

## Thermodynamic geometry and the metrics of Weinhold and Gilmore

Bjarne Andresen

*Physics Laboratory, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark*

R. Stephen Berry

*Department of Chemistry, University of Chicago, Chicago, Illinois 60637*

Robert Gilmore

*Department of Physics and Atmospheric Science, Drexel University, Philadelphia, Pennsylvania 19104*

Ed Ihrig

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

Peter Salamon

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

(Received 11 May 1987)

The thermodynamic geometries of Gibbs, Weinhold, and Gilmore are compared and the benefits of each are pointed out along with the structures which must be abandoned in order to reap the benefits. While the measurement of distances is not required (or even meaningful) in a traditional Gibbsian picture, Weinhold's metric can be used to measure distances in the equation-of-state surface. Using Weinhold's metric for more than a single state of equilibrium necessitates abandoning a Gibbsian picture of convex surfaces of thermodynamic states. Gilmore's metric, on the other hand, is compatible with standard Gibbsian thermodynamics. This metric measures distance in the potential surface of statistical mechanics rather than the equation-of-state surface of equilibrium thermodynamics.

### I. PROLOGUE

A spirited discussion has taken place in the last few years concerning possible uses of Weinhold's metric<sup>1</sup> in classical thermodynamics. Many authors<sup>2-22</sup> have used this metric to measure distances between equilibrium states of a thermodynamic system. Gilmore has argued repeatedly<sup>23,24</sup> that Weinhold's metric cannot be so used. Rather than proliferate the comment-response format, the present authors, representing both sides of the controversy, agreed to present the issues in as balanced a way as possible so that the benefits—and dangers—of adopting one view or the other are clearly apparent. We hope that we have succeeded in this task.

Regarding the earlier background of how far one can go with a geometric representation, Gibbs<sup>25</sup> warned about the importance of distinguishing “what is essential and what is arbitrary in a surface . . .” His conclusion, and that of Tisza after him, was that the equilibrium surface had no inherent metric properties. However, in light of all the works leading to this paper,<sup>1-24</sup> we can now see that Tisza's statement,<sup>26</sup> “neither the elementary nor the Riemannian theory of curvature can be applied in Gibbs space, in which no physically meaningful metric is definable” did not anticipate the benefits of introducing a metric for particular purposes at the expense of surrendering properties Gibbs emphasized.

### II. BACKGROUND

In the classical Gibbsian formulation of equilibrium thermodynamics<sup>25</sup> the set of equilibrium states is represented by the equation-of-state surface  $f(x^0, x^1, \dots, x^n) = 0$ , relating the  $n$  independent conserved extensive variables  $x^1 = U$ ,  $x^2 = V$ ,  $x^3 = N_1, \dots$ ,  $x^n = N_{n-2}$  with the entropy  $x^0 = S$ . This surface is convex and so each of its representations, such as  $S = S(U, V, \dots, N_{n-2})$ ,  $U = U(S, V, \dots, N_{n-2})$ ,  $\dots$ ,  $N_{n-2} = N_{n-2}(S, U, V, \dots, N_{n-3})$  involves a convex (or concave) function. This means in particular that the matrices of mixed second partial derivatives, or stability matrices  $\partial^2 S / \partial x^i \partial x^j = D^2 S$ ,  $\partial^2 U / \partial x^i \partial x^j = D^2 U$ ,  $\dots$ , are negative or positive semidefinite. Curvature in this space is inherited from the ambient space of the  $(x^0, x^1, \dots, x^n)$  in which the surface is embedded.

The stability matrix  $D^2 U$  was used by Weinhold<sup>1</sup> in a beautiful way as a bookkeeping device to summarize a large number of thermodynamic equalities and inequalities. Weinhold used the stability matrix  $D^2 U$  as a metric to introduce an inner-product structure on the tangent space of the equation-of-state surface at an equilibrium point. Once the tangent space was converted to an inner-product space, the Schwarz and Bessel inequalities and the Bessel equality were used to derive many of the standard thermodynamic inequalities.<sup>1,27</sup> The great vir-

tue of using the stability matrix as metric is that its matrix elements are the standard thermodynamic linear response functions, such as  $\alpha_p$ ,  $\kappa_T$ ,  $C_V$ , etc.

Three points should be emphasized: (1) Weinhold worked in the tangent space, (2) Weinhold measured angles but did not compute distances, and (3) Weinhold showed that his metric formalism for a given state of thermodynamic equilibrium is precisely equivalent to Gibbsian thermodynamics. Although Weinhold's formalism invites a Riemannian generalization of the local Euclidean metric, it does not demand it.

### III. THE DISPUTE

The crux of the controversy now hinges on the next step: whether the metric can be used to tie the tangent spaces at different points together and thereby define a global metric structure. Mathematically it is not a question of existence but rather of uniqueness which is at issue. Physically the question is whether this particular metric structure has physical relevance. The conflict arises because adopting the metric structure forces us to abandon a picture based on convex surfaces and to view the set of equilibrium states as an abstract semi-Riemannian manifold.<sup>28</sup> We stress that *the two geometrical representations of the set of equilibrium states, one as a convex hypersurface and the other as a semi-Riemannian manifold, cannot be used simultaneously*. Thus one could think in terms of the "equation-of-state surface" and interpret the semidefinite character of  $D^2U$  as expressing the convexity of this surface or one could think in terms of a semi-Riemannian manifold with  $D^2U$  as the metric matrix *but one cannot have both at the same time*.

Gilmore pointed this out<sup>23,24</sup> by inquiring into the consequences of introducing  $D^2U$  as a metric tensor on the equation-of-state surface to measure distances, and requiring that the equation-of-state surface be convex, so the Gaussian sectional curvature cannot be negative. Gilmore computed the Gaussian curvature<sup>23</sup> in terms of the Riemannian metric and curvature tensors, expressed this result in terms of second and third partial derivatives of the thermodynamic potential ( $S$  or  $U$ ), and showed that the non-negativity requirement led to a set of inequalities with physical implications for which there is no evidence whatsoever.

The dilemma comes from trying to use  $D^2U$  as a metric on the equation-of-state surface rather than on an abstract manifold of equilibrium states—that is, by wanting  $D^2U$  to be too many things. Algebraically, the second law in either setting requires that the matrix  $D^2U$  be positive semidefinite. In the Gibbsian framework this is interpreted geometrically as the convexity of the equation-of-state surface. In the alternative framework it represents the semidefiniteness of the metric matrix on the manifold of equilibrium states. One can still compute curvature<sup>10,17</sup> on this manifold; in fact such curvature turns out to equal the correlation volume<sup>2,3</sup> and can have either sign.<sup>19</sup>

Ruppeiner<sup>2-4</sup> was the first to use  $-D^2S$  as a metric tensor to measure distances in the equation-of-state sur-

face. The metric used by Ruppeiner was later shown to be conformally equivalent to Weinhold's metric:  $D^2U = -TD^2S$ .<sup>29-31</sup> Since then many authors have adopted  $D^2U$  or  $-D^2S$  as a metric tensor on the manifold of equilibrium states for a multiplicity of purposes,<sup>5-22</sup> e.g., calculating correlation volumes,<sup>2</sup> bounding dissipation in rate processes,<sup>7</sup> etc.

In order to introduce a metric structure that is compatible with the Gibbsian convex surface representation, Gilmore introduced a metric on potential surfaces which exactly reproduced the Gibbsian curvature:  $D^2U$ . In this construction a thermodynamic potential is introduced,

$$\mathfrak{U}(x^i, x^i_0) = U(x^i) - \left. \frac{\partial U}{\partial x^i} \right|_0 (x^i - x^i_0), \quad (1)$$

where  $x^i$  is an arbitrary set of extensivities,  $x^i_0$  are equilibrium values, and  $\partial U / \partial x^i = \lambda^i_0$  are the conjugate intensities at thermodynamic equilibrium. A Euclidean metric  $ds^2 = dU^2 + \sum (\lambda^i_0 dx^i)^2$  is defined on the ambient space  $\mathbb{R}^{n+1} = \{(U, x)\}$  in which this potential is introduced. The induced metric is used to define distances in the potential surface. The curvature evaluated at the equilibrium (minimum) is the Gibbsian curvature  $D^2U$ . We emphasize that this construction is not applied to the equation-of-state surface, but rather to the potential surface whose minimum is the only point on this surface which represents an equilibrium state.<sup>23</sup> This potential occurs naturally in Gibbs's formulation of statistical mechanics<sup>25</sup> where it describes the probability distribution for fluctuations around the thermodynamic equilibrium state [ $p \sim \exp(-\mathfrak{U}/kT)$ ]. This probability is replaced in the Riemannian fluctuation theory<sup>2-4</sup> by a covariant path integral formalism which works even for volumes on the order of one correlation volume.

### IV. EMBEDDINGS

A comparable construction cannot be applied to the equation-of-state surface. That is, it is not possible to define a *Euclidean* metric on the space  $\mathbb{R}^{n+1} = (x^0, x^1, \dots, x^n)$  which induces the metric  $D^2U$  on the equation-of-state surface. The easiest way to see this is by considering a multiphase region in the equation-of-state surface. In such a region the stability matrix  $D^2U$  has at least one "flat" direction (vanishing eigenvalue). All distinct states lying on a null line are nonzero distance apart in the space  $\mathbb{R}^{n+1}$  but zero distance apart according to Weinhold's metric.

A Euclidean metric in  $\mathbb{R}^{n+1}$  cannot induce the geometry of  $D^2U$  even on single phase regions of the equation-of-state surface. However, it is possible to define a nonconstant metric in  $\mathbb{R}^{n+1}$  which induces the Weinhold metric  $D^2U$  on restriction to the equation-of-state surface. Such a metric is not unique. Furthermore, the space  $\mathbb{R}^{n+1}$  with this metric is non-Euclidean. This means that one is forced to relinquish the concept of straight-line segment, in terms of which the Gibbsian concept of convexity is defined.<sup>25</sup> These results are proven in the following paper.<sup>32</sup>

### V. DISCUSSION

Gilmore's claim is that it is possible—in fact, preferable—to formulate classical thermodynamics without the concept of distance, as done originally by Gibbs.<sup>25</sup> The important quantity in such a formulation is the Gibbsian curvature tensor, or stability matrix  $D^2U$ . A metric formulation is possible on potential surfaces. In this formulation the Riemannian curvature tensor is computed from the induced metric on the potential surface.<sup>33</sup> The Gaussian sectional curvature computed from the Riemannian curvature tensor at the minimum of the potential  $\mathfrak{U}$  is identical with the Gibbsian curvature [cf. Ref. 23, Eq. (5.2)]. The metric, and an analogy with the geodesic equations of motion, has suggested some possible dynamical properties obeyed by a system on approach to thermodynamic equilibrium.<sup>23</sup>

Many authors have worked on the implications of introducing the metrics  $D^2U$  or  $-D^2S$  to measure distances in the equation-of-state surface. We stress that the metric structure on the set of equilibrium states is only semi-Riemannian as  $D^2U$  is only semidefinite. Since the directions corresponding to zero eigenvalues of the stability matrix  $D^2U$  correspond to phase changes,<sup>1</sup> a Riemannian geometry can be associated with any single-phase region. One can also use the standard construction of a Riemannian structure from a semi-Riemannian one by identifying states which can be connected by a path of zero length. Going to intensive coordinates provides one way of accomplishing this identification.

Many of the consequences of introducing the metrics  $D^2U$  or  $-D^2S$  on the equilibrium surface are now available. The geometry based on  $-D^2S$ , when restricted to the states of maximum statistical-mechanical entropy  $S_{sm} = -\sum p_i \ln p_i$ , agrees with the geometry defined by  $\partial^2 S_{sm} / \partial p_i \partial p_j = \delta_{ij} / p_j$ , where  $p_i$  is the probability of finding the system in the  $i$ th quantum state.<sup>8</sup> Wootters<sup>5</sup> has shown that this latter geometry gives distances equal to the quantum-mechanical angle between states.

Lengths of paths thus can be variously interpreted as the number of states that can be distinguished with a particular measuring apparatus,<sup>5</sup> as the number of fluctuations required to traverse the path,<sup>2</sup> and as the square root of the minimum dissipation multiplied by the number of relaxations in a finite-time process.<sup>7,11</sup> The geometry has been used to extend fluctuation theory down to regions the size of one correlation length,<sup>3,4</sup> to study dissipation in finite-time processes,<sup>7,11-14</sup> to augment renormalization-group techniques for the study of critical phenomena,<sup>16</sup> and to study molecular relaxation phenomena.<sup>12</sup> It has also been extended to irreversible dynamics.<sup>13,17</sup>

The metric structure of Weinhold also fits in nicely with the geometrical picture advanced by Hermann.<sup>34</sup> In this picture a thermodynamic system is a solution of the Pfaffian equation  $dS = \xi dX$  in the  $(2n+1)$ -dimensional space of variables  $(X, \xi, S)$ , where  $\xi$  is the set of intensive coordinates conjugate to the  $X$ . Here  $D^2S$  is the restriction of the two-form  $\sum dX_i d\xi_i$  to the solution surface.<sup>22</sup> A modification of the intrinsic geometry has been studied by Schlögl<sup>9</sup> which agrees infinitesimally, but employs the mixed "distance" function  $\sum \Delta X_i \Delta \xi_i$  for finite displacements.

By comparison, Gilmore's metric structure offers neither more nor less than Gibbsian thermodynamics. It is completely compatible with Gibbsian thermodynamics, and, in particular, the concept of convexity. It preserves the concepts which must be abandoned if Weinhold's metric is used to measure distances in the equilibrium surface. Furthermore, it offers a metric of its own whose potentialities are still unexplored. These remarks are summarized in Table I.

### VI. EPILOGUE

It is not possible to maintain simultaneously both the Gibbsian notion of convexity of the equilibrium manifold and a concept of distance based on Weinhold's metric.

TABLE I. Comparison of the consequences of using the metrics of Gilmore and Weinhold to measure distance and determine curvature.

Metric	Measure Distance	Determine Curvature
Gilmore metric over potential surfaces	Asymptotics of relaxation	Compatible with Gibbs's geometric representation of thermodynamics
	Geometry Riemannian	
	Quantum angle between states	Correlation length
	Number of states distinguished by a measuring apparatus	
Weinhold metric over equilibrium manifold	Fluctuations in a path length	Incompatible with Gibbs's geometric representation of thermodynamics
	Finite-time processes	
	Fluctuation-correlation relation	
	Dissipation	
	Renormalization groups and critical phenomena	
	Molecular relaxation	
	Irreversible dynamics	
Pfaffian geometric picture		
	Geometry semi-Riemannian	

The two are incompatible. If Weinhold's metric is used to measure distances, the Gibbsian picture of thermodynamics must be relinquished. If the Gibbsian picture is to be preserved, Weinhold's metric cannot be used to measure distances, but Gilmore's can be. Gilmore's metric is completely compatible with Gibbs's geometric interpretation of thermodynamics.

Gibbs himself was not above using different geometrical representations.<sup>1</sup> Thus it is quite possible that both representations considered here will continue to remain of physical interest. It is also possible that there is a more global perspective from which one could deduce a synthesis of the two pictures. Preference of one representation over the other must ultimately come from the physical evidence.

#### ACKNOWLEDGMENTS

We thank Professor F. Weinhold for useful comments. In addition, we would like to thank the Telluride Summer Research Center for providing us the opportunity to work together on this problem. One of us (P.S.) would like to thank the Petroleum Research Fund administered by the American Chemical Society and the Danish Natural Science Research Council for partial support of this work and R.S.B. wishes to acknowledge the support of the U.S. Department of Energy. R.G. acknowledges the support of the National Science Foundation through Grant No. PHY-84-41891 and No. PHY-85-20834.

- 
- <sup>1</sup>F. Weinhold, *J. Chem. Phys.* **63**, 2479 (1975); **63**, 2484 (1975); **63**, 2488 (1975); **63**, 2496 (1975); **65**, 559 (1976); *Acc. Chem. Res.* **9**, 236 (1976); in *Theoretical Chemistry: Advances and Perspectives*, edited by Eyring and Henderson (Academic, New York, 1978), Vol. 3, pp. 15–54.
- <sup>2</sup>G. Ruppeiner, *Phys. Rev. A* **20**, 1608 (1979); **24**, 488 (1981).
- <sup>3</sup>G. Ruppeiner, *Phys. Rev. Lett.* **50**, 287 (1983).
- <sup>4</sup>G. Ruppeiner, *Phys. Rev. A* **27**, 1116 (1983).
- <sup>5</sup>W. K. Wootters, *Phys. Rev. D* **23**, 357 (1981).
- <sup>6</sup>P. Salamon, B. Andresen, P. D. Gait, and R. S. Berry, *J. Chem. Phys.* **73**, 1001 (1983).
- <sup>7</sup>P. Salamon and R. S. Berry, *Phys. Rev. Lett.* **51**, 1127 (1983).
- <sup>8</sup>P. Salamon, J. D. Nulton, and R. S. Berry, *J. Chem. Phys.* **82**, 2433 (1985).
- <sup>9</sup>F. Schlögl, *Z. Phys. B* **59**, 449 (1985).
- <sup>10</sup>J. D. Nulton and P. Salamon, *Phys. Rev. A* **31**, 2520 (1985).
- <sup>11</sup>J. D. Nulton, P. Salamon, B. Andresen, and A. Qi, *J. Chem. Phys.* **83**, 334 (1985).
- <sup>12</sup>T. Feldmann, B. Andresen, A. Qi, and P. Salamon, *J. Chem. Phys.* **83**, 5849 (1985).
- <sup>13</sup>S. Sieniutycz and P. Salamon, *J. Phys. Chem.* **90**, 1396 (1986).
- <sup>14</sup>L. L. Campbell, *Inf. Sci. (N.Y.)* **35**, 199 (1985).
- <sup>15</sup>T. Feldmann, R. D. Levine, and P. Salamon, *J. Stat. Phys.* **42**, 1127 (1986).
- <sup>16</sup>L. Diósi, G. Forgacs, B. Lukács, and H. Frisch, *Phys. Rev. A* **29**, 3343 (1984); L. Diósi and B. Lukács, *ibid.* **31**, 3415 (1985); *Phys. Lett.*; **112A**, 13 (1985).
- <sup>17</sup>J. Casas-Vázquez and D. Jou, *J. Phys. Chem.* **83**, 4715 (1985).
- <sup>18</sup>R. D. Levine, *J. Chem. Phys.* **84**, 910 (1986).
- <sup>19</sup>G. Ruppeiner, *Phys. Rev. A* **32**, 3141 (1985).
- <sup>20</sup>K. Horn, *Phys. Rev. A* **32**, 3142 (1985).
- <sup>21</sup>P. Salamon (unpublished).
- <sup>22</sup>P. Salamon, E. Ihrig, and R. S. Berry, *J. Math. Phys.* **24**, 2515 (1983).
- <sup>23</sup>R. Gilmore, *Phys. Rev. A* **30**, 1994 (1984).
- <sup>24</sup>R. Gilmore, *Phys. Rev. A* **32**, 3144 (1985).
- <sup>25</sup>J. W. Gibbs, *Collected Works* (Yale University, New Haven, 1948), Vol. 1.
- <sup>26</sup>L. Tisza, *Generalized Thermodynamics* (MIT, Cambridge, MA, 1966), p. 106.
- <sup>27</sup>R. Gilmore, *Catastrophe Theory for Scientists and Engineers* (Wiley, New York, 1981).
- <sup>28</sup>Weinhold's review article<sup>1</sup> already emphasized that the metric geometry applies to an abstract manifold of equilibrium states.
- <sup>29</sup>R. Gilmore (unpublished). The major result of this work was conveyed to the authors of Ref. 30 prior to publication.
- <sup>30</sup>P. Salamon, J. Nulton, and E. Ihrig, *J. Chem. Phys.* **80**, 436 (1984).
- <sup>31</sup>R. Mrugała, *Physica A* **125**, 631 (1984).
- <sup>32</sup>B. Andresen, R. S. Berry, E. Ihrig, and P. Salamon, following paper, *Phys. Rev. A* **37**, 849 (1988).
- <sup>33</sup>D. J. Struik, *Differential Geometry* (Addison-Wesley, Reading, MA, 1950).
- <sup>34</sup>R. Hermann, *Geometry, Physics, and Systems* (Marcel Dekker, New York, 1973).