# Length and curvature in the geometry of thermodynamics

R. Gilmore
*Department of Physics and Atmospheric Science, Drexel University, Philadelphia, Pennsylvania 19104*
(Received 2 February 1983)

The relationship between Weinhold's metric geometry and the Riemannian geometry of thermodynamics is presented.

## I. NOTATION

The internal energy, $U$, of a system in thermodynamic equilibrium with its surroundings is a function of the extensive variables $E^1, E^2, \ldots, E^n$ (e.g., $S$, $V$, $N_i, \ldots$) which describe the system uniquely: $U = U(E^1, E^2, \ldots, E^n)$. The equation $U = U(E)$ defines an $n$-dimensional equation-of-state surface embedded in an $(n+1)$-dimensional space, $\mathbb{R}^{n+1}$, whose coordinates are $(E^1, E^2, \ldots, E^n; U(E)) = (E^\alpha; U(E))$. This surface is a manifold everywhere except at edges defined by one or more equations of Clausius-Clapeyron type.

A tangent space can be constructed through any point in the equation-of-state manifold. The coordinates of any point in the tangent space through the point $(E_0^\alpha; U(E_0))$ are $(E^\alpha; U(E_0) + \lambda_\alpha^B (E^\alpha - E_0^\alpha))$. Here $\lambda_\alpha^B$ are the values of the intensive thermodynamic variables of the heat bath (e.g., $T$, $-P$, $\mu_i, \ldots$) which are conjugate to the system's extensive variables. At equilibrium

$$U_\alpha = \left.\frac{\partial U}{\partial E^\alpha}\right|_{E_0} = \lambda_\alpha^B . \tag{1.1}$$

It is convenient to introduce the thermodynamic potential

$$\mathscr{U}(E, E_0) = U(E) - \lambda_\alpha^B (E^\alpha - E_0^\alpha) \tag{1.2}$$

for the equilibrium $E_0$. The coordinates of the surface $\mathscr{U}$ in $\mathbb{R}^{n+1}$ are $(E^\alpha; \mathscr{U}(E, E_0))$. The state of thermodynamic equilibrium $(E_0)$ is determined by the minimum value of $\mathscr{U}$. The tangent space at this point is horizontal in $\mathbb{R}^{n+1}$ with coordinates $(E^\alpha; U(E_0))$.

## II. THERMODYNAMIC IMPLICATIONS

The first law of thermodynamics ($dU = \lambda_\alpha^B dE^\alpha$) states that, to first order, the change in the system's internal energy can be determined either from the equation-of-state manifold or from the tangent space at the equilibrium point. By the second law of thermodynamics, $U(E)$ is concave upward. This means that the equation-of-state surface lies above (or on) any of its tangent spaces. The local form of this global statement of the second law is that the curvature of this surface is everywhere positive (semi)definite. The curvature of $U(E)$ is determined by the matrix of mixed second partial derivatives

$$U_{\alpha\beta} = \frac{\partial^2 U}{\partial E^\alpha \partial E^\beta} \geq 0 \text{ [positive (semi)definite]} . \tag{2.1}$$

The matrix $U_{\alpha\beta}$ [Eq. (2.1)] is positive definite in single-phase regimes. Since $U(E)$ and the potential $\mathscr{U}(E, E_0)$ differ by terms linear in the extensive thermodynamic variables $E^\alpha$, all their second- and higher-order derivatives are equal. In particular $U_{\alpha\beta} = \mathscr{U}_{\alpha\beta} = \partial^2 \mathscr{U} / \partial E^\alpha \partial E^\beta$.

## III. DISTANCE IN THE TANGENT SPACE—CURVATURE OF THE EQUILIBRIUM SURFACE

Neither the equation-of-state surface $U(E)$ nor its tangent space comes endowed with a natural measure of distance, but both are endowed with a natural measure of curvature. The tangent spaces are flat (by definition); the curvature of $U(E)$ is given by the stability matrix $U_{\alpha\beta}$ [Eq. (2.1)]. The matrix elements of this $n \times n$ matrix are the thermodynamic linear response functions (e.g., $C_V$, $\Gamma_V$, $\beta_S$).[1,2]

Since the curvature form $U_{\alpha\beta}$ is positive definite (in single-phase regions), it can be used to define distances. Weinhold used $U_{\alpha\beta}(E_0)$ to define a distance on the tangent space to the equation-of-state surface at $E_0$. Although any positive-definite $n \times n$ matrix would suffice to define a distance on the tangent space, the choice $U_{\alpha\beta}(E_0)$ was particularly fruitful. This is because standard Euclidean vector-space theorems (Schwartz inequality, Bessel equality and inequality) could easily be exploited to provide relations among the matrix elements of $U_{\alpha\beta}$, and thus provide a geometric interpretation of the equalities and inequalities which the second law of thermodynamics imposes on the thermodynamic linear response functions.[1,2]

With this choice of metric in the tangent space, the square of the distance between the point in the tangent space with coordinates $(E_0^\alpha + \Delta E^\alpha; U(E_0) + \lambda_\alpha^B \Delta E^\alpha)$ and the point of contact (equilibrium point) $(E_0^\alpha; U(E_0))$ is $U_{\alpha\beta} \Delta E^\alpha \Delta E^\beta$. To lowest order, this is twice the available energy, or twice the vertical distance between $U(E)$ and its tangent space at $E_0$, as previously noted by Salamon *et al.*[3]

Several authors have suggested the possibility of using the matrix $U_{\alpha\beta}$ to measure distances in the equation-of-state surface.[3,4] This is not possible. Such a use leads to an incorrect statement of the second law of thermodynamics. To show this (Sec. V), and to determine the appropriate measure of distance in the equilibrium manifold (Sec. VI), we review in the following sections some basic

 

mathematical procedures for studying the geometric properties of surfaces.

## IV. GEOMETRY OF SURFACES

Two important properties of surfaces must be characterized by any study of surfaces: (i) the distance between two nearby points in the surface, (ii) the curvature of the surface at a point.

Two useful methods have been developed for studying the geometry of surfaces. These methods are the extrinsic method developed by Gauss and the intrinsic method developed by Riemann.[5]

In the Gaussian approach, an $n$-dimensional surface is embedded in a Euclidean space, $\mathbb{E}^{n+1}$, of (usually) one higher dimension: $(x^1,x^2,\ldots,x^n;x^{n+1}(x^1,\ldots,x^n))$. The distance between points in $\mathbb{E}^{n+1}$ is defined by a constant positive-definite $(n+1)\times(n+1)$ matrix. The usual choice is

$$dl^2=(dx^1)^2+(dx^2)^2+(dx^{n+1})^2 . \tag{4.1}$$

The distance between nearby points in the surface is defined by the distance between these points in the Euclidean space. The curvature of the surface at a point is determined by an $n\times n$ matrix of mixed second partial derivatives $\partial^2x^{n+1}/\partial x^i\partial x^j$ (curvature matrix). In particular, if only coordinates $x^r$ and $x^s$ are allowed to vary, and the remaining $n-2$ independent coordinates are held constant, the Gaussian sectional curvature is defined by

$$K(r,s)=\det\begin{bmatrix} f_{rr} & f_{rs} \\ f_{sr} & f_{ss} \end{bmatrix} , \tag{4.2}$$

where $f(x^1,\ldots,x^n)=x^{n+1}(x^1,\ldots,x^n)$. For an ideal monatomic gas with $x^1=S$, $x^2=V$, $x^3=U(S,V)$, we have

$$K(S,V)=\det\begin{bmatrix} \dfrac{T}{C_V} & -\dfrac{T}{\Gamma_V} \\ -\dfrac{T}{\Gamma_V} & \dfrac{1}{V\beta_S} \end{bmatrix}=\frac{2}{3}\left[\frac{P}{R}\right]^2 , \tag{4.3}$$

where $PV=RT$, $C_V=\frac{3}{2}R$, $\Gamma_V=\frac{3}{2}V$, $\beta_S=\frac{3}{5}P^{-1}$.

The Gaussian approach is called extrinsic because it depends on an embedding of the $n$-dimensional surface in a space of higher dimension. The Riemannian approach is called intrinsic because it requires no such embedding.

In the Riemannian approach an $n\times n$ positive-definite real symmetric metric matrix $g_{ij}(x)$ is defined at all points on the $n$-dimensional surface. The distance between two nearby points with coordinates $(x^1,\ldots,x^n)$ and $(x^1+dx^1,\ldots,x^n+dx^n)$ is

$$dl^2=g_{ij}(x)dx^i dx^j . \tag{4.4}$$

The curvature of the surface at any point can be determined by constructing the Christoffel symbols $\Gamma^i_{jk}$ (not a tensor) and the curvature tensor $R_{ij,kl}$ from the metric tensor $g_{ij}$ as follows:[6]

$$\Gamma^i_{jk}=\tfrac{1}{2}g^{il}\left[\frac{\partial g_{lk}}{\partial x^j}+\frac{\partial g_{jl}}{\partial x^k}-\frac{\partial g_{jk}}{\partial x^l}\right] , \tag{4.5a}$$

$$R_{ij,kl}=\frac{1}{2}\left[\frac{\partial^2 g_{ik}}{\partial x^j\partial x^l}-\frac{\partial^2 g_{jk}}{\partial x^i\partial x^l}-\frac{\partial^2 g_{il}}{\partial x^j\partial x^k}+\frac{\partial^2 g_{jl}}{\partial x^i\partial x^k}\right]$$
$$+g_{rs}(\Gamma^r_{ik}\Gamma^s_{jl}-\Gamma^r_{il}\Gamma^s_{jk}) . \tag{4.5b}$$

In Eq. (4.5a), $g^{il}$ is the matrix inverse of $g_{ij}$: $g^{il}g_{lj}=\delta^i_{\ j}$.

In the event that a Riemannian surface can be embedded in a Euclidean space and thus studied also by Gaussian methods, the two approaches must provide equivalent results for the measures of distance and curvature. In particular, the Riemannian metric $g_{ij}(x)$ is the restriction of the Euclidean metric on $\mathbb{E}^{n+1}$ to the embedded surface. A concrete example of an induced metric, germain to thermodynamics, will be presented in Sec. VI. The Gaussian sectional curvature is related to the Riemannian metric and curvature tensors by[6]

$$K(r,s)=-\frac{R_{rs,rs}}{g_{rr}g_{ss}-g_{rs}g_{sr}} \tag{4.6}$$

when the Euclidean space has metric (4.1). If the metric on $\mathbb{E}^{n+1}$ is different, modifications in (4.6) must be made. For functions which are either concave or convex, all Gaussian sectional curvatures are positive.

## V. MISUSE OF THE CURVATURE FORM

Several authors have proposed using the matrix $U_{\alpha\beta}$, which measures the curvature of the equation-of-state surface, to measure distances between nearby points within this surface.[3,4] If this is to be done, the consequences of this choice cannot be neglected. The principal consequence is the ability to compute the curvature from the metric tensor $g_{\alpha\beta}=U_{\alpha\beta}$ using Eqs. (4.5) and (4.6). A trivial calculation gives

$$\Gamma^\alpha_{\beta\gamma}=\tfrac{1}{2}U^{\alpha\mu}U_{\beta\gamma\mu} , \tag{5.1a}$$

$$R_{\alpha\beta,\gamma\delta}=(\tfrac{1}{2})^2U^{\mu\nu}[U_{\alpha\gamma\mu}U_{\beta\delta\nu}-U_{\alpha\delta\mu}U_{\beta\gamma\nu}] . \tag{5.1b}$$

Using the results (5.1) to determine the Gaussian sectional curvature (4.6), we find

$$K(\alpha,\beta)=-\frac{(\frac{1}{2})^2U^{\mu\nu}[U_{\alpha\alpha\mu}U_{\beta\beta\nu}-U_{\alpha\beta\mu}U_{\beta\alpha\nu}]}{U_{\alpha\alpha}U_{\beta\beta}-U_{\alpha\beta}U_{\beta\alpha}} . \tag{5.2}$$

The second law of thermodynamics requires $U$ to be concave upward, and thus the sectional curvature to be positive. Since $U_{\alpha\alpha}U_{\beta\beta}-U_{\alpha\beta}U_{\beta\alpha}>0$ [cf. Eq. (2.1)], the choice of $U_{\alpha\beta}$ as a Riemannian metric $g_{\alpha\beta}$ on the equation-of-state surface leads to the inequalities

$$U^{\mu\nu}[U_{\alpha\alpha\mu}U_{\beta\beta\nu}-U_{\alpha\beta\mu}U_{\beta\alpha\nu}]\le 0 \tag{5.3}$$

(all pairs $\alpha,\beta$) between second and third derivatives of the internal energy.

The second law of thermodynamics places well-known constraints on the second derivatives of $U$ [i.e., Eq. (2.1)] but no known constraints on the third derivatives of $U$. We must therefore reject the choice of the Gaussian curvature form $U_{\alpha\beta}$ as the Riemannian distance form (i.e., metric tensor) $g_{\alpha\beta}$ on $U$. Such a choice is not compatible with the second law of thermodynamics.

## VI. RIEMANNIAN GEOMETRY ON THE EQUILIBRIUM MANIFOLD

The failure of the curvature (5.2) to provide a quantitative local statement of the second law of thermodynamics does not mean that the methods of Riemannian geometry cannot be applied to study the equilibrium surface $U(E)$. It simply means that an incorrect metric has been used. To determine the correct metric, we assume that the distance function in the space $\mathbb{R}^{n+1}$ in which $\mathcal{U}(E)$ is embedded is

$$dl^2=\sum_{\alpha=1}^{n}(\lambda_\alpha^B dE^\alpha)^2+d\mathcal{U}^2 . \tag{6.1}$$

In the neighborhood of the equilibrium point $(E_0^\alpha;\mathcal{U}(E_0))$ the induced metric on the $n$-dimensional potential surface $(E^\alpha;\mathcal{U}(E))$ is[5]

$$g_{\alpha\beta}=(\lambda_\alpha^B)^2\delta_{\alpha\beta}+\mathcal{U}_\alpha\mathcal{U}_\beta , \tag{6.2}$$

where

$$\mathcal{U}_\alpha=\frac{\partial U}{\partial E^\alpha}-\lambda_\alpha^B \tag{6.3}$$

is the generalized thermodynamic force acting on a system in contact with a heat bath characterized by intensive thermodynamic variables $\lambda_\alpha^B$. At equilibrium, $\mathcal{U}_\alpha=0$.

Using the choice of metric (6.2) and the expressions (4.5), another straightforward calculation for the Christoffel symbols and curvature tensor at the equilibrium point gives (recall that $\mathcal{U}_{\alpha\beta}=U_{\alpha\beta}$)

$$\Gamma_{\beta\gamma}^\alpha=0 , \tag{6.4a}$$

$$R_{\alpha\beta,\gamma\delta}=U_{\alpha\delta}U_{\beta\gamma}-U_{\alpha\gamma}U_{\beta\delta} . \tag{6.4b}$$

The relation between the Gaussian sectional curvature $K(\alpha,\beta)=U_{\alpha\alpha}U_{\beta\beta}-U_{\alpha\beta}U_{\beta\alpha}$ and the Riemannian curvature is given by (4.6), which must be modified slightly. When the coordinates are modified by scale factors, [compare (6.1) with (4.1)], the right-hand side of (4.6) must be modified by multiplying by scale factors $(\lambda_\alpha^B)^2(\lambda_\beta^B)^2$. The following expression results:

$$K(\alpha,\beta)=-\frac{(\lambda_\alpha^B)^2(\lambda_\beta^B)^2R_{\alpha\beta,\alpha\beta}}{g_{\alpha\alpha}g_{\beta\beta}-g_{\alpha\beta}g_{\beta\alpha}}=U_{\alpha\alpha}U_{\beta\beta}-U_{\alpha\beta}U_{\beta\alpha} . \tag{6.5}$$

With the choice of metric (6.1) in $\mathbb{R}^{n+1}$ and the induced intrinsic metric (6.2) on $\mathcal{U}(E)$, the Gaussian (extrinsic) and Riemannian (intrinsic) description of the equilibrium manifold are completely equivalent. Weinhold's metric geometry and the Riemannian geometry of the equilibrium surface are equivalent local formulations of the second law of thermodynamics.

## VII. SUMMARY AND CONCLUSIONS

The calculations above have been carried out in the energy representation, used by Weinhold,[1] Gilmore,[2] and Salamon *et al.*[3] The results are also valid in the entropy representation $S=S(U,V,N_i,\ldots)$, used by Ruppeiner.[4,7] The $n\times n$ curvature matrices in these two representations $[U],[S]$, are related by $[U]=-T[S]$,[8,9] where the matrix elements are second derivatives with respect to the intrinsic arguments. The equilibrium surfaces $U$ and $S$ are concave upward and concave downward, respectively. The Gaussian sectional curvature is the product of the two principal curvatures in the three-dimensional subspace $(E^\alpha, E^\beta; U;$ or $S)$. Both principal curvatures are nonnegative for the energy surface and nonpositive for the entropy surface, and so the inequality $K(\alpha,\beta)\geq 0$ is valid in either representation.

Ruppeiner introduced the metric $(S_{\alpha\beta})$ through a multivariate fluctuation argument,[4,7] claiming more generality for his metric than for Weinhold's. However, not only are the two metrics conformally equivalent,[8,9] but Gilmore has shown the equivalence of five different interpretations of $U_{\alpha\beta}$, including the two (curvature of the energy surface, description of multivariate fluctuations) discussed above.[2]

Ruppeiner's unconventional interpretation of the measure of curvature ($U_{\alpha\beta}$, Weinhold's metric) as a measure of distance on the equilibrium surface leads to

(1) the vanishing of the curvature scalar for an ideal gas;[4]

(2) the "interaction hypothesis," based on the previous finding;[7] and

(3) nontrivial relations [Eq. (5.3)] among the second and third derivatives of the internal energy (entropy).

This last feature, which has not been discussed by Ruppeiner, lies completely outside the scope of classical thermodynamics.

The correct choice of a measure of distance in the equilibrium manifold has been presented in Sec. VI. With this choice, the Riemannian curvature carries exactly the same information as the Gaussian sectional curvature.

As yet, the Euclidean metric (6.1) and the Riemannian metric (6.2) induced from it have no physical interpretation. In the neighborhood of an equilibrium point the Christoffel symbols are given by $\Gamma_{\beta\gamma}^\alpha=[\mathcal{U}_\alpha/(\lambda_\alpha^B)^2]U_{\beta\gamma}$. If these can be interpreted as forces restoring a perturbed system back to its thermodynamic equilibrium, then the relaxation equations would have the form

$$d(\delta E^\alpha)/dt+\Gamma_{\beta\gamma}^\alpha\delta E^\beta\delta E^\gamma=0 .$$

The solutions of such equations have an asymptotic time dependence (using $\mathcal{U}_\alpha=U_{\alpha\mu}\delta E^\mu$) of the form $t^{-1/2}$. The Riemannian curvature is entirely consistent with the second law of thermodynamics. The Bianchi identities are trivially satisfied, and provide no constraints on $U_{\alpha\beta}$.

## ACKNOWLEDGMENTS

This work was supported in part by National Science Foundation Grant Nos. PHY-81-02977 and PHY-83-04868.

[1]F. Weinhold, J. Chem. Phys. **63**, 2479 (1975); **63**, 2484 (1975); **63**, 2488 (1975); **63**, 2496 (1975).
[2]R. Gilmore, *Catastrophe Theory for Scientists and Engineers* (Wiley, New York, 1981).
[3]P. Salamon, B. Andreson, P. D. Gait, and R. S. Berry, J. Chem. Phys. **73**, 1001 (1980).
[4]G. Ruppeiner, Phy. Rev. A **20**, 1608 (1979).
[5]D. Laugwitz, *Differential and Riemannian Geometry* (Academic, New York, 1965).
[6]S. Weinberg, *Gravitation and Cosmology* (Wiley, New York, 1972).
[7]G. Ruppeiner, Phys. Rev. A **24**, 488 (1981).
[8]R. Gilmore (unpublished).
[9]P. Salamon, J. Nulton, and E. Ihrig, J. Chem. Phys. **80**, 436 (1984).