

On the relation between entropy and energy versions of thermodynamic length

P. Salamon, J. Nulton, and E. Ihrig

Citation: *J. Chem. Phys.* **80**, 436 (1984); doi: 10.1063/1.446467

View online: <http://dx.doi.org/10.1063/1.446467>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v80/i1>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIPAdvances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

On the relation between entropy and energy versions of thermodynamic length

P. Salamon

Department of Mathematical Sciences, San Diego State University, San Diego, California 92182

J. Nulton

Department of Mathematics, San Diego City College, San Diego, California 92101

E. Ihrig

Department of Mathematics, Arizona State University, Tempe, Arizona 85281

(Received 5 July 1983; accepted 27 September 1983)

The second derivative matrices of internal energy or of entropy may be used to define a metric structure on the set of equilibrium states of a thermodynamic system. When expressed relative to the same coordinates, the metric matrices are proportional to each other with constant of proportionality given by the negative of the absolute temperature. This establishes the conformal equivalence of the two metric structures.

The second derivative matrix D^2U of the internal energy may be used to define a Riemannian structure on the set of equilibrium states of a thermodynamic system. Since Weinhold's original observation of this fact in 1977,^{1,2} several results have appeared³⁻⁶ exploiting this structure. While Weinhold and other authors¹⁻⁵ used the Riemannian structure afforded by D^2U , Ruppeiner⁶ has chosen to use the Riemannian structure afforded by D^2S , the second derivative of the entropy. The Riemannian structures allow one to define the notion of length for fluctuations about equilibrium states^{1,2,6} as well as for thermodynamic processes proceeding via equilibrium states. We show below that these two Riemannian structures are conformally equivalent. This means that lengths of infinitesimal displacements from equilibrium (fluctuations) measured with D^2U are proportional to those measure by D^2S , although the constant of proportionality may depend on the state. Specifically we show that

$$D^2U = -T D^2S. \quad (1)$$

The above equality must be interpreted carefully; it relates the (coordinate invariant) metrics defined by U and S rather than the second derivative matrices of U and S relative to some coordinate system. To see the meaning of Eq. (1) in a specific coordinate system, we must proceed as follows: Compute the second derivative matrices of D^2U and D^2S each relative to its own natural extensive variables. Then transform to the coordinates (X_1, \dots, X_n) according to

$$D^2U(X_1, \dots, X_n) = R^T D^2U(S, V, N_1, \dots, N_{n-2}) R, \quad (2a)$$

$$D^2S(X_1, \dots, X_n) = Q^T D^2S(U, V, N_1, \dots, N_{n-2}) Q, \quad (2b)$$

where R is the Jacobian matrix of the coordinate transformation from (X_1, \dots, X_n) to $(U, V, N_1, \dots, N_{n-2})$, and Q is the Jacobian matrix of the coordinate transformation from (X_1, \dots, X_n) to $(S, V, N_1, \dots, N_{n-2})$ and R^T indicates R transpose.

Example: Consider the thermodynamic system consisting of 1 mol of an ideal gas. As is easily verified the second derivative matrix of U is

$$D^2U(S, V) = \begin{bmatrix} T/C_v & -p/C_v \\ -p/C_v & \gamma p/V \end{bmatrix}, \quad (3a)$$

while that of S is

$$D^2S(U, V) = \begin{bmatrix} -1/TU & 0 \\ 0 & -p/VT \end{bmatrix}. \quad (3b)$$

If we transform D^2U to the coordinates (U, V) using

$$R = \frac{\partial(S, V)}{\partial(U, V)} = \begin{bmatrix} 1/T & p/T \\ 0 & V \end{bmatrix}, \quad (4)$$

in formula (2a), we get

$$D^2U(U, V) = \begin{bmatrix} 1/U & 0 \\ 0 & p/V \end{bmatrix}, \quad (5)$$

in which each entry is $(-T)$ times the corresponding entry in $D^2S(U, V)$.

The general proof of Eq. (1) is most easily obtained in a coordinate free setting where the metrics are interpreted as differential two forms.^{5,7,8} In this setting we may write

$$D^2U = dTdS - dpdV + \sum_i d\mu_i dN_i \quad (6a)$$

and

$$D^2S = d(1/T)dU + d(p/T)dV - \sum_i d(\mu_i/T)dN_i, \quad (6b)$$

as may be seen by substituting the differentials of each intensive variable expanded in terms of the differentials of the extensive variables, e.g.,

$$dT = \frac{\partial T}{\partial S} dS + \frac{\partial T}{\partial V} dV. \quad (7)$$

Note that the coefficient of $dX_i dX_j$ in the resulting expansion is exactly the ij th entry in the matrix of D^2U , where $dX_i dX_j$ represents terms of the form $dSdS, dSdV, dVdV$, etc. This relationship between the coordinates of $dX_i dX_j$ and the ij th entry remains true in any coordinate system, and is the basis of the transformation rule given in Eqs. (2) above. If we now invoke the first law in the form

$$dU = TdS - pdV + \sum_i \mu_i dN_i, \quad (8)$$

substitute for dU in Eq. (6b), and expand we find

$$\begin{aligned} D^2S = & (-1/T^2)dT(TdS - pdV + \sum \mu_i dN_i) \\ & + (-pdT/T^2 + dp/T)dV \\ & + \sum (\mu_i dT/T^2 - d\mu_i/T)dN_i = (-1/T)D^2U. \end{aligned} \quad (9)$$

It is easily seen that the second derivative matrices of the Legendre transforms of U and S each computed relative to its own natural variables will yield different metrics. For example,

$$D^2H = dTdS + dpdV + \sum d\mu_i dN_i \quad (10)$$

yields a two form differing from D^2U only in the sign of the second term. These two forms are however equal when restricted to the subspace of states having the same pressure in which case the $dpdV$ term vanishes. Note that this term also vanishes if the volume is kept constant and therefore,

$$(D^2U)_v = (D^2H)_v, \quad (11)$$

where we have adopted the use of subscripts to indicate restriction to a subspace in which the subscripted variable is to be held constant. Similar statements may be made about the two forms associated with the second derivatives of the other thermodynamic potentials under suitable conditions. As further examples we note

$$(D^2U)_{N_1, \dots, N_{n-2}} = (D^2G)_{N_1, \dots, N_{n-2}}, \quad (12)$$

while

$$(D^2U)_{p,T} = (D^2G)_{p,T}. \quad (13)$$

The form of the coordinate free expressions for D^2U and D^2S suggest that the metric may be inherited from an ambient phase space^{5,7} of $2n + 1$ dimensions corresponding to n extensive variables, n conjugate intensities and a potential. In fact one may take Eqs. (6) as the definitions of D^2S and D^2U in such an ambient space. In this case however, the two metrics turn out not to be conformally equivalent.⁵ In this setting, a thermodynamic system is a surface in phase space such that $dU - TdS + pdV + \sum \mu_i dN_i$ vanishes along the

surface.^{7,5} Thus our use of the substitution for dU based on the vanishing of this differential form was crucial to the proof of conformal equivalence.

We conclude by noting the implications of Eq. (1) for thermodynamic lengths. Isothermal processes will have entropy lengths and energy lengths differing only by a factor of the square root of T (to get a positive quantity for length using a negative definite matrix it is standard practice to neglect the sign⁶). In general, the entropy length and the energy length will differ by a factor of the square root of some mean temperature during the process. Since lag times are ratios of two lengths computed at the same point,⁴ they are invariant. The conformal equivalence also assures that angles measured by one metric equal those same angles as measured by the other metric.

ACKNOWLEDGMENTS

We would like to thank R. S. Berry, M. Bynum, D. Flick, J. Molony, and F. Sullivan for helpful conversations, the Petroleum Research Fund administered by the American Chemical Society for support, and the Aspen Center for Physics for providing an excellent environment for writing this paper.

¹F. Weinhold, J. Chem. Phys. **63**, 2479, 2484, 2488, 2496 (1975); **65**, 559 (1976); Acc. Chem. Res. **9**, 236 (1976).

²F. Weinhold, Phys. Today **29**, 23 (1976).

³P. Salamon, B. Andresen, P. D. Gait, and R. S. Berry, J. Chem. Phys. **73**, 1001 (1980).

⁴P. Salamon and R. S. Berry, Phys. Rev. Lett. **51**, 1127 (1983).

⁵P. Salamon, E. Ihrig, and R. S. Berry, J. Math. Phys. **24**, 2515 (1983).

⁶G. Ruppeiner, Phys. Rev. A **20**, 1608 (1979); **24**, 488 (1981); **27**, 1116 (1983); Phys. Rev. Lett. **50**, 287 (1983). See in particular the first of these articles.

⁷R. Hermann, *Geometry, Physics, and Systems* (Marcell Dekker, New York, 1973).

⁸See, for example, R. L. Bishop and S. I. Goldberg, *Tensor Analysis on Manifolds* (Macmillan, New York, 1968).