Thermodynamic Length, Time, Speed and Optimum Path to Minimize Entropy Production

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Abstract

In addition to the Riemannian metricization of the thermodynamic state space, local relaxation times offer a natural time scale, too. Generalizing existing proposals, we relate thermodynamic time scale to the standard kinetic coefficients of irreversible thermodynamics. Criteria for minimum entropy production in slow, slightly irreversible processes are discussed. Euler-Lagrange equations are derived for optimum thermodynamic control for fixed clock-time period as well as for fixed thermodynamic time period. Only this latter requires constant thermodynamic speed as the optimum control proposed earlier. An easy-to-implement stepwise algorithm is constructed to realize control at constant thermodynamic speed. Since thermodynamic time is shown to correspond to the number of steps, thus the sophisticated task of determining thermodynamic time in real control problems can be substituted by measuring ordinary intensive variables. Most remarkably, optimum paths are Riemannian geodesics which would not be the case had we used ordinary time.
1 Introduction

Standard equations of irreversible thermodynamics have been known for many decades. Investigations on optimizing finite-time thermodynamic processes controlled by external reservoirs date from the 80’s. An instructive exposition of the problem at the time was published in Ref. [1]. Basically, the problem consists of finding the best path in the state space along which one drives the system from a given equilibrium state to another.

A particular approach to the problem of optimally controlling finite-time thermodynamic processes takes its origin from the natural geometric structure of the thermodynamic state space [2, 3, 4]. It would seem straightforward to expect that the geodesic path should somehow be related to the optimum path connecting the given initial and final equilibrium states. A few years ago it was pointed out [5, 6] that the natural relaxation time $\tau$ plays a fundamental role in devising optimum cooling strategies, e.g. in computer simulated annealing. Quite recently, Andresen and Gordon [7] have shown that the strategy of constant thermodynamic speed [5] is related to a certain minimum of entropy production. In the present work we reconsider these ideas and make a definite progress.

The problem itself is illustrated by the finite-time cooling process (Sect. 2), its dynamics is described by a phenomenological cooling-equation. Then, applying kinetic equations from standard irreversible thermodynamics, we generalize the concept of thermodynamic time and speed for any number of control variables (Sect. 3). Furthermore we invoke standard Euler-Lagrange equations to obtain the finite-time path of minimum entropy production and we make explicit the role of variational conditions. Most importantly, we prove that the optimum path is geodesical so a broader generalization of the old principle of constant thermodynamic speed is achieved. Even an older belief about the significance of Riemannian metric in thermodynamics might get justified (Sect. 4). Finally, we construct an iterative algorithm to realize thermodynamic processes at constant thermodynamic speed, also giving a genuine control-theoretic interpretation of thermodynamic time itself (Sect. 5).
2 Example: Finite-time cooling

Consider a system in thermal contact with a large reservoir and let $T$ and $T_r$ denote their respective temperatures. In general, both $T$ and $T_r$ will depend on time $t$. At the initial time $t_i$, assume the system and the reservoir are in equilibrium with each other at temperature $T_i$, i.e.,

$$T_r(t_i) = T(t_i) = T_i.$$  \hfill (1)

Then start to decrease the reservoir’s temperature $T_r$ from $T_i$ to $T_f$, consuming fixed finite time $t_f - t_i$, i.e., choose a given function $T_r(t)$ so that $T_r(t_f) = T_f$. The system’s temperature $T(t)$ decreases due to permanent heat transfer to the reservoir and will always be retarded with respect to the reservoir’s current temperature $T_r(t)$ by some positive $\Delta T(t) \equiv T(t) - T_r(t)$. Throughout this paper, we consider slightly irreversible processes when, e.g., $T_r(t)$ changes slowly enough to allow the heat transfer to satisfy Newton’s law and the following equation is expected to drive the permanent relaxation of the system’s temperature $T$:

$$\dot{T} = -\frac{1}{\tau(T)} \Delta T \tag{2}$$

provided the local relaxation time $\tau$ changes little between $T$ and $T_r$. It will be useful to re-scale the clock-time parameter. Introducing thermodynamic time $\xi$ was proposed earlier in Refs. [5, 6, 7]. The relation of the two scales relies upon the local relaxation time $\tau(T(t))$ along the cooling process:

$$d\xi = dt/\tau. \tag{3}$$

In the new variable, Eq. (2) takes a simple form:

$$T' \equiv \frac{dT}{d\xi} = -\Delta T. \tag{4}$$

We note that this equation has the following explicit solution with the initial condition $\xi_i = 0$:

$$T(\xi) = e^{-\xi} \left( T_i + \int_0^\xi T_r(\xi') e^{\xi'} d\xi' \right). \tag{5}$$

Now the basic goal is to single out "optimum" cooling paths. Following e.g. Andresen and Gordon [7] one requires that the optimum cooling happen
with maximum reversibility, i.e., at minimum total entropy production. The entropy production rate of the cooling process is

\[ \dot{\mathcal{S}} = C(T) \dot{T} \left( \frac{1}{T} - \frac{1}{T_r} \right) \]

(6)

where \( C(T) \) is the specific heat of the system. In case of sufficiently slow cooling this expression reduces to

\[ \dot{\mathcal{S}} = C(T) (\dot{T}/T)^2 \tau(T) \]

(7)

where we applied Eq. (2). The common criterium of optimum is

\[ \int_{t_i}^{t_f} \dot{\mathcal{S}} dt = \text{min.} \]

(8)

where the overall time \( t_f - t_i \) of the process is fixed. This optimum is achieved when

\[ \dot{\mathcal{S}} = \frac{C(T)}{T^2} \dot{T}^2 \tau(T) = \text{const.} \]

(9)

There is, however, a remarkable alternative to this optimum, because one can choose different boundary conditions. Instead of clock-time \( t_f - t_i \) the thermodynamic lapse \( \xi_f - \xi_i \) of the cooling can be fixed as well. Then the optimum cooling becomes different; it will correspond to constant entropy rate versus thermodynamic time:

\[ S' \equiv \tau \dot{\mathcal{S}} = \frac{C(T)}{T^2} \dot{T}^2 = \text{const.} \]

(10)

This condition has a challenging geometrical interpretation [7]. \( S' \) is the square of the thermodynamic speed of the cooling process:

\[ S' = \|T'\|^2, \]

(11)

calculated with the entropic metric defined by the quadratic norm

\[ \|dT\|^2 \equiv \frac{C(T)}{T^2} (dT)^2. \]

(12)

Hence the corresponding optimum process is called cooling at constant thermodynamic speed (cf. Refs. [4, 5, 7]). In Sect. 4 we shall prove that the principle of constant thermodynamic speed also applies for optimum finite-time thermodynamic processes affecting more (than one) variables. First, in Sect. 3 we must generalize the concept of thermodynamic length, time, and speed for such finite-time processes.
Let the equilibrium states of a given thermodynamic system be characterized by the \( n + 1 \) extensive variables; the vector \( X \equiv (X^1, X^2, \ldots, X^n) \) will parametrize the manifold of state space while \( X^{n+1} \) remains fixed. Following Refs. [2, 3, 4] one defines a metric tensor \( g \) on the manifold of equilibrium states, derived from the entropy \( S(X) \):

\[
g_{ik}(X) = -\frac{\partial^2 S(X)}{\partial X^i \partial X^k}. \tag{13}
\]

If one took the entropic intensive variables \( Y^k = \frac{\partial S}{\partial X^k}; k = 1, 2, \ldots, n \) instead of the extensive variables \( X \) then the metric tensor would be the inverse \( g^{-1} \equiv [g^{ik}] \) of \( g \equiv [g_{ik}] \). Hence, in obvious notations, the thermodynamic line-element square takes the following alternative forms:

\[
\|dX\|^2 = (dX|g|dX) = \|dY\|^2 = (dY|g^{-1}|dY). \tag{14}
\]

Consider now a certain path \( \{X(t); t_i \leq t \leq t_f\} \) in the thermodynamic state space. The thermodynamic length \( \ell \) of the path takes the (alternative) forms

\[
\ell = \int_{t_i}^{t_f} \|dX\| = \int_{t_i}^{t_f} \|dY\|. \tag{15}
\]

Obviously, the length of a path is independent of the choice of coordinates and even of the parametrization of the path itself. No intrinsic relation manifests itself between the thermodynamic length and the clock-time parameter \( t \).

In order to obtain a natural time scale along a given path, we first have to invoke standard concepts of irreversible thermodynamics. Consider a reservoir in equilibrium at some state variables \( X_r \) and bring it into contact with the system which is in equilibrium at \( X \). Then, the state of the system will converge to the state of the reservoir. The standard form of the relaxation equations reads [8]:

\[
\dot{X}^i = \gamma^{ik} \Delta Y_k \tag{16}
\]

where \( \Delta Y = Y_r - Y \) is the deviation from the equilibrium in terms of the entropic intensive variables, and \( \gamma = [\gamma^{ik}] \) is the matrix of kinetic coefficients; it is symmetric and positive. During this process of relaxation, entropy \( S \) will be produced at rate

\[
\dot{S} = (\dot{X} | \Delta Y). \tag{17}
\]
If $\Delta Y$ is small, one can write
\[ \Delta Y = -g \Delta X. \] (18)

The relaxation equation (16) takes the alternative forms:
\[ \dot{X} = -\gamma g \Delta X \quad \text{or} \quad \dot{Y} = -g \gamma \Delta Y. \] (19)

Using the equation (18) and the equation
\[ \dot{Y} = -g \dot{X} \] (20)
alternative expressions of entropy production rate (17) follow:
\[ \dot{S} = (\dot{X} | \gamma^{-1} | \dot{X}) = (\dot{Y} | (g \gamma g)^{-1} | \dot{Y}). \] (21)

Based on the above standard equations, an effective relaxation time $\tau$, depending on the path’s local direction $\dot{X}$, can be defined. Recall from Sect. 2 that the system’s path $X(t)$ is driven by a certain reservoir path $X_r(t)$ and the system’s retardation $\Delta X \equiv X - X_r$ is proportional to the current velocity $\dot{X}$ of the process:
\[ \Delta X = -(\gamma g)^{-1} \dot{X} \] (22)

In fact, this equation is formally identical with the relaxation equation (19), which remains valid if $X_r$ becomes a slowly varying function of time. Observe that the longitudinal (i.e. parallel to $\dot{X}$) projection of the above equation implies a certain effective relaxation time $\tau$. Introduce the longitudinal component of the retardation:
\[ \Delta X \parallel \equiv \frac{1}{||\dot{X}||} (\Delta X | g | \dot{X}) \] (23)

Substituting Eq. (22) yields the longitudinal relaxation equation (note that $\dot{X} \parallel = ||\dot{X}||$):
\[ \Delta X \parallel = -\tau ||\dot{X}|| \] (24)

where
\[ \tau = -\frac{1}{||\dot{X}||^2} (\Delta X | g | \dot{X}). \] (25)
This can be rewritten in the following equivalent form:

$$\tau = -\frac{1}{\|\dot{X}\|^{2}} (\dot{X}|\gamma^{-1}|\dot{X}). \quad (26)$$

Indeed, as it is clearly seen from this form, the effective relaxation time $\tau$ is positive and only depends on the direction of $\dot{X}$ but not on its magnitude (as long as it is moderate). Eq. (26) have the compact form

$$\tau = \frac{\dot{S}}{\|X\|^2}, \quad (27)$$

showing up $\tau$’s invariance if one changes the representation of the states from extensive variables $X$ to intensive ones $Y$, for instance.

Having introduced the effective relaxation time $\tau$, the notion of thermodynamic time $\xi$ can now be extended for paths in more dimensions. Formally, we retain the old definition (3) of the element of thermodynamic time $\xi$:

$$d\xi = dt/\tau \quad (28)$$

which now depends on the direction of the speed $\dot{X}$. Sometimes, a vector of thermodynamic speed $X'$ (or $Y'$) will be more useful than $\dot{X}$ (or $\dot{Y}$):

$$X' \equiv \frac{dX}{d\xi} = \tau \dot{X} \quad \text{or} \quad Y' \equiv \frac{dY}{d\xi} = \tau \dot{Y}. \quad (29)$$

The common (scalar) thermodynamic speed $\dot{X}$ corresponds to the invariant norm(s) $\|X'\| = \|Y'\|$ of the vector(s) (29) so an extension of the notion of thermodynamic speed for more dimensions has been performed. The entropy production $S' = \tau \dot{S}$ per unit thermodynamic time can also be considered. From Eq. (27) we obtain:

$$S' \equiv \tau \dot{S} = \|X'\|^2 \quad (30)$$

This means that the dimensionless entropy production rate $S'$ is equal to the squared thermodynamic speed, as is expected from the single variable case in Sect. 2.
4 Optimum paths minimizing entropy production

Consider a certain path \( \{ Y(t) \} \) corresponding to a finite-time thermodynamic process connecting the initial state \( Y_i \equiv Y(t_i) \) with the final one \( Y_f \equiv Y(t_f) \). Remember that a thermodynamic path \( \{ Y(t) \} \) is the solution to the ”cooling” equation (2) having now the following general form [cf. Eq. (19)]:

\[
\dot{Y} = g \gamma (Y_r - Y),
\]

(31)
driven by the given reservoir path \( \{ Y_r(t) \} \). The system’s path has a small retardation \( \Delta Y(t) \) behind the reservoir path. In the slow process approximation Eq. (21) applies and the total entropy production will depend on the path as follows:

\[
S_{fi} \equiv \int_{t_i}^{t_f} \dot{S} dt = \int_{t_i}^{t_f} (\dot{Y} | (g \gamma g)^{-1} | \dot{Y}) dt.
\]

(32)

Let us find the path minimizing the overall entropy production, among paths connecting the fixed initial and ending points at a fixed time lapse \( t_f - t_i \). An analogy with Lagrange’s variational principle can be established if we identify the Lagrange-function as \( \dot{S}/2 \). Then, minimizing paths are found to obey the following Euler–Lagrange– equations:

\[
\frac{d}{dt} ((g \gamma g)^{-1} \dot{Y})^k = \frac{1}{2} (\dot{Y} \frac{\partial (g \gamma g)^{-1}}{\partial Y_k} | \dot{Y}).
\]

(33)

Obviously, the entropy production rate (21) is an integral of the above differential equation:

\[
\dot{S} = (\dot{Y} | (g \gamma g)^{-1} | \dot{Y}) = \text{const}.
\]

(34)

which is the mathematical counterpart of the energy conservation rule in mechanics. In our case this means that the entropy minimizing path corresponds to a constant entropy production rate, as was pointed out in Sect. 2 for the single variable cooling process.

An equivalent Euler equation could be obtained had we chosen the extensive variables \( X \) to parametrize the paths. Actually we have chosen the intensive ones since in typical experimental situations the reservoir’s intensive variables are under our control (cf. Sect. 2).
In certain cases (see Sect. 5) it would be interesting to find the path minimizing $S_{fi}$ at the condition that the thermodynamic time $\xi_f - \xi_i = \int_{t_i}^{t_f} dt/\tau$ be kept fixed and the clock-time $t_f - t_i$ might be varied. In this case, one suitably replaces all $t$-dependences by $\xi$-dependences. From rate (30), one obtains the following equation for the total entropy production:

$$S_{fi} \equiv \int_{\xi_i}^{\xi_f} S' d\xi = \int_{\xi_i}^{\xi_f} \|Y'\|^2 d\xi. \quad (35)$$

At fixed $\xi_i, \xi_f$, the minimum of entropy production is achieved if the path $Y(\xi)$ satisfies the following Euler-Lagrange equations:

$$\frac{d}{d\xi} \left( g^{-1}Y' \right)^k = \frac{1}{2}(Y'|\partial g^{-1}\partial Y_k|Y'). \quad (36)$$

The entropy production rate versus thermodynamic time $\xi$ will be an integral of this Euler-Lagrange equation:

$$S' = \|Y'\|^2 = \text{const.} \quad (37)$$

Thus the minimizing path corresponds to constant $S'$. On the other hand, $S'$ is equal to the squared invariant norm of the thermodynamic speed $Y'$ defined by Eq. (29). Hence the optimum path is of constant thermodynamic speed. An equivalent result could be obtained in $X$-variables. The constancy of the thermodynamic speed is merely a consequence of a much remarkable feature of optimum paths: they are geodesics of the Riemann–metricized manifold of thermodynamic states.

5 An easy control of optimum cooling

It follows from the previous Section that the Riemannian geometric structure of the thermodynamic state space has an intrinsic relation with the processes of maximum reversibility at fixed thermodynamic lapse rather than clock-time. We are going to show that optimum cooling processes can easily be controlled by using thermometers instead of clocks! The method is straightforward to implement for the simultaneous control of more thermodynamic parameters.
We propose a stepwise control strategy to approximate the optimum process at constant thermodynamic speed. Assume that we change the reservoir temperature stepwise between $T_i$ and $T_f$:

$$T_i \equiv T_0 = T_{r0} > T_{r1} > T_{r2} > \ldots > T_{rN} = T_f,$$

and the cooling strategy goes like this. First we lower the reservoir temperature to $T_{r1}$ suddenly, and we wait for the system to become equilibrated to a given extent $\epsilon$, i.e. its temperature $T$ will be as close to $T_{r1}$ as

$$T_1 = \epsilon T_{r1} + (1 - \epsilon) T_i.$$

Then we move to the next iteration by lowering the reservoir temperature to $T_{r2}$ and letting the system’s temperature $T$ to equilibrate to the same extent $\epsilon$, identified by $T_2 = \epsilon T_{r2} + (1 - \epsilon) T_1$. In general:

$$T_{n+1} = \epsilon T_{r,n+1} + (1 - \epsilon) T_n, \quad (n = 0, 1, \ldots, N - 1). \quad (38)$$

If all steps are so small that the change of the relaxation time $\tau(T)$ is negligible at the step’s scale then the relaxation equation (2) holds and each step will have the same lapse

$$\delta \xi = \log(1 - \epsilon)^{-1} \quad (39)$$

of thermodynamic time. Hence, the number $N$ of small steps required to realize the cooling process from $T_i$ to $T_f$, provided the quality of each relaxation has had the common characteristic value $\epsilon$, will be proportional to the thermodynamic time lapse $\xi_f - \xi_i$ of the cooling path:

$$N = \frac{\xi_f - \xi_i}{\log(1 - \epsilon)}. \quad (40)$$

The smaller the defect of relaxations $1 - \epsilon$ the bigger number of iterations will be necessary to achieve the same cooling $T_i \rightarrow T_f$.

To assure constant thermodynamic speed in average we choose steps $T_{r1}, T_{r2}, \ldots$ in such a way that the same thermodynamic length $\delta \ell$ defined by (12) belong to all corresponding segments $\|T_i - T_1\|, \|T_1 - T_2\|, \ldots$:

$$\frac{C(T_n)}{T_n^2} |T_{n+1} - T_n|^2 = \delta \ell^2, \quad (n = 0, 1, \ldots, N - 1) \quad (41)$$

From equations (38,41) one obtains:

$$T_{r,n+1} = \left(1 - \frac{\delta \xi/\epsilon}{\sqrt{C(T_n)}}\right) T_n, \quad (n = 0, 1, \ldots, N - 1). \quad (42)$$
Now we can summarize the iterative algorithm of cooling. Given the current temperature $T_n$ of the system, one decreases the reservoir's temperature according to Eq. (42) and lets the system relax until the condition (38) becomes valid. This procedure is then iterated for $T_{n+1}$, e.t.c. One can see by inspection that the same average thermodynamic speed

$$v = \frac{\delta \ell}{|\log(1 - \epsilon)|}$$

(43)

belongs to each steps and consequently to the whole process as well. So this stepwise algorithm approaches the theoretical optimum process of constant thermodynamic speed [9]. We need no clocks to measure time but thermometers to measure temperatures and the $a priori$ knowledge of the specific heat function $C(T)$ of the system in hand.

In the general case when more thermodynamic variables are to be controlled one has to derive the geodesic path between the initial and final equilibrium states in advance and then apply the stepwise algorithm along the geodesic path. It is worth noting that in simulated annealing [5] the above algorithm can not be directly applied since the annealed system’s temperature and specific heat are known but statistically. We nevertheless think that our results could be adapted to computer simulated statistical systems.

A few words are needed to interprete the condition of fixed thermodynamic time when looking for the optimum control. It may often happen that it is not the clock-time of a given thermodynamic process that is the economically or technologically relevant quantity. Rather than clock-time, the number of iterated technological steps might better characterize the amount of relevant facilities (computer capacity, special materials, or just money) that can be consumed to bring the system from its initial state into a prescribed final one. In such cases the clock-time period of the process is of less interest to be fixed in advance. The step number is rather to be fixed. The condition of fixed-in-advance step number is equivalent to the condition of fixed-in-advance thermodynamic time, as shown by Eq. (40). It may eventually happen that the thermodynamic time (proportional to the step number) takes the place of the clock-time. The overall clock-time needed to perform a single cooling step might not be dominated by the clock-time of the relaxation but by the clock-time of the technological adjustment before and after the relaxation. In this case, the gross time of the stepwise process will be
proportional to its thermodynamic time. Actually, the fixed-in-advance thermodynamic time becomes the relevant condition in designing the finite-time thermodynamic process and, consequently, minimum entropy production will be achieved along the geodesic path in thermodynamic state space.

6 Conclusion

We have extended the notion of the relaxation time \( \tau \) from one dimension to an arbitrary number of dimensions. Thus the thermodynamic time can be deduced for multi-dimensional thermodynamic processes, too, in a straightforward way. As a consequence, the optimum control of a thermodynamic process based on the thermodynamic time scale can be achieved with any number of variables to be controlled. We have seen that the optimum path should be followed as close as possible by the process in hand as the geodesic is uniquely marked out between the initial and the desired final states. In addition, the proposed stepwise driving force for the process can be arranged by measuring ordinary thermodynamic variables e.g. temperature, concentration etc.

A remarkable result of the present analysis is that the path of minimum irreversible entropy production in fixed thermodynamic time becomes a geodesic of the Riemannian space of thermodynamic states introduced a decade ago. Thus far Riemannian structure was seen only in its influence in infinitesimal neighbourhoods, e.g., on thermodynamic fluctuations. Now we have shown within the context of standard irreversible thermodynamics that some finite time thermodynamic processes, when optimum, follow the shortest paths of the Riemannian space. The result is valid in an arbitrary number of dimensions and proves for the first time the distinguished role of geodesics in driven irreversible processes. Our result is based on the usual expansion of the irreversible entropy production up to the second order in speeds. Of course, the given interpretation for geodesics is restricted to not too high speeds and rates. (This, however, would not at all restrict the ultimate value of the interpretation. Recall the analogous case in space-time geometry: it is not the too large objects but the small enough ones that will follow geodesics.) These results may turn out to form a basis for amplifying the benefits of finite-time thermodynamics both in theory and in practice.

After the completion of our work we became aware of a related report by
Spirkl and Ries [10]. Whereas they do not use Riemann-geometrical terms there seem to be significant coincidences between our results.

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of the entropy production in the stepwise process versus that in the continuous process: \( S_{fi}(\text{step}) = \left( 1 + \ell C_{av}^{-1/2} / N + O(1/N^2) \right) S_{fi}(\text{cont}) \), where \( \ell \) is the thermodynamic length of the continuous path and \( C_{av}^{-1/2} \) is the average of \( C^{-1/2}(T_n) \) over \( n = 1, 2, \ldots, N \).

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