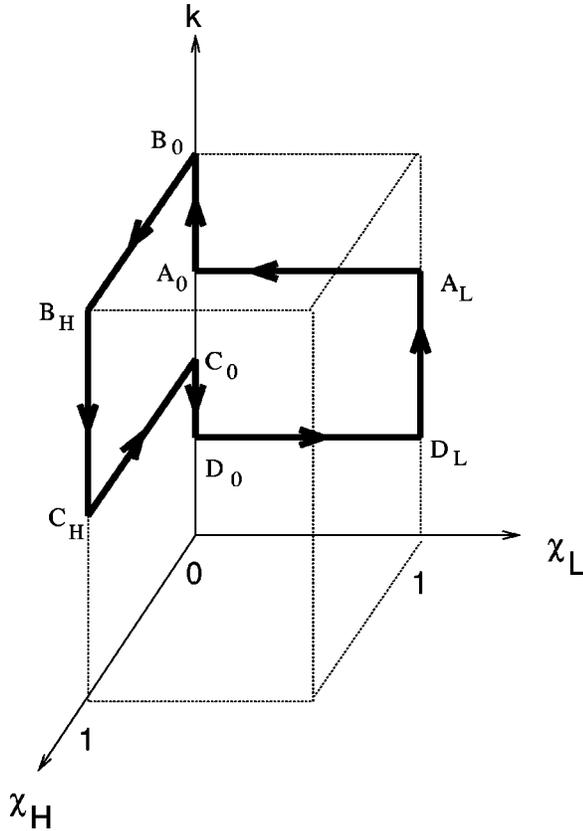


FIG. 2. The cycle undergone by the control parameters. The various legs of this cycle correspond to the following processes of the system: isothermal processes ($B_H \rightarrow C_H$ and $D_L \rightarrow A_L$), adiabatic processes ($A_0 \rightarrow B_0$ and $C_0 \rightarrow D_0$), and the remaining processes where only one of the two control parameters of the couplers is changed (i.e. $\chi_H \neq 0$ exclusively or $\chi_L \neq 0$) while k is kept constant.

$$\frac{dx}{dt} = \frac{p}{m}, \quad (14a)$$

$$\frac{dp}{dt} = -kx - \frac{\partial \phi_H}{\partial x} - \frac{\partial \phi_L}{\partial x}, \quad (14b)$$

$$\gamma_H \frac{dy_H}{dt} = -\frac{\partial \phi_H}{\partial y_H} + \xi_H(t), \quad (14c)$$

$$\gamma_L \frac{dy_L}{dt} = -\frac{\partial \phi_L}{\partial y_L} + \xi_L(t). \quad (14d)$$

We consider the gears of the heat bath and the system to be “tightly connected” (i.e., completely engaged) for $\chi_\alpha = 1$, that is, the interaction $\phi_\alpha(x - y_\alpha, 1)$ is so strong that the difference $x - y_\alpha$ is fixed except for a small thermal fluctuation around its mean value, while these gears are “disconnected” (i.e., completely disengaged) for $\chi_\alpha = 0$, that is, $\phi_\alpha(x - y_\alpha, 0) \equiv 0$. We have neglected the inertia effect related to y_H and y_L , as they would play only a secondary role for our analysis.

The protocol by which we control the parameters is represented in the space of (k, χ_H, χ_L) as shown in Fig. 2. In the figure, the paths along the axis $(\chi_H, \chi_L) = (0, 0)$ correspond to adiabatic processes, while the vertical paths with

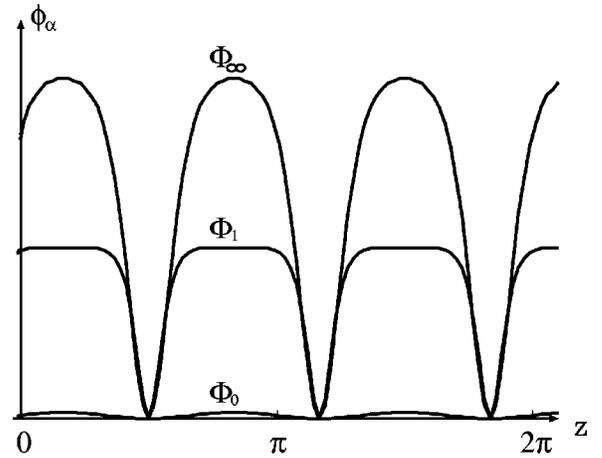


FIG. 3. The profiles of the interaction potential ϕ_α are given as functions of $z \equiv x - y_\alpha$ for three typical values of the maximum of ϕ_α , Φ_0 , Φ_1 , and Φ_∞ , where $\Phi_0 \ll T_\alpha \ll \Phi_1 < \Phi_\infty$ (see the text).

$(\chi_H, \chi_L) = (1, 0)$ and $(\chi_H, \chi_L) = (0, 1)$ correspond to isothermal processes. The values of k corresponding to the four horizontal paths are the parameters.

IV. REVERSIBLE AND IRREVERSIBLE WORK OF OPERATING THE COUPLERS

As we discussed in Sec. I, the operation of the couplers can never be made quasistatic, because the time scale of this operation inevitably becomes shorter than the equilibration time for the system when the coupling between the system and a heat bath becomes either absent or extremely tight. In addition to the work due to these irreversible processes, there is also reversible work associated with operation of the couplers.

Figure 3 illustrates the generic features of the potential $\phi_\alpha(z, \chi_\alpha)$ for three different values of χ_α . Here Φ_0 , Φ_1 , and Φ_∞ represent the height of each potential profile. We assume that the height of $\phi_\alpha(z, \chi_\alpha)$ is a monotonically increasing function of χ_α and satisfies $\max_z \phi(z, 0) = 0$, $\max_z \phi(z, \chi_{\alpha 0}) = \Phi_0 (\ll T_\alpha)$, $\max_z \phi(z, \chi_{\alpha 1}) = \Phi_1 (\gg T_\alpha)$, and $\max_z \phi(z, 1) = \Phi_\infty (> \Phi_1)$ with $0 < \chi_{\alpha 0} < \chi_{\alpha 1} < 1$.

There are two situations in which the time scale of measurement and/or operation cannot exceed the equilibration time of the system. One is when the height of ϕ_α is very small, and the other is when the height of ϕ_α is very large. Let us assume that the regime $0 < \chi_\alpha < \chi_{\alpha 0}$ corresponds to the former case; that is, for $\max_z \phi_\alpha(z, \chi_\alpha) \leq \Phi_0$, the interaction ϕ_α is so weak that the equilibration time of the system with the heat bath ($T = T_\alpha$) is beyond the time scale of measurement and/or operation. We call this the *loose regime*. Then we assume that the regime $\chi_{\alpha 1} < \chi_\alpha < 1$ corresponds to the latter case; that is, for $\max_z \phi_\alpha(z, \chi_\alpha) \geq \Phi_1$, the interaction ϕ_α is so strong that the equilibration time characterized by the over-barrier transition of z (see Fig. 3) is again beyond the time scale of measurement and/or operation. In particular, we assume that for $\chi_\alpha = 1$ there occur essentially no thermal activation events over the barrier Φ_∞ . We call this the *tight regime*. In the remaining regime, $\chi_{\alpha 0} \leq \chi_\alpha \leq \chi_{\alpha 1}$ we assume that the operation can be carried out in a manner that arbitrarily closely approximates the quasistatic limit. Note

that what Kramers calls the ‘‘small viscosity’’ and ‘‘large viscosity’’ cases in Ref. [10] correspond, respectively, to the limits of the loose and tight regimes.

We now evaluate the work

$$W_\alpha(\chi_{\alpha 1} \rightarrow \chi_{\alpha 2}) \equiv \int_{\chi_\alpha = \chi_{\alpha 1}}^{\chi_{\alpha 2}} \frac{\partial \phi_\alpha[x(t) - y_\alpha(t), \chi_\alpha(t)]}{\partial \chi_\alpha} d\chi_\alpha(t) \quad (15)$$

for the loose and tight regimes using Eq. (6). We will describe the case of $\alpha = H$ for concreteness. (The case of $\alpha = L$ can be treated similarly.) In the loose regime (the processes near B_0 and C_0 in Fig. 2), $W_H(0 \rightarrow \chi_{H0})$ is of order Φ_0 and is small ($\ll T_H$), although this work may be mostly irreversible. Since Φ_0 is associated with the lower limit of quasistatic operation, the time scale of the operation is required to be large enough to satisfy the condition $\Phi_0 \ll T_H$.

In the tight regime (the processes near B_H and C_H in Fig. 2), the situation is more subtle. The contribution to $W_H(\chi_{H1} \rightarrow 1)$ consists of (i) the contribution produced when z moves around the valley regions of $\phi_H(z, \chi_H)$ with $\phi_H \lesssim \Phi_1$ and (ii) the contribution produced when z visits, by rare thermal excitation, the barrier regions of ϕ_H . To simplify the analysis we exclude the former contribution by assuming that $\partial \phi_H(z, \chi_H) / \partial \chi_H = 0$ for z in the valley regions of ϕ_H (Fig. 3) in the tight regime. (This assumption is only technical; one can reach the conclusion of this paragraph without it.) The evaluation of the contribution (ii) above is carried out as follows. The probability of finding z in the barrier region is $\sim e^{-\Phi_1/T}$, and for such values of z the change of χ_H from χ_{H1} to 1 results in an amount of work $\sim (\Phi_\infty - \Phi_1)$. Thus we have $W_H(\chi_{H1} \rightarrow 1) \sim e^{-\Phi_1/T} (\Phi_\infty - \Phi_1) \sim e^{-\Phi_1/T} \Phi_\infty$. Because the time scale of operation is sufficiently large to allow large values of Φ_1 , the conditions $e^{-\Phi_1/T} \Phi_\infty \ll T$ and $\Phi_\infty \gg T$ can be satisfied simultaneously. In conclusion, the irreversible part of the work associated with both the loose regime and the tight regime can be made as small as we wish by making the time scale of the operation sufficiently long in these regimes. The same conclusion holds for the case of $\alpha = L$.

The quasistatic work associated with the change of χ_α within the region $\chi_{\alpha 0} \leq \chi_\alpha \leq \chi_{\alpha 1}$ can be evaluated using Eq. (8). Below we show that such quasistatic work cancels exactly when summed over the consecutive operations of connection to and disconnection from a heat bath. Again, considering the case of $\alpha = H$, we denote by $F(T_H, k, \chi_H, 0 (= \chi_L))$ the Helmholtz free energy of the composite system of the harmonic oscillator and the couplers, $\{p, x, y_H, y_L\}$:

$$e^{-F(T_H, k, \chi_H, 0)/T_H} \equiv 2\pi \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \int_0^{2\pi} dy_H \times \exp \left\{ -\frac{1}{T_H} \left[\frac{p^2}{2m} + \frac{kx^2}{2} + \phi_H(x - y_H, \chi_H) \right] \right\}. \quad (16)$$

Note that here $\chi_L = 0$ and the factor 2π in front of the integration on the RHS comes from the phase integration over y_L . Performing the integration over y_H first, we have

$$F(T_H, k, \chi_H, 0) = -\frac{T_H}{2} \ln \frac{(2\pi)^4 (T_H)^2 m}{k} + \tilde{F}(T_H, \chi_H, 0), \quad (17)$$

with \tilde{F} defined by

$$e^{-\tilde{F}(T_H, \chi_H, 0)/T_H} = \int_0^{2\pi} dz e^{-\phi_H(z, \chi_H)/T_H}. \quad (18)$$

The first term on the RHS of Eq. (17) is independent of χ_H , while \tilde{F} is independent of k . Using the notation of Eq. (15), we find from Eq. (17) that $W_H(\chi_{H0} \rightarrow \chi_{H1}) = \tilde{F}(T_H, \chi_{H1}, 0) - \tilde{F}(T_H, \chi_{H0}, 0)$ along $B_0 \rightarrow B_H$ in Fig. 2, and $W_H(\chi_{H1} \rightarrow \chi_{H0}) = \tilde{F}(T_H, \chi_{H0}, 0) - \tilde{F}(T_H, \chi_{H1}, 0)$ along $C_H \rightarrow C_0$. These two cancel exactly:

$$W_H(\chi_{H0} \rightarrow \chi_{H1}) + W_H(\chi_{H1} \rightarrow \chi_{H0}) = 0. \quad (19)$$

The actual time interval required to change χ_α between $\chi_{\alpha 0}$ and $\chi_{\alpha 1}$ is finite, say, t_{01} . The irreversible work due to this finiteness has been shown to be $O(t_{01}^{-1})$ quite generally [4]. Thus the irreversible work associated with the process in which χ_α is changed between $\chi_{\alpha 0}$ and $\chi_{\alpha 1}$ can be made as small as we wish by making the time scale of operation sufficiently long.

For later use, we now also estimate the heat exchanged upon the operation of the couplers. As we have shown above, the amount of work in the loose and tight regimes can be made arbitrarily small. Also, changes in the parameters χ_α lead to only small changes of the internal energy of the composite system. These facts together with the energy balance principle [see Eq. (7)] lead to the conclusion that the heat exchanged in these two regimes can be made as small as we wish. Next, the heat exchanged during the quasiequilibrium processes with $\chi_{\alpha 0} < \chi < \chi_{\alpha 1}$ is assessed as follows. From Eq. (17) the ensemble average of the internal energy of the composite system is given by $T_H + [1 - T_H(\partial/\partial T_H)]\tilde{F}(T_H, \chi_H, 0)$. If we define by $\langle Q(B_0 \rightarrow B_H) \rangle$ the average heat influx to the composite system during the quasiequilibrium operation along $B_0 \rightarrow B_H$, the condition of energy balance, Eq. (11), yields $\langle Q(B_0 \rightarrow B_H) \rangle = -T_H(\partial/\partial T_H)[\tilde{F}(T_H, \chi_{H1}, 0) - \tilde{F}(T_H, \chi_{H0}, 0)]$. This heat cancels exactly the average heat input $\langle Q(C_H \rightarrow C_0) \rangle$ similarly defined along $C_H \rightarrow C_0$:

$$\langle Q(B_0 \rightarrow B_H) \rangle + \langle Q(C_H \rightarrow C_0) \rangle = 0. \quad (20)$$

In the same manner, we can show the cancellation of both the work and the heat during the quasistatic part of the operation of coupler along $D_0 \rightarrow D_L$ and $A_L \rightarrow A_0$.

V. MATCHING THE ‘‘TEMPERATURE’’ OF THE SYSTEM AND A HEAT BATH

Here we study the meaning of the idea of matching the ‘‘temperature’’ of the small system with that of a heat bath. For comparison, we note that this meaning is unambiguous for an isolated macroscopic thermodynamic system, for which the energy and the temperature are simultaneously well-defined quantities, and, in order to realize a reversible Carnot cycle, the temperature of the system should be the

same as that of the heat bath with which it makes contact. In contrast, for isolated small systems, the energy takes a definite value, while the temperature is not generally well defined. We will show in this section that if the small system is a harmonic oscillator the concept of the temperature is still useful, and reversibility can be obtained as in macroscopic systems. Discussion regarding the general case is given in Sec. VII A.

Suppose that a coupler is operated quasistatically up to the edge of a loose regime ($\chi_L = \chi_{L0}$ along $A_L \rightarrow A_0$ or $\chi_H = \chi_{H0}$ along $C_H \rightarrow C_0$ in Fig. 2). The energy of the oscillator in this situation fluctuates as a function of time and, although the temporal fluctuation of the energy is very slow, it still obeys the canonical distribution at the temperature of the heat bath (T_L for A_0 and T_H for C_0) up to a small error of $O(\Phi_0) (\ll T_a)$. By the definition of the loose regime, further weakening the connection results in a situation in which there is no appreciable exchange of energy between the system and the heat bath (see Sec. I and IV). Then complete disconnection leaves an isolated system whose energy is distributed according to the canonical distribution corresponding to the temperature of the heat bath. This is in fact true even if the small system is not a harmonic oscillator.

For a harmonic oscillator, however, both the energy distribution in the canonical ensemble and the transformation of the system's energy through the quasistatic adiabatic process have special features. The energy distribution in the canonical ensemble at temperature T , $P_{\text{can}}(E; T)$, is independent of the parameter k :

$$P_{\text{can}}(E; T) = \frac{1}{T} e^{-E/T}. \quad (21)$$

(See Appendix A for a derivation.) Thus, at A_0 and C_0 , the energy of the oscillator is distributed according to $P_{\text{can}}(E; T_L)$ and $P_{\text{can}}(E; T_H)$, respectively. If the oscillator has a specific (initial) energy E and undergoes the quasistatic adiabatic process represented as $A_0 \rightarrow B_0$ or $C_0 \rightarrow D_0$ in Fig. 2, its energy $E(k)$ changes so that the value $J(E, k)$ given by Eq. (A3) remains constant [11]:

$$J(E(k), k) = \frac{E(k)}{2\pi} \sqrt{\frac{m}{k}} = \text{const}. \quad (22)$$

The relation (22) determines the change of the energy distribution when the system undergoes a quasistatic adiabatic process through the change of k : For a change from k to k' , the altered distribution $P'(E')$ must obey $P_{\text{can}}(E, T)dE = P'(E')dE'$ with $E'/(2\pi\sqrt{k'/m}) = E/(2\pi\sqrt{k/m})$. Thus we obtain the energy distribution of a canonical ensemble after the change in k , $P'(E') = P_{\text{can}}(E', T')$, with T' being defined by $T/\sqrt{k} = T'/\sqrt{k'}$. However, we note that this simple situation is due to the special nature of the harmonic oscillator system. The general case is discussed in Sec. VII A.

With these facts in mind, we can now characterize the condition for a quasiequilibrium transition between adiabatic processes and subsequent isothermal processes: (1) The energy distribution of the system before the connection with the heat bath must be that of a canonical ensemble; (2) the temperature characterizing this canonical ensemble must be

the same as that of the heat bath in question. The reason is that, under these conditions, the system upon connection behaves statistically *as if* it had been in contact with the heat bath for a long time. Note that the connection should be begun through a sufficiently weak interaction $\sim \Phi_0$ (see Sec. IV). In our case with the protocol described by Fig. 2, we require that $T' = T_H$ at B_0 and $T' = T_L$ at D_0 hold. Denoting the value of k between A_0 and A_L as k_A , that between B_0 and B_H as k_B , etc., the condition for a quasiequilibrium connection to the heat bath is given explicitly as follows:

$$\frac{T_L}{\sqrt{k_A}} = \frac{T_H}{\sqrt{k_B}}, \quad \frac{T_H}{\sqrt{k_C}} = \frac{T_L}{\sqrt{k_D}}. \quad (23)$$

VI. EFFICIENCY

A. How is the Carnot limit approached?

We now evaluate the maximal overall efficiency. We must take into account (i) the operation of the couplers, (ii) the isothermal processes, and (iii) the adiabatic processes.

(i) We assume that, by making the time in the loose and tight regimes sufficiently long, the intrinsically irreversible work and heat flow can be made as small as we wish. The remaining part of the operation of the couplers is assumed to be made under quasiequilibrium conditions. The accompanying work and heat flow cancel exactly when summed over an infinite number of consecutive connections and disconnections from the heat bath [see Eqs. (19) and (20)].

(ii) For the isothermal parts of the cycle, $B_H \rightarrow C_H$ and $D_L \rightarrow A_L$, we assume a quasistatic change of k . The accompanying work is then given using the general formula Eq. (8). For the part $B_H \rightarrow C_H$, $F(T, a)$ in Eq. (8) is replaced by $F(T_H, k, \chi_H, 0)$ of Eq. (17), and the work done by the system is $(T_H/2)\ln(k_B/k_C)$, which we denote by $-W(B_H \rightarrow C_H)$. Similarly, for the part $D_L \rightarrow A_L$ the work is $-W(D_L \rightarrow A_L) = (T_L/2)\ln(k_D/k_A)$. Then, from relation (23), we have

$$-W(B_H \rightarrow C_H) - W(D_L \rightarrow A_L) = \frac{T_H - T_L}{2} \ln\left(\frac{k_B}{k_C}\right). \quad (24)$$

(iii) For the adiabatic part of the cycle, $A_0 \rightarrow B_0$ and $C_0 \rightarrow D_0$, we also assume a quasistatic change of k . The energy of the system then obeys the law (22) and the amounts of work done by the system in the adiabatic processes $-W(A_0 \rightarrow B_0)$ and $-W(C_0 \rightarrow D_0)$ are given by $-W(A_0 \rightarrow B_0) = E(k_A)(1 - \sqrt{k_B/k_A})$ and $-W(C_0 \rightarrow D_0) = E(k_C)(1 - \sqrt{k_D/k_C})$. As the energies E_A and E_C obey the distribution Eq. (21) with $T = T_L$ and $T = T_H$, respectively, their statistical averages are $\langle E_A \rangle = T_L$ and $\langle E_C \rangle = T_H$ [up to a small error of $O(\Phi_0)$]. Using Eq. (23), we then have

$$\begin{aligned} & -\langle W(A_0 \rightarrow B_0) \rangle - \langle W(C_0 \rightarrow D_0) \rangle \\ & = T_L \left[1 - \sqrt{\frac{k_B}{k_A}} \right] + T_H \left[1 - \sqrt{\frac{k_D}{k_C}} \right] = 0. \end{aligned} \quad (25)$$

While we obtain this simple result in the present case, it is important to note that the cancellation of the contributions from the adiabatic processes on the average is not a generic feature of the Carnot cycle (consider, for example, nonideal gases).

The heat influx from the high temperature heat bath is evaluated as follows. While the work during the isothermal quasiequilibrium processes is a nonfluctuating quantity [see Eq. (8)], both the energy influx from the heat bath and the system's energy fluctuate subject to the constraint of energy balance described by Eq. (7). From Eqs. (17) and (18) we can show that the average internal energy of the composite system with degrees of freedom $\{p, x, y_H, y_L\}$ is independent of the parameter k . Therefore, the statistical average of the heat influx during the isothermal process $B_H \rightarrow C_H$, which we denote by $\langle Q(B_H \rightarrow C_H) \rangle$, satisfies

$$0 = \langle Q(B_H \rightarrow C_H) \rangle + W(B_H \rightarrow C_H). \quad (26)$$

Thus we have

$$\langle Q(B_H \rightarrow C_H) \rangle = \frac{T_H}{2} \ln \left(\frac{k_B}{k_C} \right). \quad (27)$$

As we have seen in Sec. IV, there is no net heat flow due to the quasistatic part of the operation of the coupler [see Eq. (20)], while the heat transfer associated with the loose and tight regimes can be made as small as we wish.

Collecting the above results, the maximal overall efficiency η_{\max} of the cycles is reduced to the following formula:

$$\eta_{\max} = - \frac{W(B_H \rightarrow C_H) - W(D_L \rightarrow A_L)}{\langle Q(B_H \rightarrow C_H) \rangle}. \quad (28)$$

Then, using Eqs. (24) and (27), we have

$$\eta_{\max} = 1 - \frac{T_L}{T_H}. \quad (29)$$

We would like to stress that the attainment of this efficiency (whose expression is familiar from textbook treatments) is not due to the quasistatic operation of the whole system. In the situation we consider, we have seen that some parts of the cycle can never be carried out quasistatically, due to the intrinsically irreversible operation of the couplers (Sec. IV), as well as the intrinsic irreversibility resulting from the noncanonical energy distribution of the system caused by the adiabatic processes (Sec. V).

B. Statistics over a finite number of cycles

The maximal efficiency Eq. (29) obtained above represents exclusively the ratio of the total work done by the system to the total energy influx from the high temperature heat bath through an infinite number of cycles. Here we consider the efficiency for a single cycle, η_{loc} , which can be written as

$$\eta_{\text{loc}} = \frac{[(T_H - T_L)/2] \ln(k_B/k_C) - \delta_W}{(T_H/2) \ln(k_B/k_C) + \delta_Q}, \quad (30)$$

with

$$-\delta_W = -W(A_0 \rightarrow B_0) - W(C_0 \rightarrow D_0)$$

and

$$\delta_Q = \{Q(B_0 \rightarrow B_H) + Q(C_H \rightarrow C_0)\} + \left\{ Q(B_H \rightarrow C_H) - \frac{T_H}{2} \ln \left(\frac{k_B}{k_C} \right) \right\}. \quad (31)$$

We first note several properties of η_{loc} .

(1) The deviations δ_W and δ_Q do not vanish, even in the quasiequilibrium limit, since the system continues to exchange energy with a heat bath until the moment that it is disconnected from the heat bath.

(2) If we choose the initial point of an individual cycle to be somewhere between D_L and A_L , then the values of $\eta_{\text{loc}} - \langle \eta_{\text{loc}} \rangle$ for different cycles are statistically independent. In fact, the statistical deviations of $W(A_0 \rightarrow B_0)$ and $W(C_0 \rightarrow D_0)$ are mutually uncorrelated because of the intervening isothermal Markov processes $B_H \rightarrow C_H$ and $D_L \rightarrow A_L$, while $W(A_0 \rightarrow B_0)$ and $Q(B_0 \rightarrow B_H)$ are statistically correlated through the shared point B_0 , as are $Q(C_H \rightarrow C_0)$ and $W(C_0 \rightarrow D_0)$ through the point C_0 .

(3) One can define the excess output $-\dot{W}$ by

$$-\dot{W} \equiv (\eta_{\text{loc}} - \eta_{\max}) \left[\frac{T_H}{2} \ln \left(\frac{k_B}{k_C} \right) + \delta_Q \right] = -\delta_W - \eta_{\max} \delta_Q. \quad (32)$$

A positive value of $-\dot{W}$ implies that we happened to get more work than that expected from the Carnot maximal efficiency (i.e., $-\delta_W > \eta_{\max} \delta_Q$). Such a situation can result through fluctuations, and it is not in contradiction with the second law of thermodynamics. However, we may then ask how many cycles on average we must carry out before we first obtain a cumulative excess output $-\dot{w}_n \equiv \sum_{i=1}^n (-\dot{W}_i)$, where $-\dot{W}_i$ is the excess output of the i th cycle and n is the total number of consecutive cycles. The point of this question can be understood in terms of the following apparent paradox: Suppose one monitors $-\dot{w}_n$ as a function of n and stops when it becomes positive for the first time. If one could repeat such a procedure of monitor and stop indefinitely many times, one could construct a perpetual machine of the second kind. This, of course, would be in contradiction with the second law of thermodynamics. A pitfall of this false argument is that, although for a given sequence of cycles, the condition $-\dot{w}_n > 0$ will be satisfied at some finite n with probability 1, the *average* over separate sequences of the smallest value of n with positive $-\dot{w}_n$ is divergent. This fact is closely related to the fact that the one-dimensional random walk is ‘‘null recurrent’’ (see Appendix B).

VII. DISCUSSION

A. Irreversibility resulting from contact with a heat bath

In Sec. V we used the fact that for the harmonic oscillator system, as a result of quasistatic adiabatic process, the energy changes in such a manner that the energy distribution remains in canonical form, with simply a change of the temperature, $T \rightarrow T'$. However, the harmonic oscillator represents a special system, and this is not generically the case with any Hamiltonian. More generally, the energy distribution $P_{\text{can}}(E, T)$ is distorted into some noncanonical form

$P'(E)$ as a result of the quasistatic adiabatic process. When an ensemble of systems following the distribution $P'(E)$ is brought into (weak) contact with a heat bath of arbitrary temperature T' , the energy distribution *irreversibly* relaxes to the canonical form $P_{\text{can}}(E, T')$. This is the case even if T' is chosen so that $\int EP'(E)dE = \int EP_{\text{can}}(E, T')dE$, i.e., even in the case that no net heat is transferred on the average from the bath to the system. The relevance of this irreversible relaxation to the energetics of small systems requires further scrutiny. This will be discussed in more detail in a separate paper [12].

B. Irreversible adiabatic process

The adiabatic process in the Carnot cycle is a mechanical process. The ergodic invariant theorem [13] tells us that, under quasistatic and adiabatic change of a system parameter, say a , by a finite amount, the phase volume enclosed by the energy surface defined by the system's energy at each moment, $J(E, a)$ [see Eq. (A2) for a definition], remains constant. The theorem does not assume the thermodynamic limit nor the presence or absence of chaotic trajectories. Contrastingly, for a nonquasistatic process $J(E, a)$ can either increase or decrease, depending on both the nature of the change of a and the initial conditions of the system.

In the context of the present paper, however, it is most meaningful to confine ourselves to only "macroscopic" external operations, excluding "demonic" ones that depend on detailed information of the system. More precisely, we focus on an unprejudiced choice of the initial conditions among those with a given energy, and also focus only on statistical averages of the energy, rather than considering particular results obtained from particular initial conditions. Sato [14] has recently studied a harmonic oscillator under a time-dependent force $m\ddot{x} = -x + a(t)$ as the simplest nontrivial example of a system with only macroscopic external operations. Here, the change of $a(t)$ amounts to a horizontal displacement of the potential. He showed analytically, as one can easily confirm, that for an arbitrary function $a(t)$ the energy of the oscillator $(m/2)\dot{x}^2 + \frac{1}{2}(x - a)^2$ is strictly non-decreasing *if* the average is taken with respect to the initial condition over all initial conditions represented by states with a given energy, i.e., over a microcanonical ensemble. Only in the limit of a quasistatic process ($|da/dt| \rightarrow 0$) is the energy unchanged.

This example demonstrates the irreversibility of a mechanical system of nonmacroscopic size with properly defined macroscopic operation. A recent numerical work [15] investigating a harmonic oscillator with time-dependent spring constant $m\ddot{x} = -k(t)x$ reveals the same phenomena when $k(t)$ is constrained to return to its initial value. In the present context of the analysis of the efficiency of Carnot cycle (Sec. VI), these findings are both natural and important, since, if the case were different, one could find a functional form for $k(t)$ for which the adiabatic work on the system would be less than what we expect for a quasistatic process, and the whole cycle could be used to construct a perpetual machine of the second kind. (Note that in the analysis of Sec. VI we have excluded only marginally the existence of such a perpetual machine if the loss due to the other sources is made arbitrarily small.)

It is desirable to obtain a general proof (or counterevidence) of the irreversibility resulting from nonquasistatic processes. A related analysis using path probabilities has been performed for chaotic systems [16]. However, we suspect that the essential mechanism of the irreversibility related to the characterization of macroscopic operators, which are ignorant of the initial microscopic state of the system, can be elucidated without resort to chaotic statistics. It is also a future problem to scrutinize the case in which the topology of the energy contour surface in the phase space ($\mathcal{H}_a = E$) changes at some parameter value, say a_c . In such cases, quasistatic processes cannot be extended across a_c [17].

C. Control of processes by the system itself

As in the case of the ordinary macroscopic Carnot cycle, we have introduced control parameters $\{k, \chi_H, \chi_L\}$. We assumed that the values of these parameters are changed by some external agent whose dynamics are external to the equation of motion of the system.

In fact, however, there are many "self-controlled" energy transducers that contain their own control systems. In such cases, the identification of the control system is more or less a matter of interpretation. In the macroscopic world, dc electric motors and steam engines are examples, while motor proteins, such as myosins, kinesins, and dyneins, etc., are microscopic examples [24,25]. Theoretically, the so-called Feynman ratchet and pawl system [6] has been proposed as a microscopic energy transducer working by itself between hot and cool heat baths. In this model, the role of the control system is played either by the pawl or by the ratchet, depending on which of these two is in direct contact with the cool heat bath. The stochastic energetics of this model have been analyzed [3,18]. Büttiker's model [19] is another self-controlled microscopic transducer. In this model a massive particle moves while in contact with a heat bath of position-dependent temperature $T(x) = T_H$ or T_L . In this model, the inertia of the particle serves to switch the particle's environment from $T = T_H$ to $T = T_L$, or vice versa. The stochastic energetics of this model have also been analyzed [20,21]. Some people have claimed that the Carnot limiting efficiency $\eta_{\text{max}} = 1 - T_L/T_H$ can be attained in Feynman's ratchet and pawl system (see [6] and [22]) and in Büttiker's model (see [23]). With the exception of the original work by Feynman *et al.* [6], where no implementation details are given, these studies introduced into their analyses some "gate" mechanism. A study of the energetics of such systems, including the action of these gates, has not yet been made.

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APPENDIX A: DERIVATION OF EQ. (21)

For a general Hamiltonian \mathcal{H}_a with a parameter a , the energy distribution $P_{\text{can}}^{\mathcal{H}_a}(E;T)$ corresponding to the canonical ensemble at temperature T is

$$P_{\text{can}}^{\mathcal{H}_a}(E;T,a) = W(E,a)e^{[F(T,a)-E]/T}, \quad (\text{A1})$$

with

$$W(E,a) \equiv \frac{\partial J(E,a)}{\partial E},$$

$$J(E,a) \equiv \int_{E > \mathcal{H}_a} d\Gamma, \quad (\text{A2})$$

$$e^{-F(T,a)/T} \equiv \int e^{-\mathcal{H}_a/T} d\Gamma,$$

where $\int d\Gamma$ denotes the phase integral. Here, J , or $S \equiv \log J$, is an adiabatic invariant.

In the text, \mathcal{H}_a is that of an isolated harmonic oscillator, $p^2/2m + kx^2/2$, and we take its spring constant k as a . The calculation of $J(E,k)$ is straightforward, yielding

$$J(E,k) = \frac{E}{2\pi} \sqrt{\frac{m}{k}}. \quad (\text{A3})$$

$W(E,a)$ is, therefore, independent of E . Thus from Eq. (A1) we reach Eq. (21). In general, however, $W(E,a)$ depends on E , and $P_{\text{can}}^{\mathcal{H}_a}(E;T)$ is not simply an exponential $\sim e^{-E/T}$.

APPENDIX B: NULL-RECURRENCE PROPERTY

As $\{-\dot{W}_i\}$ are statistically independent of each other, $-\dot{w}_n$ constitutes a one-dimensional discrete random walk. To simplify the argument we assume that $-\dot{W}_i$ takes only the values ± 1 randomly. If we denote by f_{2n} the probability that at the $(2n-1)$ th step the random walker comes to the position $+1$ for the first time, it is known that

$$f_{2n} = \frac{1}{n2^{2n+1}} \binom{2n}{n} \approx \frac{1}{\sqrt{4\pi n}^{3/2}}.$$

The fact that f_{2n} is normalized ($\sum_{n=1}^{\infty} f_{2n} = 1$) implies that this event occurs with probability 1 at some n . On the other hand, it is also true that

$$\sum_{n=1}^{\infty} (2n-1)f_{2n} = \infty,$$

which is referred to as the null-recurrence property. Thus if we are to wait until the position of the walker becomes positive for the M th time, with $M \geq 1$, then the ‘‘waiting time’’ is, *on the average*, infinite.

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