# Quasistatic processes as step equilibrations

J. Nulton,<sup>a)</sup> P. Salamon, B. Andresen,<sup>b)</sup> and Qi Anmin Department of Mathematical Sciences, San Diego State University, San Diego, California 92182

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The proportionality between the square of the distance traversed as measured in thermodynamic length and the minimum associated dissipation of a process is established in a new context independent of dynamical laws. A quasistatic thermodynamic process consisting of K steps, each equilibrating with an appropriate reservoir, is optimized with respect to the position of the steps and the allocation of the total time  $\tau$  for the process among the steps. It is found that the steps should be of equal thermodynamic length. For large K the bounds based on thermodynamic length are recovered.

# I. INTRODUCTION

The present paper is a step toward understanding how time enters into thermodynamic considerations by examining the dependence of the dissipation associated with a thermodynamic system traversing a sequence of states in a certain time  $\tau$ . It turns out that the dissipation is closely linked to the distance<sup>1</sup> traversed along such a sequence of states in the natural thermodynamic geometry defined by the second derivative of either the internal energy or the entropy of the system.<sup>2,3</sup> The present paper sheds new light on this link between geometry and dissipation.

While in the present paper we restrict our view to the macroscopic level where the sequence of states consists of states of equilibrium, we remark that our statements remain valid if the sequence of states consists of states of local thermodynamic equilibrium or to distributions in a statistical mechanical state space.<sup>4</sup> In the event that the sequence of distributions happen to represent equilibrium states, the conclusions of the three pictures coincide.<sup>1,4</sup> The importance of the geometry appears to transcend all levels; in fact, the notion of distance in the space of distributions has been shown to coincide at the quantum mechanical level<sup>5</sup> with the angle in Hilbert space between the initial and final quantum states of the system.

The question we now wish to address is how the dissipation associated with bringing a system along a given quasistatic locus varies as a function of the total time alloted to the process. While in general this depends on how the total time is allocated, i.e., at what rate different portions of the process are run, the *minimum* dissipation behaves very simply for large times. This minimum dissipation is proportional to the square of the distance L traversed, and inversely proportional to the total time of the process  $\tau$ . The constant of proportionality is the mean value of the slowest time scale  $\epsilon$  in the system. In symbols<sup>1,3</sup>

$$\Delta A^{u} \gg L_{U}^{2} \epsilon / \tau,$$

$$\Delta S^{u} \gg L_{S}^{2} \epsilon / \tau,$$
(1)

where  $\Delta A^{\mu}$  and  $\Delta S^{\mu}$  are the change in the availability and entropy of the universe and  $L_{U}$  and  $L_{S}$  are the lengths of the paths traversed as measured by the metrics based, respectively, on internal energy and entropy.

With hindsight, the early finite time thermodynamic work on heat engines<sup>6–10</sup> pointed the way to this result. The general formulation of minimum entropy production in finite time heat engines<sup>10</sup> noted that a natural parametrization of the problem involved the entropy change of the working fluid. With hindsight, the key result

 $\Delta S^{\,u} \ge 4\sigma^2/k\tau \tag{2}$ 

retained its simplicity only when parametrized in terms of the entropy change  $\sigma$  of the working fluid. The finding may now be interpreted as showing that the losses in those engines are due purely to making the working fluid involved traverse the sequence of states in time  $\tau$  subject to the relaxation times characteristic for "Newton's Law Thermodynamics"<sup>10</sup> which assumed instantaneous relaxation in all degrees of freedom save the thermal contact which has time constant 1/k. The losses involved can, in retrospect, be easily computed from tables of distances and, relaxation times.

For shorter times the inequalities (1) remain valid but at the cost of complexity in the mean relaxation times  $\epsilon$  which are easily evaluated only for the linear regime. In some sense our results for shorter times merely shuffle the complexity of dissipation in real processes into a convenient parametrization:  $\epsilon$ . How useful this approach will prove depends on how easily a physics of mean relaxation times can be worked out. Progress in this direction would benefit greatly from experimental tools analogous to Watt's instrument to generate an indicator diagram for a working fluid in a steam engine. Such tools would provide easy access to the path followed by a system participating in a process and would thereby make  $\epsilon$ observable.

Our present task is to arrive at the proportionality between  $L^2$  and dissipation in a manner manifestly independent of specific dynamical laws by viewing the process as a sequence of small equilibrations. The fact that this proportionality is recovered in this manner is further evidence that the connection between distance and dissipation is fundamental. Furthermore, the arguments involved reveal some interesting physics surrounding the nature of the mean relaxation time  $\epsilon$ .

#### II. A K-STEP PROCESS

We treat a simplified quasistatic process as the limit of processes which consist of K-step equilibrations during

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<sup>&</sup>lt;sup>a)</sup> Permanent address: Department of Mathematics, San Diego City College, San Diego, CA 92101.

<sup>&</sup>lt;sup>b)</sup> Permanent address: Physics Laboratory 2, University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen 0, Denmark.

which the system moves through a succession of points on a given quasistatic locus. We investigate the asymptotically optimal placement of these steps along the locus as  $K \rightarrow \infty$ .

Consider a path  $\gamma$  from an initial state to a final state on the Gibbs surface in thermodynamic configuration space, i.e., the surface relating all the extensive variables of the system  $U, V, S, N_1, N_2, ...$ , at equilibrium. Callen<sup>11</sup> calls such a path a quasistatic locus. Below we investigate one sense in which this locus can be made to correspond with a real process taking place in finite time.

Let a finite number of points be selected and numbered successively along this locus from initial state 0 to final state K. We may envision a real process whereby the system is transported through these states, not along the exact locus, but in K steps where in the k th step the system in state k - 1 is allowed to equilibrate with a reservoir having intensities appropriate to state k or, equivalently, to a very large copy of the system in state k. Such a process will be called a K-step process associated with the path  $\gamma$ .

If we were to allow the number of steps K to increase indefinitely while the spacing of the steps is made uniformly smaller, we would approach the classical ideal limit of the reversible process. However, any K-step process for which the "distance" between consecutive states in the process is greater than a standard fluctuation must be irreversible. It must also take place in a finite period of time. In this way the path  $\gamma$  is made to correspond to a real process proceeding at a nonvanishing rate. As an example to clarify the concept, imagine heating a glass of water from 20 to 50 °C in a threestep process by first placing it in a room at 35 °C, then moving it to a room at 40 °C, and finally to a room at 50 °C. At each stage the glass of water remains until it matches the room's temperature. By this procedure, less availability is lost (or entropy produced) than if the glass were left to equilibrate in the 50 °C room from the beginning, due to the lower temperatures at which most of the heat is delivered. It is essential to obtaining a reversible process in the limit  $K \rightarrow \infty$ that the system at each step interact with the environment with which it will be in equilibrium at the end of that step. This gives the smallest dissipation among all (one-step) equilibrations. Equilibrating toward different environments while suffering the same displacement, would dissipate more and thus could not give general bounds since processes exist (e.g., the K-step processes discussed above) which proceed by K equilibrations but which dissipate less. Two examples of such undesirable processes are (i) the three-step heating of the glass of water from 20° to 50° in rooms at 135°, 140°, and 150° and (ii) the step-wise expansion of a gas in a cylinder equipped with a piston which is stopped by a series of pins at preset volumes, but otherwise working against zero outside pressure. The bound derived later in this paper will, of course, also be valid for these processes since their dissipation is much larger than for a K-step process as defined here. This very fact, however, renders them unrelated to the problem of establishing a lower bound on dissipation.

We show below that the dissipation in such processes is related to the thermodynamic length of  $\gamma$ . Toward this goal we first derive the expansion for dissipation in a single small equilibration, i.e., an equilibration where the initial state is already so close to equilibrium that higher than second order terms in a power series expansion of the entropy may be neglected. Then we use this result to deduce the dissipation in a K-step process for large K. In the final section we consider the problem of time allocation to the various steps and again recover expressions which closely resemble the bounds on dissipation in Ref. 1.

### **III. DISSIPATION IN A SINGLE SMALL EQUILIBRATION**

Let us turn first to measures of irreversibility for a single equilibration step of the process. There are two closely related measures:  $\Delta S^{\mu}$ , the entropy produced in the universe and  $-\Delta A^{\mu}$ , the availability dissipated in the universe, i.e., the loss of potential work.

We first consider  $\Delta S^u$  by taking the entropy view of Massieu.<sup>11</sup> That is, we regard the entropy S of the system as a function of its natural extensive variables  $U, V, N_1, N_2, ...,$  which we will denote generically by  $X_i$ , i = 1 to m. The intensities conjugate to  $X_i$  will be denoted by  $Y_i = \partial S / \partial X_i$ , and the second derivatives by  $\sigma_{ii} = -\partial^2 S / \partial X_i \partial X_i$ .

A second order power series expansion of S about equilibrium yields

$$S = S^{0} + \sum_{i} Y_{i}^{0}(X_{i} - X_{i}^{0})$$
$$- \frac{1}{2} \sum_{ij} \sigma_{ij}^{0}(X_{i} - X_{i}^{0})(X_{j} - X_{j}^{0}),$$

where the superscript zero denotes equilibrium values. If we let  $\Delta S = S^0 - S$  and  $\Delta X_i = X_i^0 - X_i$  denote the deviations from the equilibrium values and assume that these are small, this expansion may be written

$$\Delta S = \sum_{i} Y_{i}^{0} \Delta X_{i} + 1/2 \sum_{ij} \sigma_{ij}^{0} \Delta X_{i} \Delta X_{j}.$$
<sup>(4)</sup>

The corresponding entropy change of the reservoir-like environment, whose intensive quantities  $Y_i^{en}$  are constant, due to its infinite size, is

$$\Delta S^{\,\rm en} = \sum_{i} Y^{\rm en}_{\,i} \Delta X^{\rm en}_{\,i}. \tag{5}$$

Since at equilibrium  $Y_i^{en} = Y_i^0$ , and conservation of matter and energy insures that  $\Delta X_i^{en} = -\Delta X_i$ , Eqs. (4) and (5) may be added to obtain the total entropy production in the small equilibration of the system from  $X_i$  to  $X_i^0$ ,

$$\Delta S^{u} = 1/2 \sum_{ii} \sigma_{ij}^{0} \Delta X_{i} \Delta X_{j}$$
(6a)

or in matrix notation,

$$\Delta S^{\,u} = 1/2\Delta \, \mathbf{X}^{t} \boldsymbol{\sigma}^{0} \Delta \, \mathbf{X}. \tag{6b}$$

To examine the loss of availability in a small equilibration we take the energy view and regard the internal energy of the system U as a function of its natural extensive variables  $S, V, N_1, N_2, \dots$ . To distinguish these variables and their conjugates from the symbols  $X_i$ ,  $Y_i$  used in the entropy discussions we add a tilde,  $\tilde{X}_i$  and  $\tilde{Y}_i = \partial U/\partial \tilde{X}_i$ , and call the components of the matrix of second derivatives  $\tilde{\sigma}_{ij}^2 = \partial^2 U/\partial \tilde{X}_i \partial \tilde{X}_j$ . Then the maximum work that can be extracted as the system

(3)

undergoes changes  $d\tilde{X}_i$  at intensities  $\tilde{Y}_i$  in contact with a reservoir of intensities  $\tilde{Y}_i^0$  is equal to the availability dissipated in the corresponding spontaneous process,

$$-dA^{u} = \sum_{i} (\widetilde{Y}_{i}^{0} - \widetilde{Y}_{i}) d\widetilde{X}_{i} = \sum_{i} \widetilde{Y}_{i}^{0} d\widetilde{X}_{i} - dU.$$
(7)

Since the  $\tilde{Y}_{i}^{0}$  are constant equilibrium values, we have for the finite changes during the equilibration

$$-\Delta A^{u} = \sum_{i} \widetilde{Y}_{i}^{0} \widetilde{X}_{i} - \Delta U.$$
(8)

Combining this with a second order Taylor expansion of U about equilibrium,

$$U - U^{0} = -\Delta U$$
  
=  $-\sum_{i} \widetilde{Y}_{i}^{0} \Delta \widetilde{X}_{i} + \frac{1}{2} \sum_{ij} \widetilde{\sigma}_{ij}^{0} \Delta \widetilde{X}_{i} \Delta \widetilde{X}_{j},$   
(9)

we have in matrix notation

$$-\Delta A^{u} = 1/2\Delta \widetilde{\mathbf{X}}^{t} \widetilde{\boldsymbol{\sigma}}^{0} \Delta \widetilde{\mathbf{X}}.$$
 (10)

It should be remembered that the X in Eq. (6b) and  $\tilde{X}$  in Eq. (10) represent different sets of coordinates. Nevertheless, we have shown elsewhere<sup>3</sup> that  $\sigma$  and  $\tilde{\sigma}$  are related as quadratic forms in a manner independent of coordinates by

$$\tilde{\boldsymbol{\sigma}} = T\boldsymbol{\sigma},\tag{11}$$

where T is the temperature. This allows us to combine Eqs. (6) and (10) in the form

$$-\Delta A^{\,\,u} = T\Delta S^{\,\,u},\tag{12}$$

which is consistent with the interpretation of work lost as "uncompensated heat."

#### **IV. DISSIPATION IN A K-STEP PROCESS**

Now let us return to the K-step process and focus on the entropy view; a precisely analogous argument may be given for the energy view.

For the k th step of the process we may write [cf. Eq. (6b)]

$$\Delta S_{k}^{u} = 1/2\Delta \mathbf{X}^{t} \boldsymbol{\sigma}^{k} \Delta \mathbf{X} = D_{k}^{2}/2, \qquad (13)$$

where  $\sigma^k$  is evaluated at the k th equilibrium state, and where, for short equilibration steps so that  $\sigma$  is essentially constant,

$$D_k = \sqrt{\Delta \, \mathbf{X}^t \boldsymbol{\sigma}^k \Delta \, \mathbf{X}} \tag{14}$$

can be identified with the length of the step as measured by the Riemannian metric  $\sigma$ . For the whole process the Cauchy-Schwarz inequality gives

$$\Delta S^{u} = 1/2 \sum_{k} D_{k}^{2} \ge 1/2K \left(\sum_{k} D_{k}\right)^{2} = L^{2}/2K, \quad (15)$$

where  $L = \sum_k D_k$  is the thermodynamic length, <sup>1</sup> L of the Kstep process, and equality is attained only when all  $D_k$ 's are equal. Thus, since L is the length of the whole path  $\gamma$  irrespective of partitioning, minimum dissipation is attained when the K steps of the process are spaced such that the lengths of all the steps are the same when measured in the metric  $\sigma$ . Note that the above arguments solve the problem of the optimal location of the steps along  $\gamma$  provided each of the *K*-equilibration steps is small. The Appendix examines this optimization problem further in a more general context, calculates necessary conditions for optimality, and proves that the step size in an optimal *K*-step process goes uniformly to zero as *K* goes to infinity.

#### **V. OPTIMAL ALLOCATION OF TIME**

In the previous section we found the optimal allocation of step sizes along the process, viz. constant steplength. Now we let each step k equilibrate for time  $\tau_k$  in contact with the reservoir of intensities  $\mathbf{Y}_k^0$  so that the duration of the total process is

$$\tau = \sum_{k} \tau_k. \tag{16}$$

However, in the k th step it is not possible for the system to completely reach the state  $X_k^0$  which is in equilibrium with the reservoir in the time  $\tau_k$  (or in any finite time for that matter), rather the system ends in  $X_k$  so that the entropy production of the step becomes

$$\Delta S_{k}^{u} = -\mathbf{Y}_{k}^{0} \cdot (\mathbf{X}_{k} - \mathbf{X}_{k-1}) + [S(\mathbf{X}_{k}) - S(\mathbf{X}_{k-1})].$$
(17)

For  $\tau_k$  large compared to the largest relaxation time  $\epsilon_k$  of the interaction

$$\mathbf{X}_{k} = \mathbf{X}_{k}^{0} + \mathbf{V}_{k} e^{-\tau_{k}/\epsilon_{k}},\tag{18}$$

where  $\mathbf{V}_k$  is the eigendirection corresponding to the eigenvalue  $1/\epsilon_k$  for the linearized dynamics near  $\mathbf{X}_k^0$ .

The total dissipation sums to

$$\Delta S^{u} = -\sum_{k} \mathbf{Y}_{k}^{0} \cdot (\mathbf{X}_{k}^{0} - \mathbf{X}_{k-1}^{0}) + (S_{\text{final}} - S_{\text{initial}}) + \sum_{k} \mathbf{V}_{k} \cdot (\mathbf{Y}_{k+1}^{0} - \mathbf{Y}_{k+1}^{0}) e^{-\tau_{k}/\epsilon_{k}}, \quad (19)$$

in which the only time dependence is in the last term. In writing the overall change of entropy of the system as the constant  $S_{\text{final}} - S_{\text{initial}}$  we have neglected the small difference  $X_k^0 - X_k$  at the end of the last step.

For brevity we define

$$C_k = \mathbf{V}_k \cdot (\mathbf{Y}_{k+1}^0 - \mathbf{Y}_k^0) \tag{20}$$

which for small  $\Delta X_k$  is the dot product between the net displacement and the direction of approach relative to the metric. Then we minimize the entropy production with respect to the time allocation subject to the constraint (16) with Lagrange multiplier  $\lambda$ ,

$$\lambda = \frac{\partial \Delta S^{u}}{\partial \tau_{k}} = C_{k} e^{-\tau_{k}/\epsilon_{k}} (-1/\epsilon_{k}).$$
<sup>(21)</sup>

Using Eq. (21) and invoking the constraint (16) we find

$$\ln(-\lambda) = -\left[\tau + \sum_{k} \epsilon_{k} \ln\left(\frac{\epsilon_{k}}{C_{k}}\right)\right] / \sum_{k} \epsilon_{k}$$
(22)

and

$$\tau_{k} = \frac{\epsilon_{k}}{\sum_{l} \epsilon_{l}} \tau + \epsilon_{k} \left( \frac{\sum_{l} \epsilon_{l} \ln(\epsilon_{l}/C_{l})}{\sum_{l} \epsilon_{l}} - \ln\left(\frac{\epsilon_{k}}{C_{k}}\right) \right). (23)$$

This gives the following total entropy production with optimal time allocation:

$$\Delta S^{u} = -\sum_{k} \mathbf{Y}_{k}^{0} \cdot (\mathbf{X}_{k}^{0} - \mathbf{X}_{k-1}^{0}) + (S_{\text{final}} - S_{\text{initial}}) + \exp\left(-\tau \sum_{k} \epsilon_{k}\right) \\ \times \exp\left[-\sum_{k} \epsilon_{k} \ln(\epsilon_{k}/C_{k}) / \sum_{k} \epsilon_{k}\right] \sum_{k} \epsilon_{k}, (24)$$

which has a simple exponential time dependence  $e^{-n}$ , where  $n = \tau/\Sigma_k \epsilon_k = \overline{\tau}_k/\overline{\epsilon}_k$  is the average number of relaxation times in each step.

As it stands, the lower bound in Eq. (15) goes to zero as the number of steps K goes to infinity. However, the individual steps lose their meaning when they last less than one relaxation time, so the largest meaningful K is the number of relaxation times in the total process  $K = \tau/\overline{\epsilon}_k$ . Then the bound cannot become less than roughly

$$\Delta S^{u} \geqslant \overline{\epsilon}_{k} L_{S}^{2} / 2\tau. \tag{25}$$

Analogously in the energy view<sup>1,3</sup>

$$\Delta A^{u} \geqslant \overline{\epsilon}_{k} L^{2}_{U} / 2\tau.$$
<sup>(26)</sup>

Here we have assigned subscripts S and U to distinguish the lengths of the process as measured in the two metrics  $\sigma$  and  $\tilde{\sigma}$ .

It is interesting to note several reduced forms of the time allocation in Eq. (23). For sufficiently large  $\tau$ , the ratio  $\tau_k/\epsilon_k$  is independent of k, so the process spends an equal number of relaxation times on each step. For smaller  $\tau$  the second term becomes significant. We define the probability distribution

$$p_m = \epsilon_m / \sum_l \epsilon_l \tag{27}$$

and write Eq. (23) in the form

$$\tau_k = p_k \tau + \epsilon_k \left[ \frac{\ln(\epsilon_m/\epsilon_k)}{\ln(\epsilon_m/\epsilon_k)} - \frac{\ln(C_m/C_k)}{\ln(c_m/c_k)} \right],$$
(28)

where the bars denote the means computed with respect to the distribution in Eq. (27). Note that if all the  $\epsilon_k$  are equal, the first term in the bracket vanishes, while if all the dot products  $C_k$  are equal, the second term vanishes. This will be the case, e.g., if the directions of approach  $V_k$  coincide with the displacements  $\Delta X_k^0$ , i.e., if the system moves along the quasistatic locus. Then the  $C_k$  are constant by the results of the previous section since the  $C_k$  then become the squares of the lengths of the segments.

## **VI. CONCLUDING REMARKS**

We have examined the minimum dissipation in a K-step process along a quasistatic locus  $\gamma$ . When the number of steps K goes to infinity, the optimal step size goes uniformly to zero. In this limit the minimum is  $L^2/2K$ , where L is the thermodynamic length of  $\gamma$ . Furthermore, the minimum is achieved for equal length steps. For large times, the time allocation to step k is proportional to the largest relaxation time of the system at state k.

K-step processes, besides providing excellent intuition for why it should take a certain amount of dissipation to bring a system through a given sequence of equilibrium states, are interesting in their own right. They are involved whenever control on a system is naturally exercised in steps, e.g., when there is a cost to touching the controls. This fact has already been exploited to find strategies which minimize losses in adaptive coding through an evolving channel,<sup>12</sup> and we are currently exploiting it to choose optimal annealing schedules in applications of simulated annealing.<sup>13</sup>

The primary achievement of the present paper, however, was to establish in a new context, independent of any dynamical laws the inseparable link between dissipation and thermodynamic length.

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# APPENDIX

The optimality arguments for step length (Sec. IV) and duration (Sec. V) of a K-step process implicitly assumed that all steps become small as K increases, not leaving any large gaps. This Appendix gives proof that this is actually the case, and points up the dependence of this fact on the convexity of the entropy function.

Suppose we are given a one-to-one function X(t):  $[a,b] \rightarrow \mathbb{R}^n$  with range  $\gamma$  and a strictly convex function  $\phi:\mathbb{R}^n \rightarrow \mathbb{R}$ , both being suitably differentiable. Here  $\phi$  plays the role of S or -U. For t and t' in the closed interval [a,b], define

$$f(t,t') = \phi(t') - \phi(t) + \nabla \phi(t) \cdot [\mathbf{X}(t) - \mathbf{X}(t')] \quad (A1)$$

as a general expression for the dissipation (entropy produced or availability dissipated). Here, for brevity, we have let  $\phi(t) = \phi[\mathbf{X}(t)]$ . Note that the strict convexity of  $\phi$  guarantees that

$$f(t,t') > 0$$
 for  $t = t'$ . (A2)

The graph of  $\phi$  is a hypersurface in  $\mathbb{R}^{n+1}$ , and f(t,t') may be interpreted as the vertical distance from the surface to its tangent plane at X(t), as measured from the point X(t'). Let  $P = \{t_0, t_1, ..., t_K\}$  be a partition of the interval [a, b] with  $a = t_0 \leq t_1 \leq ... \leq t_K = b$ . Define

$$||P|| = \max_{i} |t_i - t_{i-1}|,$$
(A3)

$$F(P) = \sum_{i=1}^{k} f(t_i, t_{i-1}).$$
(A4)

We will prove the following theorem consisting of assertions (i), (ii), and (iii):

(i) For each K > 0, there is an optimal partition  $P_K^*$  such that

$$F(P_K^*) = \inf F(P_K), \tag{A5}$$

where the infimum is taken over all partitions  $P_K$  of [a,b] into K subintervals.

(ii)  $\|\mathbf{P}_{K}^{*}\|$  decreases monotonically to zero as K goes to infinity.

(iii) The optimal partition satisfies the extremal equations

$$\begin{aligned} \mathbf{X}(t_{i}^{*}) \cdot \left[ \nabla \phi \left( t_{i+1}^{*} \right) - \nabla \phi \left( t_{i}^{*} \right) \right] \\ &= \dot{\mathbf{X}}(t_{i}^{*})^{t} D^{2} \phi \left( t_{i}^{*} \right) \left[ \mathbf{X}(t_{i}^{*}) - \mathbf{X}(t_{i-1}^{*}) \right] \\ &\text{ for } i = 1, ..., K - 1. \end{aligned}$$
(A6)

**Proof:** Part (i) follows at once. The set of (K + 1)-tuples  $(t_0, ..., t_K)$  corresponding to partitions of [a, b] form a compact set in  $\mathbb{R}^{K+1}$ . F, as a function of  $t_0, ..., t_K$  is continuous, and, therefore, assumes its minimum value on the set.

Part (iii) expresses, by direct calculation, the necessary conditions that  $\partial F/\partial t_i$ , i = 1,...,K - 1 must vanish at the minimum.

As for part (ii) it is clear that  $\delta_K = ||P_K^*||$  decreases monotonically. We will show that if  $\delta_K$  did not converge to zero, the numbers  $F(P_K^*)$  would be bounded away from zero. We will then show this contradicts the optimality of P by exhibiting a sequence  $\tilde{P}_K$  for which

$$\lim_{K \to \infty} F(\tilde{P}_K) = 0. \tag{A7}$$

Suppose, contrary to (ii), that  $\delta_K \ge \delta > 0$  for all K. That is, for each K, there is a maximal subinterval  $[t'_{(K)}, t''_{(K)}]$  of the partition  $P_K^*$  with the  $t''_{(K)} - t'_{(K)} \ge \delta > 0$ . We may suppose, by going to a subsequence if necessary, that  $t'_{(K)}$  and  $t''_{(K)}$ converge to t' and t", respectively, where, of course,  $t'' - t' \ge \delta$ . It then follows from Eq. (A2) that  $f(t', t'') = \epsilon > 0$ . Thus, by continuity, for  $K_0$  large enough,

$$F(P_{K}^{*}) \geq f(t_{(K)}^{\prime}, t_{(K)}^{\prime\prime}) > \epsilon/2 > 0 \text{ for all } K \geq K_{0}.$$
(A8)

We will now exhibit the sequence  $\tilde{P}_K$  promised above which will contradict Eq. (A8) and complete the proof of the theorem. Let the partition  $\tilde{P}_K$ , for each K, be defined by

$$\tilde{t}_i = a + i(b - a)/K, \quad i = 0,...,K.$$
 (A9)

We will show that

$$f(\tilde{t}_i, \tilde{t}_{i-1}) \leq Q(b-a)^2 / K^2, \quad i = 1, ..., K,$$
 (A10)

where

$$Q = \max\{\partial^2 f / \partial t^2(s,t) : s, t \in [a,b]\}.$$
 (A11)

For fixed r, define g(t) = f(r,t). Direct calculation shows g(r) = g'(r) = 0, so, by Taylor's theorem, there is an s between r and t for which

$$g(t) = \frac{1}{2}g''(s)(t-r)^2.$$
 (A12)

This result, expressed in terms of the function f, and letting  $t_i = r$  and  $\tilde{t}_{i-1} = t$ , yields Eq. (A10). Summing this over i yields

$$F(\widetilde{P}_K) \leqslant Q(b-a)^2 / K, \tag{A13}$$

from which the desired result [Eq. (A7)] follows at once. This completes the proof of the theorem.

Note that Eq. (A6) has a simple interpretation if the steps are small enough to justify the approximation

$$\nabla \phi(t_{i+1}^*) - \nabla \phi(t_i^*) \approx D^2 \phi(i) [X(t_{i+1}^*) - X(t_i^*)].$$
(A14)

Then

$$\dot{\mathbf{X}}(t_{i}^{*})^{t}D^{2}\phi(t_{i}^{*})[\mathbf{X}(t_{i+1}^{*}) - 2\mathbf{X}(t_{i}^{*}) + \mathbf{X}(t_{i-1}^{*})] = 0.$$
(A15)

This says that the velocity vector  $\dot{\mathbf{X}}$  is perpendicular to the second difference of  $\mathbf{X}$  (the acceleration) with respect to the metric  $D^2\phi$ , a familiar condition for a constant speed curve.

<sup>1</sup>P. Salamon and R. S. Berry, Phys. Rev. Lett. 51, 1127 (1983).

- <sup>2</sup>F. Weinhold, J. Chem. Phys. **63**, 2479, 2484, 2488, 2496 (1975); **65**, 559 (1976).
- <sup>3</sup>P. Salamon, J. Nulton, and E. Ihrig, J. Chem. Phys. 80, 436 (1984).
- <sup>4</sup>P. Salamon, J. Nulton, and R. S. Berry, J. Chem. Phys. 82, 2433 (1985).
- <sup>5</sup>W. K. Wooters, Phys. Rev. D 23, 357 (1981).
- <sup>6</sup>F. L. Curzon and B. Ahlborn, Am. J. Phys. 43, 22 (1975).
   <sup>7</sup>M. H. Rubin, Am. J. Phys. 46, 647 (1978); Phys. Rev. A 19, 1272, 1277
- <sup>'</sup>M. H. Rubin, Am. J. Phys. **46**, 647 (1978); Phys. Rev. A **19**, 1272, 1277 (1979); **22**, 1741 (1980).
- <sup>8</sup>D. Gutkowicz-Krusin, I. Procaccia, and J. Ross, J. Chem. Phys. **69**, 3878 (1978).
- <sup>9</sup>P. Salamon and A. Nitzan, J. Chem. Phys. 74, 3546 (1981).
- <sup>10</sup>P. Salamon, A. Nitzan, B. Andresen, and R. S. Berry, Phys. Rev. A 21, 2115 (1980).
- <sup>11</sup>H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).
- <sup>12</sup>J. D. Flick, P. Salamon, and B. Andresen, IEEE Trans. Inf. Theory (submitted).
- <sup>13</sup>S. Kirkpatrick, C. D. Gelatt, Jr., and M. P. Vecchi, Science 220, 671 (1983).