

# Length in statistical thermodynamics

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A theorem is proved establishing the equality of "lengths" calculated with the entropy-based metric  $\partial^2 S / \partial X_i \partial X_j$  used by Ruppeiner and with a metric based on the information-theoretic entropy  $\max(-\sum p_j \ln p_j)$ .

## INTRODUCTION

The matrix of second derivatives ( $\partial^2 U / \partial X_i \partial X_j$ ) (or  $D^2 U_{ij}$ ) of internal energy  $U$  with respect to extensive variables  $\{X_i\}$  is a second fundamental form—the "stiffness" matrix, in Tisza's nomenclature<sup>1</sup>—in the space of  $U, X_1, \dots, X_d$ . Weinhold<sup>2</sup> showed that the First and Second Laws of thermodynamics endow their matrix with the properties of a metric or first fundamental form, but in the space of  $X_1, \dots, X_d$ . Some time later, Ruppeiner<sup>3</sup> developed a number of relations based on the corresponding set of second derivatives of the entropy. Salamon, Nulton, and Ihrig<sup>4</sup> showed that the two metrics,  $D^2 S$  and  $D^2 U$ , are conformally equivalent, i.e., proportional with constant of proportionality given by the thermodynamic temperature  $T$ .

As a result of its intimate connection to the dissipation and irreversibility associated with finite-time behavior,<sup>5</sup> the "thermodynamic length" of the path of a process computed in the  $X_1, \dots, X_d$  space using either the Weinhold or Ruppeiner metric takes on a special significance for connecting reversible thermodynamic processes with the behavior of real systems. It is especially tempting to pursue the use of the entropy form of the metric because of the possibility of extending the concept of thermodynamic length to processes passing through states more general than just those for which thermodynamic variables are defined. One would like to be able to use the power of the theorems of Ref. 5 to compute the minimum loss of availability for processes in which the system may be well out of equilibrium along its course. The crux of the question of this possibility is whether the probabilistic, so-called "maximum entropy" definition of entropy leads to a measure equivalent to  $D^2 S$  as introduced by Ruppeiner, and how general the conditions on a population distribution must be for the theorems of Ref. 5 to apply.

This note presents proof that under suitable circumstances,  $S_p$ , the entropy defined by a probability distribution, gives a length in the space of probability distributions that is equal to the length calculated with the thermodynamic entropy  $S_x$  in the space of the extensive

variables, whenever both are well defined. (The former may exist in situations in which the latter may not be defined.) We also make some comments regarding the correspondence between probabilistic and thermodynamic forms for the entropy, and the calculation of irreversibility from these.

## STATEMENT OF THE THEOREM

Consider an ensemble of systems whose quantum states  $j = 0, 1, \dots$  are occupied with probabilities  $p_0, p_1, \dots, p_n$ . Suppose that these probabilities satisfy the "maximum entropy" condition, that is, the  $p_j$ 's maximize the sum

$$\mathcal{S} = -\sum_j p_j \ln p_j, \quad (1)$$

subject to a set of constraints

$$\sum_j a_{rj} p_j(t) = X_r(t), \quad r = 0, \dots, d, \quad (2)$$

specifying the values of the  $d$  macroscopic degrees of freedom given in terms of the extensive variables  $X_r$ . The equation with  $r = 0$  incorporates the constraint  $\sum p_i = 1$ , by means of the requirements  $X_0 = a_{0j} = 1$ , for  $j = 0, 1, \dots, n$ . We call the maximum of Eq. (1) subject to Eq. (2) the probabilistic entropy  $S_p$ .

The probabilities satisfying the maximization condition and the constraint equations conform to the Boltzmann distribution

$$p_j(t) = \exp \left[ -\sum_{r=1}^d y_r(t) a_{rj}(t) \right] / Q(t), \quad (3)$$

where each  $y_r(t)$  is a Lagrange multiplier appropriate to one of the constraint equations (2) at time  $t$  and the partition function  $Q(t)$  has been used to eliminate the multiplier  $y_0(t)$ .

Since maximizing  $\mathcal{S}$  in Eq. (1) subject to Eq. (2) is a convex programming problem,<sup>6</sup> the solution  $P = (p_0, \dots, p_n)$  is unique for each possible value of  $X = (X_1, \dots, X_d)$ . As the  $d$ -tuple  $X$  runs through its set of possible values, the corresponding  $P$ 's run through a  $d$ -dimensional

subspace of the  $n$ -dimensional space of probability distributions  $P$ . The correspondence  $\sigma$  between  $X$  and the unique optimal  $P$  for given  $X$  allows us to identify points on the  $d$ -dimensional subspace of optimal  $P$ 's and the  $d$ -dimensional space of macroscopic states  $X$ . Such identification is common, albeit implicit, in most statistical mechanical calculations. With this identification, the probabilistic entropy  $S_p$  can be considered a coordinate transformed version of  $S_x$ , i.e.,

$$S_x = S_p \circ \sigma, \quad (4)$$

where  $\circ$  indicates function composition. It is not true however, that the second derivative matrices of  $S$  computed in any coordinate system define the same metric.<sup>4</sup> Our theorem asserts that  $X$  or  $P$  are good coordinates in the sense that the second derivative matrix of the entropy in either of these coordinates defines the same metric.

The theorem can now be stated explicitly. Given a distribution,  $P = (p_0, \dots, p_j, \dots, p_n)$  maximizing Eq. (1) while satisfying Eq. (2) and a thermodynamic entropy  $S_x$  for the system with extensive variables  $X = (X_1, \dots, X_r, \dots, X_d)$ , then, over the same interval of time, the lengths

$$L_x \equiv \int [\dot{X} D^2 S_x \dot{X}]^{1/2} dt \quad (5)$$

and

$$L_p \equiv \int [\dot{P} D^2 S_p \dot{P}]^{1/2} dt \\ = \int \left[ \dot{P} \begin{pmatrix} p^{-1} & 0 & \dots \\ 0^1 & p_2^{-1} & \\ \vdots & & \ddots \end{pmatrix} \dot{P} \right]^{1/2} dt \quad (6)$$

are equal.

Before giving proofs of this theorem, some remarks are in order. It has been conjectured by Levine that the time evolution of "most" systems proceeds along a path maximizing Eq. (1) and satisfying Eq. (2) although the appropriate constraints may not be known. If this conjecture is correct, then  $\mathcal{S}$  would usually be  $S_p$ . The power of our theorem depends on the validity of Levine's conjecture, so it is obviously of interest to try to establish the range of its validity. Parallel to this is the question of how generally the constraints on a system can be written in the form (2). To the extent that both the Levine conjecture and the linearity of constraint expressions are generally satisfied, the thermodynamic length can be evaluated from the time-varying probability distributions, without any need for explicit reference to the macroscopic equations of state. This in turn means that from the time-varying probabilities and a knowledge of the relevant relaxation times, one can compute the minimum dissipation by using the theorems of Ref. 5. That is, we have constructed a bridge between the microscopic probability distributions and the dissipation. This bridge is especially important in view of Wootters<sup>7</sup> result which shows that the shortest distance  $L_p$  is equal to the angle  $|2 \cos^{-1} \langle \Psi_1 | \Psi_2 \rangle|$  in Hilbert space between the wave functions of the initial and final states.

We now present two very different proofs of this theorem. The first is based on the connection between lengths and dissipations in a sequence of step equilibrations.<sup>8</sup> The second is a direct change of coordinates on the subspace of optimal  $P$ 's from the  $p_j$ 's to the constraint variables  $X_r$  in Eq. (2).

### Proof 1

Consider a process in which a system is driven from its initial state to its final state by a sequence of  $N$  steps, each of which begins when the intensive variables of the surroundings are set to new values different from those of the system. During the  $i$ th step, the system relaxes to within fluctuations of a new equilibrium, with the probability distributions changing from  $P^{i-1}$  to  $P^i$ . The  $p_j$ 's at the endpoints of each segment thus lie along the desired path  $P(t)$  and by letting  $N$  grow large, we can make the actual process approximate  $P(t)$ .

Schlögl<sup>9</sup> and later Procaccia and Levine<sup>10</sup> showed that when a system with probabilities  $P$ , equilibrates to a state whose probabilities are  $P_3^0$ , then the entropy produced in this process is

$$\Delta S = \sum_j p_j \ln(p_j/p_j^0). \quad (7)$$

Now consider the sequence of  $N$  steps which together yield the entropy production

$$\Delta S^T = \sum_{i=1}^N \Delta S^i \\ = \sum_{i=1}^N \sum_j p_j^i \ln(p_j^i/p_j^{i+1}). \quad (8)$$

As the steps are made smaller so  $P^{i+1}$  approaches  $P^i$ ,  $\Delta S^T$  approaches zero. Using a second order expansion of the logarithm we get

$$\Delta S^T \approx \frac{1}{2} \sum_{i=1}^N \left[ \sum_j (p_j^i)^{-1} (p_j^{i+1} - p_j^i)^2 \right] \rightarrow 0 \\ \text{as } N \rightarrow \infty. \quad (9)$$

However the product  $N \Delta S^T$  does not go to zero:

$$N \Delta S^T \approx \frac{1}{2} \sum_{i=1}^N \sum_j \frac{1}{p_j^i} \frac{(p_j^{i+1} - p_j^i)}{1/N} (p_j^{i+1} - p_j^i) \\ \approx \frac{1}{2} \sum_i \int \frac{1}{p_j} \frac{dp_j}{dt} dp_j \\ = \frac{1}{2} \int \dot{P} D^2 S_p \dot{P} dt, \quad (10)$$

where  $t$  here is simply a parameter of the path which changes by  $1/N$  between point  $i$  and point  $i + 1$ . This integral has a value dependent on parametrization; its minimum value is  $L_p^2$ , which is only attained for constant speed, i.e., for

$$[\dot{P} D^2 S_p \dot{P}]^{1/2} \text{ const.}$$

Hence, the  $P^i$ 's chosen optimally fall at equal intervals along the path, and the minimum of  $N \Delta S^T$  over choices

of intermediate distributions  $P^i$ ,  $i = 1, \dots, N$  in the limit of large  $N$  becomes

$$\begin{aligned} \text{Min}(N\Delta S^T) &= \frac{1}{2}L_x^2 \\ &= \frac{1}{2}\left[\int (\dot{P}D^2S_p\dot{P})^{1/2}dt\right]^2. \end{aligned} \quad (11)$$

In a similar fashion it has been shown previously<sup>8</sup> that

$$\text{Min } N\Delta S^T = \frac{1}{2}L_x^2, \quad (12)$$

where the minimum is taken over intermediate  $X^i$ . Since lengths must be nonnegative, we conclude that  $L_x = L_p$ .

## Proof 2

The necessary conditions for the maximality of  $S_p$ , subject to the constraints (2), may be expressed as

$$\frac{\partial S_p}{\partial p_i} = \sum_m y_m a_{mi}, \quad i = 0, \dots, n. \quad (13)$$

In fact, Eq. (3) is obtained from Eq. (13) by solving explicitly for  $p_i$  in terms of  $y_1, \dots, y_d$ , the multiplier  $y_0$  being eliminated by means of the constraint  $\sum p_i = 1$ . Equation (3) is substituted into Eq. (2) and inverted to obtain  $y_m$  ( $m = 1, \dots, d$ ), and therefore, also  $p_i$  ( $i = 0, \dots, n$ ), as functions of  $X_1, \dots, X_d$ . Then both sides of Eqs. (13) and (2) may be regarded as functions of the  $X$ 's, and may be differentiated to obtain

$$\frac{\partial}{\partial X_s} \left( \frac{\partial S_p}{\partial p_i} \right) = \sum_m \frac{\partial y_m}{\partial X_s} a_{mi} \quad (14)$$

and

$$\sum_i a_{mi} \frac{\partial p_i}{\partial X_r} = \delta_{mr}. \quad (15)$$

Here we have used the fact that the  $a_{mi}$  are constants.

On the other hand, by the chain rule, we have

$$\frac{\partial}{\partial X_s} \left( \frac{\partial S_p}{\partial p_i} \right) = \sum_j \frac{\partial^2 S_p}{\partial p_j \partial p_i} \frac{\partial p_j}{\partial X_s}. \quad (16)$$

Equating the right sides of Eqs. (14) and (16), multiplying by  $\partial p_i / \partial X_r$ , and summing over  $i$ , we obtain

$$\sum_{i,j} \frac{\partial^2 S_p}{\partial p_j \partial p_i} \frac{\partial p_j}{\partial X_s} \frac{\partial p_i}{\partial X_r} = \sum_m \frac{\partial y_m}{\partial X_s} \sum_i a_{mi} \frac{\partial p_i}{\partial X_r}. \quad (17)$$

Equation (15) may be used to simplify the right-hand side of Eq. (17) to yield

$$\sum_{i,j} \frac{\partial^2 S_p}{\partial p_j \partial p_i} \frac{\partial p_j}{\partial X_s} \frac{\partial p_i}{\partial X_r} = \frac{\partial y_r}{\partial X_s}. \quad (18)$$

Now, to express this result in terms of time derivatives, multiply Eq. (18) by  $\dot{X}_r \dot{X}_s$ , sum over both  $r$  and  $s$  and incorporate the chain rule

$$\dot{p}_k = \sum_m (\partial p_k / \partial X_m) \dot{X}_m, \quad (19)$$

on the left-hand side:

$$\sum_{i,j} \frac{\partial^2 S_p}{\partial p_j \partial p_i} \dot{p}_i \dot{p}_j = \sum_{r,s} \frac{\partial Y_r}{\partial X_s} \dot{X}_r \dot{X}_s. \quad (20)$$

This expresses the desired equivalence of Eqs. (5) and (6) as soon as we have verified

$$y_r = \partial S_x / \partial X_r, \quad (21)$$

so that we may replace  $\partial y_r / \partial X_s$  in Eq. (21) with  $\partial^2 S_x / \partial X_s \partial X_r$ .

Equation (21) is a consequence of the general fact that the derivative of an objective function with respect to a constraint is the corresponding Lagrange multiplier. Nevertheless, a direct proof may be quickly obtained as follows. Differentiate Eq. (4) to obtain

$$\frac{\partial S_x}{\partial X_r} = \sum_i \frac{\partial S_p}{\partial p_i} \frac{\partial p_i}{\partial X_r}. \quad (22)$$

Substitute Eq. (13) and interchange sums to obtain

$$\frac{\partial S_x}{\partial X_r} = \sum_m y_m \sum_i a_{mi} \frac{\partial p_i}{\partial X_r} = y_r. \quad (23)$$

The last equality uses Eq. (15) once again.

## A TANTALIZING OBSERVATION

The comparison of the standard forms for

$$\Delta S_x = \int \sum_r dX_r (y_r - y_r^{\text{ext}}) \quad (24)$$

and

$$\begin{aligned} \Delta S_p &= \sum_j p_j (\ln p_j - \ln p_j^0) \\ &= \int \sum_j dp_j (\ln p_j - \ln p_j^0) \end{aligned} \quad (25)$$

suggests an interesting identification. We may consider the  $dp_j$ 's analogous to the differentials of the extensive variables  $dX_r$ , and the logarithms  $\ln p_j$  as the analogs of the intensive variables  $y_r$ . Naturally the system requiring the full probabilistic description of all the  $p_j$ 's has far more dimensions required for its specification. However the form of Eq. (25) shows that:

$$\left( \frac{\partial \Delta S}{\partial p_j} \right)_{pk} = \ln(p_j/p_j^0). \quad (26)$$

It is a bit discomfoting to see a variable that ought to be an intensive quantity conjugate to  $p_j$  seeming to be a function of  $p_j$  alone. However the left-hand side of Eq. (26) does not contain an arbitrary zero of entropy, and the right-hand side depends on  $p_j^0$  as well as on  $p_j$ , which in turn depends on the temperature and the entire level structure of the system.

To close, we give a simple illustration. Consider a two level system with partition function  $1 + e^{-\beta}$ , i.e., energy levels 0 and 1 ( $\beta = 1/kT$ ). In this case, the only

thermodynamic variable is  $u$ , the average energy, given by the constraint

$$u = (0)p_0 + (1)p_1 = p_1. \quad (27)$$

This provides the only equation of state:

$$u = \frac{e^{-\beta}}{1 + e^{-\beta}}. \quad (28)$$

Taking the thermodynamic point of view,  $S'(u) = dS/du = k\beta$ , and, using Eq. (28) to calculate the second derivative, the thermodynamic form becomes

$$(dL_x)^2 = -S''(u)du^2 = \frac{k}{u(1-u)} du^2. \quad (29)$$

On the other hand, using the fact  $p_0 + p_1 = 1$ , the probabilistic form is

$$\begin{aligned} (dL_p)^2 &= \frac{1}{p_0} (dp_0)^2 + \frac{1}{p_1} (dp_1)^2 \\ &= \frac{1}{p_1(1-p_1)} (dp_1)^2. \end{aligned} \quad (30)$$

Whence, in view of Eq. (27), we have the equivalence of

the forms (29) and (30). Using Eqs. (29) or (30) in Eqs. (5) or (6), respectively, gives

$$\begin{aligned} L_x = L_p &= 2 \arctan \exp(\beta/2) \Big|_{u_1}^{u_2} \\ &= \arccos(1 - 2u) \Big|_{u_1}^{u_2}. \end{aligned} \quad (31)$$

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<sup>1</sup> L. Tisza, *Generalized Thermodynamics* (MIT, Cambridge, MA, 1966).

<sup>2</sup> F. Weinhold, *J. Chem. Phys.* **63**, 2479, 2484, 2488 (1975).

<sup>3</sup> G. Ruppeiner, *Phys. Rev. A* **20**, 1608 (1979); **24**, 488 (1981); *Phys. Rev. Lett.* **50**, 287 (1983).

<sup>4</sup> P. Salamon, J. Nulton, and E. Ihrig, *J. Chem. Phys.* **80**, 436 (1984).

<sup>5</sup> P. Salamon and R. S. Berry, *Phys. Rev. Lett.* **51**, 1127 (1983).

<sup>6</sup> J. Stoer and C. Witzgall, *Convexity and Optimization* (Springer, New York, 1970).

<sup>7</sup> W. K. Wootters, *Phys. Rev. D* **23**, 357 (1981).

<sup>8</sup> J. Nulton, P. Salamon, B. Andresen, and Qi Anmin, *J. Chem. Phys.* (to be published).

<sup>9</sup> F. Schlögl, *Z. Phys.* **191**, 81 (1966); **198**, 559 (1967).

<sup>10</sup> I. Procaccia and R. D. Levine, *J. Chem. Phys.* **65**, 3357 (1976).