A Simple Example of Control to Minimize Entropy Production

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Abstract

This paper treats the simple example of heating a system from a given initial to a given final temperature with minimum entropy production. The allowed control for the process is the selection of K temperatures for intermediate heat baths. The problem is sufficiently simple to allow analytic approaches and we compare the optimal solution with the solution prescribed by equal thermodynamic distance (ETD). We find that ETD coincides with the optimum if the heat capacity is constant. For a temperature-dependent heat capacity, ETD deviates from the exact optimum. ETD however matches the optimal solution to second order in $1/K$.

1. Introduction

This paper treats a simple example of controlling a thermodynamic system in a multi-step process by a sequence of contacts with generalized baths. The example illustrates the asymptotically optimal control known as equal thermodynamic distance (ETD) in a simple enough context to be analytically accessible. The simple example treated here maps directly onto problems of industrial significance including diabatic distillation.

The example grew out of a controversy regarding the approximate optimality of different schemes for controlling the temperatures of trays in a diabatic distillation column [1–6]. The scheme presented here controls the temperature steps so as to maintain a constant thermodynamic distance at each step. One competing scheme maintained a constant average thermodynamic force (EOF) at each step. It is found that ETD works better for the present example. We therefore present a detailed comparison only between ETD and the true optimum and merely comment on the comparison to EOF along the way.

2. Coffee Cup Motel

We are interested in calculating the amount of entropy generated in multistep processes. The present paper treats a simple example of such a process. In discussing this example, we have found it useful to think in terms of an analogy we have dubbed *Coffee Cup Motel*. In the analogy, our goal is to heat a cup of coffee while minimizing entropy production. Suppose that there is a motel which has K vacant rooms, and each room's temperature can be set arbitrarily. Each room is adjusted to be a little hotter than the previous room (Fig. 1a). By allowing the coffee cup to equilibrate to a room's temperature and then moving the cup to the next room at a higher temperature, we are able to heat the coffee with very little entropy production. The coffee is brought into the first room with a temperature T_o and it equilibrates to its final value T_f in the last room. The optimization problem is to choose the temperatures of the intermediate rooms such that the total entropy production is as small as possible. We stress that the problem assumes complete equilibration at each step.
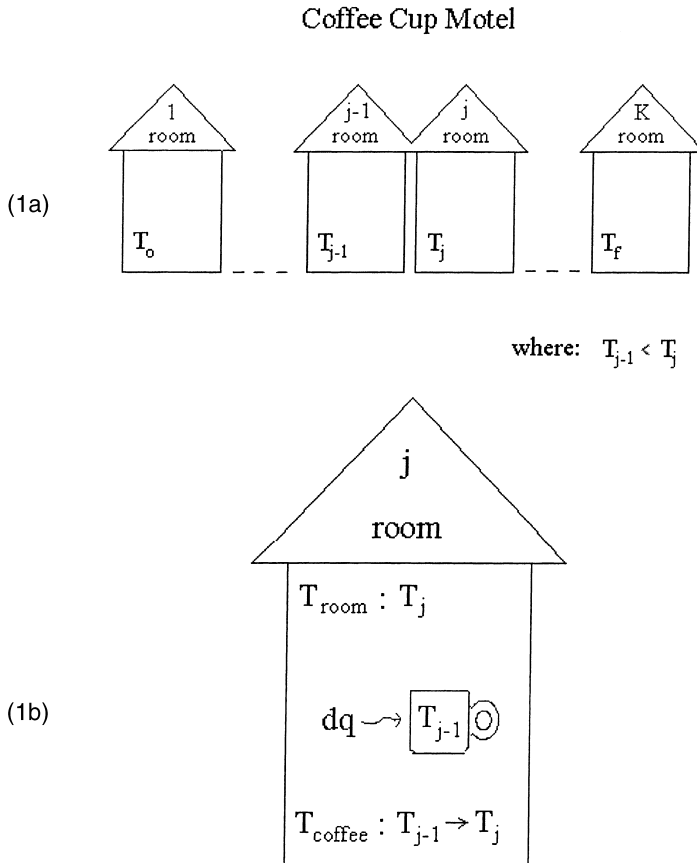
Coffee Cup Motel

Fig. 1. The figure depicts a caricature process wherein a cup of coffee is heated by moving it to successively hotter rooms.

The solution to this problem is found to depend on the heat capacity of the coffee cup. In the next section we analyse the case in which the coffee cup has a constant heat capacity, C. It is then found that the approximate optimization method ETD reproduces the exact solution, as does EOF. In the fourth section we analyse the consequences of a temperature-dependent heat capacity, $C(T)$. This leads to differences between the approximate optimization principles and the exact solution. In a concluding section these results are put into a wider perspective.

3. Entropy Production for a Constant Heat Capacity

At each equilibration step, a small amount of entropy is generated due to the heat exchange between the room and the coffee (Fig. 1b). The entropy generated in an infinitesimal flow of heat $dq = CdT$ from the coffee cup at temperature T to the room at constant temperature T_j is

$$dS_u = dS_{cup} + dS_{room} = C\left(\frac{1}{T} - \frac{1}{T_j}\right)dT. \tag{1}$$

Integrating to equilibrium in room j, the total change in the entropy is

$$(\Delta S_u)_j = \int_{T_{j-1}}^{T_j} dS_u = C\left(\ln\frac{T_j}{T_{j-1}} - \frac{T_j - T_{j-1}}{T_j}\right), \tag{2}$$

where we note that the heat capacity of the room is large compared to C. To calculate the total entropy generated throughout the K rooms of the overall heating process, we need to sum over the K steps to get

$$\Delta S_u = \sum_{j=1}^{K}(\Delta S_u)_j = C\left(\ln\frac{T_f}{T_o} - K + \sum_{j=1}^{K}\frac{T_{j-1}}{T_j}\right). \tag{3}$$

Once T_f and T_o are specified, the $K - 1$ intermediate temperatures can be chosen arbitrarily. The temperature steps are optimal when the total entropy production (3) is a minimum.

3.1. Minimum Entropy Production

A necessary condition for minimizing entropy production is stationarity with respect to a small change in each intermediate temperature, T_i, for $0 < i < K$. To obtain this condition for some given i, it is convenient if we first identify all those terms of (3) that depend on T_i. Placing those terms at the beginning, we obtain

$$\Delta S_u = C\frac{T_{i-1}}{T_i} + C\frac{T_i}{T_{i+1}} + \cdots, \tag{4}$$

where the ellipsis represents terms that do *not* depend on T_i.

The stationarity condition is now easily calculated:

$$\frac{\partial \Delta S_u}{\partial T_i} = C\left(-\frac{T_{i-1}}{T_i^2} + \frac{1}{T_{i+1}}\right) = 0, \tag{5}$$

or equivalently,

$$\frac{T_{i-1}}{T_i} = \frac{T_i}{T_{i+1}}. \tag{6}$$

This holds for each $i, 0 < i < K$, showing that, in the optimal scheme, consecutive temperatures all have a constant ratio. This constant ratio, γ, can be determined by the condition

$$\gamma^K = \frac{T_0}{T_1} \cdot \frac{T_1}{T_2} \cdots \frac{T_{k-1}}{T_f} = \frac{T_o}{T_f}. \tag{7}$$

This enables us to write the common ratio explicitly as

$$\frac{T_{i-1}}{T_i} = \left(\frac{T_f}{T_o}\right)^{-1/K}. \tag{8}$$

Now substituting (8) into (3), allows us to formulate the minimum total entropy production as a function of the number of steps K.

$$\Delta S_u^{OPT}(K) = C\ln\frac{T_f}{T_o} - CK + CK\left(\frac{T_f}{T_o}\right)^{-1/K} \tag{9}$$

3.2. Equal Thermodynamic Distance (ETD)

Equal thermodynamic distance gives a prescription for the optimal sequence of temperatures by requiring that the thermodynamic distance traversed on each step T_{j-1} to T_j be the same. This thermodynamic distance is found as an integral over the metric in the thermodynamic variable space, and will be detailed below. This prescription has been shown to be optimal for large K in a sense to be specified below [7]. The thermodynamic distance between two states of a system is the integral of the line element

$$dL = \sqrt{-dX^t D^2 S dX} \tag{10}$$

where X is the column vector of extensive variables of the system and $D^2 S$ is the matrix of second derivatives of the entropy S with respect to the X's [8].

The example in this paper has only one thermodynamic degree of freedom and thus dL takes the form

$$dL = \sqrt{-dU D^2 S dU} = \sqrt{|D^2 S|} \cdot |dU|, \tag{11}$$

where U is the internal energy of the system. Using

$$dU = CdT \tag{12}$$

and

$$\frac{d^2S}{dU^2} = \frac{d}{dU}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{dT}{dU} = \frac{-1}{CT^2} \tag{13}$$

allows us to express the length element dL as

$$dL = \sqrt{\frac{C}{T^2}(dT^2)}. \tag{14}$$

We integrate (14) to obtain the length $L(T_{j-1}, T_j)$.

$$L(T_{j-1}, T_j) = \int_{T_{j-1}}^{T_j} \frac{\sqrt{C}}{T}dT = \sqrt{C}\ln\left(\frac{T_j}{T_{j-1}}\right) \tag{15}$$

Since in the ETD scheme we need to keep $L(T_{j-1}, T_j)$ constant [7], (6) immediately follows. ETD therefore reproduces the optimal solution for this simple example with constant heat capacity. One may do a similar analysis using a constant average thermodynamic force. This also results in (6) for the temperatures. We thus find that for a constant heat capacity

$$\Delta S_u^{ETD} = \Delta S_u^{EOF} = \Delta S_u^{OPT}. \tag{16}$$

4. Entropy Generation for an Arbitrary Heat Capacity

Integrating (1) to equilibrium in room j, the total change in the entropy now becomes

$$(\Delta S_u)_j = \int_{T_{j-1}}^{T_j} dS_u = \int_{T_{j-1}}^{T_j} C(T)\left(\frac{1}{T} - \frac{1}{T_j}\right)dT. \tag{17}$$

For notational convenience, we introduce

$$D(T) \equiv \int_{T_o}^{T} C(T)dT. \tag{18}$$

This results in

$$(\Delta S_u)_j = \int_{T_{j-1}}^{T_j} \frac{C(T)}{T}dT + \frac{D(T_{j-1}) - D(T_j)}{T_j}. \tag{19}$$

To calculate the total entropy generated throughout the *K* rooms of the overall heating process, we need to sum over the *K* steps to get

$$\Delta S_u = \sum_{j=1}^{K} (\Delta S_u)_j = \int_{T_o}^{T_f} \frac{C(T)}{T} dT + \sum_{j=1}^{K} \frac{D(T_{j-1}) - D(T_j)}{T_j}. \tag{20}$$

To minimize this expression, we are again faced with the problem of choosing the $K - 1$ intermediate temperatures.

4.1. Minimum Entropy Production (OPT)

We use stationarity as a necessary condition. To obtain this condition for some given *i*, it is convenient if we first identify all those terms of (20) that depend on T_i. Placing those terms at the beginning, we obtain

$$\Delta S_u = \frac{D(T_{i-1}) - D(T_i)}{T_i} + \frac{D(T_i) - D(T_{i+1})}{T_{i+1}} + \cdots, \tag{21}$$

where the ellipsis represents terms that do *not* depend on T_i.

The stationarity condition is now easily calculated:

$$\frac{\partial \Delta S_u}{\partial T_i} = C(T_i) \left(\frac{1}{T_{i+1}} - \frac{1}{T_i} \right) - \frac{D(T_{i-1}) - D(T_i)}{T_i^2} = 0. \tag{22}$$

This condition can be rearranged to give

$$T_{i+1} = \frac{T_i}{1 + \dfrac{D(T_{i-1}) - D(T_i)}{T_i C(T_i)}}. \tag{23}$$

Note that this is a second order difference equation which may be solved by a shooting method[1].

4.2. Equal Thermodynamic Distance (ETD)

We may again integrate (14) to obtain the thermodynamic distance $L(T_{i-1}, T_i)$

$$L(T_{i-1}, T_i) = \int_{T_{i-1}}^{T_i} \frac{\sqrt{C(T)}}{T} dT. \tag{24}$$

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[1]Since T_o is given, we can iteratively adjust the value of T_1 until the desired value is obtained for $T_K = T_f$.

Thus the T_i's are chosen to give

$$\int_{T_{i-1}}^{T_i} \frac{\sqrt{C(T)}}{T} dT = \frac{1}{K} \int_{T_o}^{T_f} \frac{\sqrt{C(T)}}{T} dT. \tag{25}$$

Note that as a difference equation, this is only first order and thus may be solved explicitly without the need for the trial and error of the shooting method required for OPT.

4.3. A Numerical Example

As expected, in all three schemes (OPT, ETD, and EOF), ΔS_u approaches zero as K approaches infinity. This is in fact the case for any scheme in which all the temperature changes $T_{i+1} - T_i$ approach zero. Numerical comparisons of performance of the schemes OPT, ETD, and EOF were carried out for large but finite K on a number of examples. When the heat capacity does not vary appreciably, the agreement is very good for all K. This is not surprising since both ETD and EOF are exact when the heat capacity is a constant. Accordingly, we chose an example with a large change in $C(T)$ over the temperature range of interest. We consider the problem of heating (and melting) a block of slightly impure ice (e.g. ice coffee) from 223.15 K to 323.15 K. In this case, the heat of fusion gives a very large spike in the heat capacity at T_{melt}. The actual heat capacity curve for one mole of water with 0.01 molal impurities is shown in Figure 2.
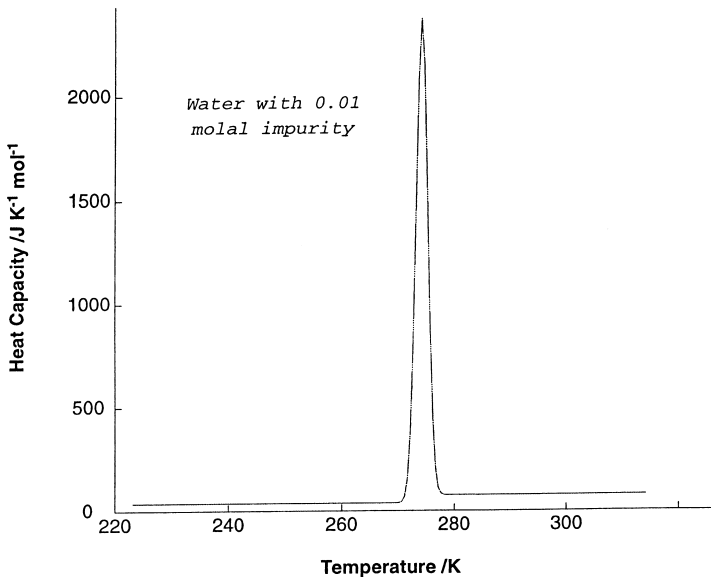

Fig. 2. The figure shows the heat capacity of the ice-water system with 0.01 molal impurity heated from 223.15 K to 323.15 K.
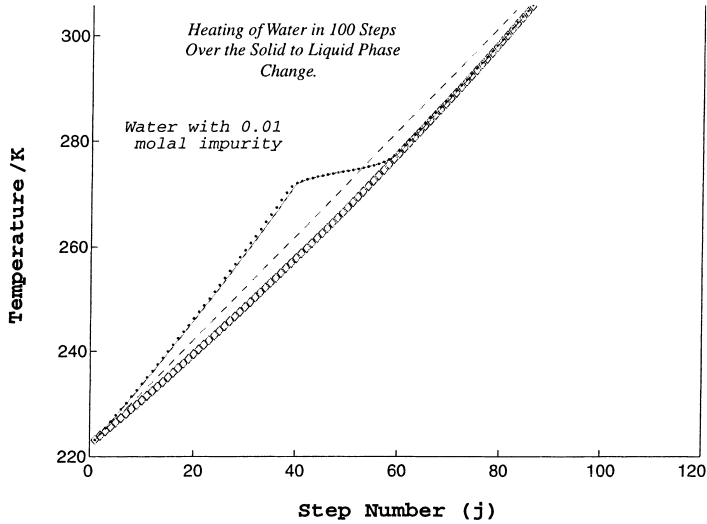
Fig. 3. The figure shows the temperature profiles for the four schemes OPT (dotted), ETD (solid), LIN (dashed) and EOF (diamonds) for heating the ice-water system with 0.01 molal impurity from 223.15 K to 323.15 K

Table 1. Entropy production for heating the block of ice with 0.01 molal impurity from 273.15 K to 373.15 K in 100 steps.

Scheme	ΔS_u
OPT	0.0507
ETD	0.0508
LIN	0.0765
EOF	0.0779

For illustration, two additional schemes are compared here also. The first, LIN, uses a linear temperature profile. The second, EOF, uses a profile based on keeping the average thermodynamic force during each step constant. The temperature profiles for $K = 100$ are shown in Figure 3. Note that both OPT and ETD slow down significantly for the phase transition while LIN and EOF do not. The corresponding values of the entropy production are shown in table 1.

4.4. Asymptotic Optimality

The K-dependence of ΔS_u, in the asymptotic limit, for all four of our schemes takes the form

$$\Delta S_u \approx \frac{A}{K}, \tag{26}$$

where A is a constant, independent of K, but characteristic of the particular scheme, and, of course, dependent on the heat-capacity function $C(T)$. In general,

$$A_{OPT} = A_{ETD}, \tag{27}$$

which reflects the usual statement [7, 8] that ETD is asymptotically optimal. When we calculate these coefficients[2], we find the general result that

$$A_{OPT} = A_{ETD} = \frac{1}{2} \left(\int_{T_o}^{T_f} \frac{\sqrt{C(T)}}{T} dT \right)^2. \tag{28}$$

5. Discussion and Conclusions

We now summarize our findings for the simple example. When the heat capacity is independent of the temperature, both ETD and EOF reproduce the exact optimal solution. When the heat capacity C depends on the temperature T, ETD gives a temperature sequence that matches the minimum entropy production to order $1/K^2$ [9]. The arguments presented here lead only to a first order match.

The coffee-cup-motel as a thermodynamic process is much more general than it appears at first glance. It applies *mutatis mutandis* to the problem of bringing a thermodynamic system with n degrees of freedom from an initial state to a final state along any given path for which the temperature is an acceptable parameter. One example of particular note is the sequence of temperatures that should be maintained on the successive trays in a diabatic distillation column[3]. It can be shown that, for binary distillation, assuming complete equilibration on each tray, this is equivalent to a coffee-cup problem [8] in which the "coffee" is a coexisting 2 phase mixture where the amounts of the liquid and vapor phases are given by the flows V and L for a minimum reflux column with an infinite number of trays. Figure 4 shows the constant pressure coexistence heat capacity for separating a 50% (by mole) mixture of benzene and toluene to various purities. Note that $C(T)$ changes by a factor of four which is much less than in the melting ice example.

EOF also reproduces the optimal schedule exactly for constant heat capacity and does well for heat capacities varying by as much as 50%. This probably accounts for the good performance of the EOF temperature schedules in columns with not very high purity requirements for which the heat capacity does not vary much (see Fig. 4). A numerical comparison of the ETD and EOF schemes was carried out for small K [4, 5]. In their study, one can see the approach of the ETD scheme to the optimal scheme for the largest value of K used. The required values of K were deemed too large to be of interest in that study. The lack of fit of EOF in [4] led to the procedure where the flux-force expression was minimized with an increased number of

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[2]The derivation of these formulas is rather long. The interested reader is referred to [9].
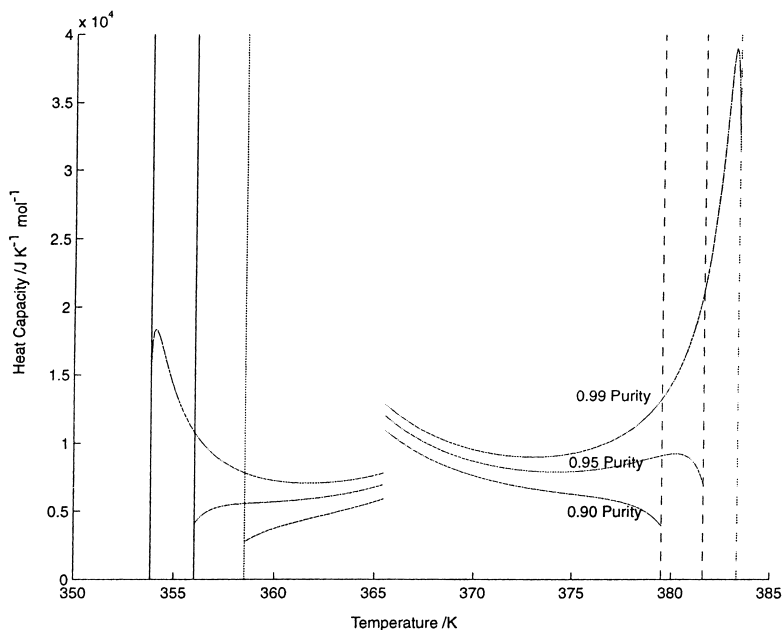[3]Columns in which every tray is equipped with a heat exchanger.

Fig. 4. The effective heat capacity as a function of temperature for a distillation process separating a 50% mixture of benzene and toluene to 90%, 95%, and 99% purities. The discontinuity at 366 K corresponds to the feed point.

constraints [2]. The nature of the optimal path will vary according to constraints [1, 10], and EOF is only valid if the transport paths are parallel [11].

If a certain total time, large compared to the relaxation time of the system, is alloted for the K equilibrations, the optimal allocation of such time has the system spending an equal number of relaxation times on each step. This is the so-called constant thermodynamic speed cooling schedule in which the distance traversed per relaxation time is constant. In the EOF scheme the time spent in rooms close to the melting temperature would increase since the relaxation time depends on the heat capacity. This would bring the EOF solution closer to OPT and ETD. We remark that if the temperature can be continuously varied, rather than varied in the stepwise fashion discussed here, a fixed total time implies that constant entropy production rate is the correct asymptotic principle [12, 13, 14]. For stepwise control, however, ETD gives the correct asymptotic result and works quite well even for moderate number of steps [2, 3].

Acknowledgements

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