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Constant thermodynamic speed for minimizing entropy production in thermodynamic processes and simulated annealing

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For an arbitrary finite-time thermodynamic or information-based process we derive a lower bound on cumulative entropy production, as well as the associated optimal operating strategy for minimizing entropy production. The optimal path corresponds to a fixed rate of entropy production in the system, provided the rate of change is calculated in terms of the natural dimensionless time scale of the system. The constant thermodynamic speed algorithm for simulated annealing is derived from first principles and shown to be the leading term in a general expansion which represents the optimal solution. The results are valid for uniform systems (no spatial gradients) in which the involved intensive thermodynamic quantities are uniquely defined. The method and conclusions are easily extended to other objective functions, such as minimal loss of availability, and to assorted thermodynamic control variables.

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I. INTRODUCTION

The minimization of dissipation is often an important objective in thermodynamic and information-based systems. In thermodynamic systems this translates into minimizing entropy production, minimizing loss of availability or, in general, minimizing the loss of a potential work, which is equivalent to minimizing loss of the appropriate free energy function. Helmholtz free energy is one specific example for the (T,V,N) ensemble (the canonical ensemble), i.e., systems in which temperature T, volume V, and number of particles N are constant. However, *any* free energy corresponding to its particular statistical ensemble may be appropriate to the problem under consideration; for example, minimizing loss of Gibbs free energy for the (T,p,N) ensemble, where p denotes pressure. An earlier optimization of molecular diffusion through a membrane at constant T, V, and μ, μ being the chemical potential of the system [1], would appropriately have been carried out with a grand canonical ensemble.

In information-based problems such as simulated annealing [2,3], entropy production has an analogy in terms of the number of questions asked or the number of computer iterations performed [4]. Simulated annealing refers to stochastic simulation procedures for dealing with complex combinatorial optimization problems with a formal analogy to statistical thermodynamics. Many annealing schedules or cooling strategies have been proposed [2,3,5–14]. The aim optimally is to find that cooling strategy which minimizes entropy production in the entire process for given initial and final states or, alternatively, arrives at the lowest energy state in a given time.

In all these cases one can relate to the problem in thermodynamic terms. A given system must be brought from a given initial state to a final state in a fixed, finite time (or, equivalently, with fixed, finite resources, such as fixed heat exchanger area in heat exchange problems) with the least total dissipation. Note the distinction between this problem and a seemingly similar one analyzed in traditional irreversible thermodynamics. The problem solved here is a global or integral one, in which cumulative dissipation over the complete path is to be minimized. The traditional problem is of a local or differential nature, in which one considers and minimizes the rate of dissipation at each instant of time (see, for example, [15–17]). The two problems are not equivalent and consequently can have markedly different solutions.

The system's environment is the control through which we drive the system. Thus the system does not evolve according to some nominally naturally occurring kinetic equation, but rather is actively controlled so as to follow the optimal path. In most problems considered to date, a single control variable only has been considered; for example, temperature. Analyses are easily extended, however, to problems with more than one control variable. For clarity of illustration and presentation we will restrict our analysis here to the single control variable problem.

We will derive a lower bound on entropy production, as well as the operating strategy that minimizes entropy production in a finite-time process, for any spatially uniform thermodynamic system. The validity of the optimal path is independent of the degree of nonlinearity of the system, as long as all thermodynamic state variables are well defined and no gradients exist within the system. Coupling of the system to the surroundings naturally in-

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volves differences of intensive state variables of nonnegligible magnitude. We then show how this optimal operating strategy can be translated into a specific algorithm for how the system's temperature should evolve in time in terms of the system's relaxation time and heat capacity. The algorithm emerges as a series expansion about small deviations from equilibrium.

Previously, an algorithm for simulated annealing studies had been derived based on operating at constant thermodynamic speed [18,6,9]. The constant thermodynamic speed strategy has proven superior to other proposed paths in a large number of instances [6–8], but not in all cases [10,11]. Our derivation will show clearly how one arrives at the constant thermodynamic speed strategy from first principles, why it is limited to problems where deviations from equilibrium are small, and how to improve the algorithm by retaining progressively more terms in the series expansion that represents the nominally exact result.

Our starting point is requiring minimization of cumulative entropy production, and our control variable is temperature (pertinent to simulated annealing and to problems in heat transfer, be it heating or cooling). For problems where the goal is minimization of loss of potential work (i.e., minimization of dissipation of the relevant free energy), our method is easily adapted to that particular objective, and the algorithm for the optimal path can be derived analogously. Furthermore, the control variable can be chemical potential in mass transfer problems, magnetic field in magnetic systems, stress in elastic systems, or whatever the appropriate intensive thermodynamic variable may be. Optimal thermodynamic operating strategies previously derived for problems in heat transfer [19] and heat engine design [20] follow as special cases of the more general result derived here.

II. MINIMUM ENTROPY PRODUCTION PATH

In this section we will derive a lower bound on the entropy produced in the universe ΔS^u when a system is taken from a state described by the initial extensive variables $\mathbf{X}_i = (U_i, V_i, N_i, \ldots)$ to a state described by the final values $\mathbf{X}_f = (U_f, V_f, N_f, \ldots)$ during a fixed time τ, where U denotes internal energy, V volume, and N particle number of the system. We will also derive the optimal operating strategy that will achieve the minimum entropy production; for example, optimal heating rates in heat exchange or optimal cooling schedules in simulated annealing.

In [21] it was shown that a lower bound on loss of availability could be calculated from analysis of the rate of change of internal energy. The same argument enables one to calculate a lower bound on entropy production from analysis of the rate of change of entropy [22]. The general statement would be that a lower bound on dissipation of any thermodynamic free energy can be calculated by analysis of the rate of change of its corresponding extensive variable (e.g., internal energy U for Helmholtz free energy, enthalpy H for Gibbs free energy, entropy S for entropy production, etc.).

In analogy to the analysis of [21], the instantaneous entropy production dS^u can be expressed in terms of changes in the conjugate extensive variables $\mathbf{X}$ and intensive variables $\mathbf{Y}$ by

$$dS^u = \Delta\mathbf{Y}\cdot d\mathbf{X} \ , \tag{2.1}$$

where

$$\mathbf{Y} = \left[\frac{\partial S}{\partial U}, \frac{\partial S}{\partial V}, \frac{\partial S}{\partial N}, \ldots \right] = \left[\frac{1}{T}, \frac{p}{T}, -\frac{\mu}{T}, \ldots \right] .$$

μ denotes the chemical potential and S the entropy of the system; $\Delta\mathbf{Y} = \mathbf{Y} - \mathbf{Y}^e$ is the difference in intensity between the system's value $\mathbf{Y}$ and the environment's value $\mathbf{Y}^e$ that gives rise to the flow of extensity $d\mathbf{X}$ from the environment to the system. Our goal is to derive that operating strategy, or environment path, $\mathbf{Y}^e(t)$ (t=time), which will take the system from $\mathbf{X}_i$ to $\mathbf{X}_f$ in time τ while producing as little entropy as possible along the way.

An earlier attempt to derive the optimal operating strategy for $\mathbf{Y}^e(t)$ relied upon a hypothesis that the system always be kept a fixed number of standard deviations in energy from the environment's energy [9]. Our derivation stems directly from the requirement of minimal entropy production and can generate the optimal operating strategy as an expansion, the leading term of which is the same as the result of [9]. This leading term, however, turns out to be the overwhelmingly dominant term in problems where the process time is long compared to the system's relaxation time (e.g., for well-annealed systems in simulated annealing).

Our derivation provides a direct connection to statistical mechanics and information theory [9] and makes the ensuing bound on entropy production and the calculation of the optimal path immediately applicable to simulated annealing. We limit our analysis to one pair of conjugate variables, U and $1/T$, in order to make the derivation more transparent. Note that all the steps in the derivation are easily extended to any set of conjugate thermodynamic variables.

In this simple formulation the intensity difference can be expressed as an expansion about equilibrium between system and environment (the superscript e denotes properties of the environment),

$$\begin{aligned} \Delta Y &= (1/T) - (1/T^e) \\ &= \frac{\partial}{\partial U}\left[\frac{\partial S}{\partial U}\right]\Delta U + \frac{1}{2}\frac{\partial^2}{\partial U^2}\left[\frac{\partial S}{\partial U}\right]\Delta U^2 + \cdots \\ &= \frac{\partial^2 S}{\partial U^2}\Delta U + \frac{1}{2}\frac{\partial^3 S}{\partial U^3}\Delta U^2 + \cdots \ , \end{aligned} \tag{2.2}$$

where $\Delta U = U - U^e$ is the deviation of system energy from its hypothetical value U^e if it were in equilibrium with the environment. The first term on the right-hand side of Eq. (2.2) includes the thermodynamic metric $D^2S = \{\partial^2 S/\partial X_i \partial X_j\}$ first introduced by Weinhold at a point [23] and later extensively studied by Salamon and co-workers [24–26,18]. Evaluating the derivatives in Eq. (2.2) yields

$$\frac{1}{T} - \frac{1}{T^e} = \frac{-1}{CT^2}\Delta U + \frac{\theta(T)}{C^2T^3}\Delta U^2 + \cdots \ , \tag{2.3}$$

where we have defined

$$\theta(T)=1+\frac{T}{2C}\frac{\partial C}{\partial T} . \tag{2.4}$$

Next we need the phenomenological connection between the degree of deviation from equilibrium ΔU and the resulting extensity flow dU/dt. This is where the nonequilibrium nature of the process enters. However, since this will in general be a complicated relation, we use the functional form of its asymptotic behavior for small ΔU,

$$\frac{dU}{dt}=\frac{-1}{\varepsilon(T)}\Delta U . \tag{2.5}$$

As long as we use the instantaneous apparent relaxation time $\varepsilon(T)$, this is not an approximation. Rather, $\varepsilon(T)$ is the local inherent unit of time of the system and is defined by Eq. (2.5). The natural (dimensionless) time scale ξ for the process is therefore given by [27]

$$d\xi=\frac{dt}{\varepsilon(T)} \tag{2.6}$$

so that Eq. (2.5) can be rewritten as

$$\frac{dU}{d\xi}=-\Delta U . \tag{2.7}$$

A similar definition of "local time" has been used to advantage in solving the highly nonlinear Stefan problem [28].

We now have the tools to calculate

$$\Delta S^u=\int_{\mathbf{X}_i}^{\mathbf{X}_f}\Delta\mathbf{Y}\cdot d\mathbf{X}=\int_{\xi_i}^{\xi_f}\frac{dS^u}{d\xi}d\xi , \tag{2.8}$$

where, using Eqs. (2.2) and (2.7),

$$\begin{aligned}\frac{dS^u}{d\xi}&=-\frac{\partial^2 S}{\partial U^2}\left[\frac{dU}{d\xi}\right]^2+\frac{1}{2}\frac{\partial^3 S}{\partial U^3}\left[\frac{dU}{d\xi}\right]^3+\cdots\\&=\frac{1}{CT^2}\left[\frac{dU}{d\xi}\right]^2\left[1+\frac{\theta(T)}{CT}\frac{dU}{d\xi}+\cdots\right] .\end{aligned} \tag{2.9}$$

The first term on the right-hand side of Eq. (2.9),

$$\frac{1}{CT^2}\left[\frac{dU}{d\xi}\right]^2=-\frac{dU}{d\xi}D^2S\frac{dU}{d\xi}=\left[\frac{dL_s}{d\xi}\right]^2=v_s^2 , \tag{2.10}$$

is the square of the thermodynamic speed v_s^2, namely, it is the square of the natural-time derivative of the thermodynamic length L_s [9] calculated with the entropy metric $-D^2S$.

The constant thermodynamic speed path used in [6] and derived in [9] follows by recognizing that

$$\left|\frac{dU}{d\xi}\right|=\left|\frac{dU}{dT}\right|\left|\frac{dT}{d\xi}\right|=C\varepsilon\left|\frac{dT}{dt}\right| , \tag{2.11}$$

so that with Eq. (2.10) one obtains

$$\frac{dT}{dt}=\frac{v_s T}{\varepsilon\sqrt{C}} . \tag{2.12}$$

Equation (2.12) may be interpreted to mean that the fractional change in temperature with time should be proportional to the ratio of the thermodynamic speed to the root-mean-square fluctuations in the energy, so the smaller the fluctuations in energy the faster can be the temperature change. An alternative form [7] of Eq. (2.12),

$$v_s=\frac{\langle E\rangle-E_{\mathrm{eq}}(T)}{\sigma} , \tag{2.13}$$

where $\langle E\rangle$ is the average energy of the system, $E_{\mathrm{eq}}(T)$ the energy the system would have if it were in equilibrium with the environment at temperature T, and σ the standard deviation of E, shows this interpretation even more clearly.

The derivation in [9] assumes that the optimal path at all times is a constant number of standard deviations from equilibrium; this leads to v_s being constant. However, the assumption that the optimal path should have *constant* thermodynamic speed need not be invoked to arrive at Eq. (2.12).

We continue the general derivation in the spirit of the original derivation of the dissipation bound [21] by now applying the Cauchy-Schwarz inequality to Eq. (2.8) while using Eq. (2.9) to obtain

$$\begin{aligned}\Delta S^u&=\int_{\xi_i}^{\xi_f}\frac{1}{CT^2}\left[\frac{dU}{d\xi}\right]^2\left[1+\frac{\theta(T)}{CT}\frac{dU}{d\xi}+\cdots\right]d\xi\\&\geq\frac{1}{\Xi}\left[\int_{\xi_i}^{\xi_f}\frac{1}{T\sqrt{C}}\left|\frac{dU}{d\xi}\right|\left|1+\frac{\theta}{CT}\frac{dU}{d\xi}+\cdots\right|^{1/2}d\xi\right]^2 ,\end{aligned} \tag{2.14}$$

with $\Xi=\xi_f-\xi_i$ being the total duration of the process in natural dimensionless time units.

The bound in Eq. (2.14) is one of the main results of this paper. It states that the entropy production in the process is not just non-negative, as insured by traditional thermodynamics, but greater than or equal to a positive path-dependent quantity divided by the process duration. The general conclusion is of course the same as in the original derivation [21], but two major differences exist: (i) The metric expansion of the intensity difference Eq. (2.2) is carried beyond the first term and thus is not limited to processes very close to equilibrium and to constant heat capacity; (ii) the ongoing relaxation of the system is incorporated by a modification of the time scale (and thus kept within the integral rather than taken out in an averaged fashion as was done in [21]).

The equality (lower bound) in Eq. (2.14) is achieved when the integrand is a constant, i.e., when

$$\frac{dS^u}{d\xi}=v_s^2\left[1+\frac{\theta(T)}{CT}\frac{dU}{d\xi}+\cdots\right]=\text{const} . \tag{2.15}$$

Consequently, constant rate of entropy production, when expressed in terms of natural time, is the path or operating strategy which produces the least overall entropy.

Again using Eqs. (2.10) and (2.11), one can express the optimal path, Eq. (2.15), in a form similar to Eq. (2.12):

$$\frac{dT}{dt}\left[1+\frac{\theta(T)\varepsilon(dT/dt)}{T}+\cdots\right]^{1/2}=\text{const}\times\frac{T}{\varepsilon\sqrt{C}}\ . \tag{2.16}$$

The constant thermodynamic speed algorithm, Eq. (2.12), is thus the leading term of the general solution in an expansion about equilibrium behavior. In principle, any desired degree of accuracy can be achieved by retaining an adequate number of terms in the expansion Eq. (2.9). This, of course, presupposes that all thermodynamic state variables are well defined throughout.

III. EXAMPLES AND DISCUSSION

A. Thermodynamics

First we consider optimal strategies that have been derived for various thermodynamic systems in light of the path derived above, Eq. (2.15), namely, that the optimal path is the one along which the rate of entropy production is constant, provided the time scale used is the intrinsic dimensionless one defined in Eq. (2.6). In [20] it was shown that for any system obeying a linear transfer law with constant coefficients, e.g., Newtonian heat transfer, the optimal path (for minimizing entropy production) corresponds to a constant rate of entropy production (with respect to clock time). To first order in Eqs. (2.15) and (2.16) that is equivalent to constant thermodynamic speed [9].

This can be viewed as a special case of Eq. (2.15) in which the relaxation time is constant (as opposed to depending on temperature). In fact, it provides a clear generalization of the definition of "linear" system for which constant rate of entropy production with respect to clock time corresponds to the optimal path: a system for which

$$\frac{d\mathbf{X}}{dt}=a+b\mathbf{Y}\ , \tag{3.1}$$

where a and b are constants, and in which the relaxation time is constant. Note that a linear system's heat capacity C and thermal conductance κ *may* be temperature-dependent as long as their ratio $\varepsilon=C/\kappa$ is constant. Hence the conclusion of [20] extends to a broader class of systems than originally realized.

An illustrative special case arises when the heat capacity is independent of temperature and with no requirements for the relaxation time. Then Eq. (2.15) sums to a simple analytical expression,

$$\frac{dS^u}{d\xi}=\frac{v_s^2}{\left[1-\frac{v_s}{\sqrt{C}}\right]} \tag{3.2}$$

which, by Eq. (2.12), is constant when

$$\frac{d\ln T}{dt}=\frac{\text{const}}{\varepsilon}\ , \tag{3.3}$$

i.e., the optimal temperature path can be obtained by solution of Eq. (3.3) regardless of the distance from equilibrium.

As noted in [19], the theorem of [20] for linear systems is clearly not valid for nonlinear systems such as non-Newtonian heat transfer laws like radiative heat transfer. Examination of similar calculations of optimal paths for highly nonlinear systems, e.g., in the liquid-solid phase transition (classical Stefan problem) [29], reveals a similar conclusion. Equation (2.15) does, however, correctly describe the optimal path for these nonlinear systems. In these instances our new theorem does not offer a new solution; rather it provides a simpler, faster way of arriving at the correct answer and places these results within the framework of a universal observation.

The validity of our results is restricted to uniform systems, i.e., no spatial gradients. A notable exception is the Stefan problem (solid-liquid phase transition) where our results are valid, provided the system proper is taken to be the moving phase boundary, with the solid and liquid regions viewed as the thermal couplings to the surroundings [29].

In general, when spatial gradients exist within the system, the optimization procedure is far more complicated than depicted here. Several approaches have been proposed: (i) introduction of an entire field of controls on the system to regulate the internal dissipation [30]; (ii) application of spatially varying reservoirs around the surface of the system with subsequent averaging of the energy and/or mass exchanges [31]; (iii) using average effective thermodynamic state variables for the system as a whole and collecting all the internal irreversibilities into a single entropy production term. These situations are beyond the scope of this paper.

The main results of this paper, the bound Eq. (2.14) and the optimal path Eq. (2.15), contain two new notions: (i) an untruncated expansion of the driving force of the process, Eq. (2.2); and (ii) derivatives with respect to the intrinsic time ξ, Eq. (2.6). The latter implies that the optimal process slows down when the relaxation time increases. For glasses and spin glasses [32] this may lead to an essential standstill. In essence the reference frame now follows the system rather than the observer. This idea is also used in relativity and for solid-liquid phase change problems [28].

B. Simulated annealing

Problems in which a significant new degree of accuracy and new solutions may emerge come from simulated annealing. In simulated annealing studies one usually is searching for a cooling schedule that will minimize entropy production [4]. In most problems for which simulated annealing is employed, heat capacities and relaxation times cannot be known at the outset and are estimated at each step of the annealing based on the entire past history [8]. Both can vary markedly with temperature.

The value of the cooling schedule of Eq. (2.12), derived originally in [9,6], can now be understood as limited to systems which are close to equilibrium, or equivalently, for which the observation time is long compared to system relaxation time. In these cases, the correction terms noted in Eqs. (2.15) and (2.16) will be small, if not negligible.

This will not be the case when the system being cooled is not close to equilibrium. Indeed, the inferiority of the path Eq. (2.12) relative to other cooling strategies has been noted for simulated annealing problems where the observation time is relatively short [10,11]. We additionally note that it fails to reproduce the optimal path in nonlinear systems such as the phase-change problem [28].

The result derived here, however, does provide a better algorithm in principle. The degree to which the system deviates from equilibrium and from linearity will determine the number of terms one must retain in the expansion of Eqs. (2.15) and (2.16). Therefore we would suggest that simulated annealing studies for which the constant thermodynamic speed algorithm has not succeeded to provide satisfactory results be performed with the optimal algorithm derived here. If systems that are not very far from equilibrium are chosen, then only a small number of terms in the expansion of Eqs. (2.15) and (2.16) need be retained (i.e., the series converges rapidly).

IV. SUMMARY

Our fundamental finding is that the optimal strategy for driving any thermodynamic or information-based process so as to minimize entropy production is to insure that the rate of entropy production is constant when expressed in terms of the natural dimensionless time scale of the system (clock time divided by the system's relaxation time). This observation provides a universal framework for understanding the findings of earlier studies on optimal paths for simple linear systems, and what was considered to be the apparent dearth of a universal basis for determining the optimal path of processes that are nonlinear and/or not close to equilibrium.

In simulated annealing the constant thermodynamic speed algorithm [18,6,9] can now be derived from first principles and can be shown to be the leading term in an expansion in deviations from equilibrium behavior. This not only explains why the constant thermodynamic speed algorithm failed for markedly nonlinear systems and for systems not close to equilibrium, but also provides the correction terms with which the optimal cooling schedule can be generated. An immediate test of this observation would be to anneal systems for which the constant thermodynamic speed algorithm had proven inferior to alternative strategies with the new cooling schedule derived here, provided an adequate number of terms in the expansion is retained.

Our detailed derivation has been restricted to the minimization of entropy production and to a single control variable (temperature). However, the method presented here is easily generalized to cover:

(i) The minimization of dissipation of any thermodynamic free energy (equivalently, minimization of loss of potential work) provided the appropriate thermodynamic ensemble is defined; e.g., availability, Helmholtz free energy, Gibbs free energy, grand canonical ensemble (T, V, and μ constant), etc.

(ii) Any appropriate intensive control variable, such as chemical potential for problems in mass transfer, magnetic field for magnetic systems, etc.

(iii) Systems with more than one control variable, in which case our scalar equations become vectorial equations, but the conceptual and mathematical paths to solve for the optimal strategy are qualitatively unmodified.

Note that the fundamental conclusion must apply to these seemingly different but equivalent problems. Namely, the optimal path for minimizing the loss of availability, for example, is the strategy in which there is a constant rate of change of availability when the rate of change is calculated with the natural dimensionless time scale of the system. As such, one in principle now has an algorithm for minimizing dissipation based on *any* free energy criterion with respect to *any* appropriate intensive variable (or number of intensive control variables) for systems that may be nonlinear and/or not close to equilibrium.

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