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# Reply to "Comment on 'Length and curvature in the geometry of thermodynamics'"

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Previous authors have introduced a Riemannian surface $[(S,V),U_{\alpha\beta}(S,V)]$, and claimed that this surface could be identified with the surface $U=U(S,V)$ for a substance in thermodynamic equilibrium. No proof has ever been offered of this supposed equivalence. The paper commented on showed that such a proof is not possible unless a new class of thermodynamic inequalities were to exist (they do not). The two preceding Comments also fail to provide a proof that these two surfaces can be identified. In the present Comment we prove once again, citing fundamental theorems of differential geometry, that this identification is not possible. We show specifically that any Riemannian metric chosen to measure distances in the equilibrium surface must lead, through the curvature tensor, to a Gaussian sectional curvature which is everywhere positive semidefinite if the convexity condition of the second law of thermodynamics is not to be violated. Two previous choices of metric do not possess this property.

For a substance in thermodynamic equilibrium depending on $n$ independent extensive thermodynamic variables, the equilibrium surface is an $n$-dimensional surface in the space of $n+1$ extensive thermodynamic variables: $f(U,S,V,N,\ldots,E^{n+1})=0$. This surface is convex in the energy representation $U=U(S,V,\ldots,E^{n+1})$ [concave in the entropy representation $S=S(U,V,\ldots,E^{n+1})$] by the second law of thermodynamics.[1,2] Convexity means that the surface lies everywhere above each tangent plane ($n=2$) or tangent space ($n>2$). In the following we will restrict consideration to $n=2$ and to the energy representation $U=U(S,V)$ for concreteness. Conversion to the entropy representation can be carried out without difficulty, and extension to $n>2$ variables will be discussed toward the end of the response. In this concrete case the energy surface $U=U(S,V)$ is a two-dimensional surface embedded in the three-dimensional space $\mathbb{R}^3$ of thermodynamic variables $(U,S,V)$, and convexity means that both principal curvatures are positive (non-negative in multiphase regimes).

The study of two-dimensional surfaces embedded in three-dimensional space is the subject of classical differential geometry. These studies have been carried out in two distinct ways.[3,4] In the first ("Gaussian") approach, a notion of distance, or metric, is introduced in the embedding space $\mathbb{R}^3$. The distance between two nearby points in the surface $z=z(x,y)$ is defined as the distance between these points, considered as points in $\mathbb{R}^3$. This identification induces a metric tensor $g(x,y)$ on the surface. The quadratic form based on $g$ is called the first fundamental form of the surface.[3,4] The curvature of the surface $z=z(x,y)$ is determined by a second tensor $L(x,y)$ on the surface. The quadratic form based on $L$ is called the second fundamental form of the surface.[3,4] The two fundamental forms $g$ (measuring distance) and $L$ (measuring curvature) are not unrelated, but must obey the Gauss-Codazzi equations.[3,4] The Gaussian sectional curvature $K(x,y)$, which is the product of the two principal curvatures at $(x,y)$, is the ratio of determinants of these two forms: $K=\det L/\det g$.[3,4] Gauss was able to determine one of the invariants of $L$, its determinant, as a function of the metric tensor $g$ and its first and second partial derivatives. This showed that a property of the surface which appeared to depend on embedding was, in fact, an intrinsic property of the surface. The importance which Gauss attached to this result is reflected by the name he gave to it: *theorema egregium.* The inverse problem was resolved by Bonnet, who proved that if $g_{\alpha\beta}(x,y)$ is a real symmetric positive-definite tensor and $L_{\alpha\beta}(x,y)$ is a real symmetric tensor, with $g$ and $L$ obeying the Gauss-Codazzi equations, then there exists a surface $z=z(x,y)$ in $\mathbb{R}^3$ with $g$ and $L$ as its first and second fundamental forms, and this surface is unique up to rigid motions. This theorem is called the fundamental theorem of surface theory.[3,4]

The second approach to the study of surfaces was proposed by Riemann.[3,4] He dispensed completely with embeddings, studying only the intrinsic properties of surfaces. In this approach only the parameter space $[(x,y)$ of $\mathbb{R}^2]$ is used, and a metric tensor $g(x,y)$ is introduced on this parameter space, making it, in general, non-Euclidean. Riemann showed that the intrinsic curvature properties, in particular, the Gaussian sectional curvature of the Riemannian space $[(x,y),g(x,y)]$, could be determined from the (Riemann) curvature tensor $R_{\alpha\beta,\gamma\delta}$, which was constructed from $g$ and its first and second partial derivatives. Different choices of metric can give the domain $x^2+y^2<1$ in $\mathbb{R}^2$ the metric and curvature properties of a hemisphere, one sheet of a two-sheeted hyperboloid, a saddle, etc.[3–5] Metrics which exhibit these properties can be constructed starting from (6.2) of Ref. 6. The question of whether an arbitrary two-dimensional Riemannian manifold $[(x,y),g(x,y)]$ could be isometrically embedded in a three-dimensional Euclidean space is more difficult. Although a global embedding is not always possible, a result of Janet and Cartan showed that a local embedding was always possible.[3,7]

The space $\mathbb{R}^3$ of thermodynamic variables $(U,S,V)$ has, *a priori,* no natural notion of distance. However, an equilibrium surface $U=U(S,V)$ is everywhere convex.[1,2] Therefore, the matrix $U_{\alpha\beta}(S,V)$ of mixed second partial derivatives, or stability matrix, is positive (semi)definite. This matrix describes the curvature of the equilibrium surface, and is therefore the second fundamental form of the surface. Ruppeiner,[8] and also Salamon, Andresen, Gait, and Berry[9] have chosen to adopt $U_{\alpha\beta}(S,V)$ as the Riemann metric tensor on the parameter space $(S,V)$:

 

$g_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$. They have made the claim, but nowhere proved, that the Riemannian space so defined can be identified with the equilibrium surface. This is a nontrivial claim, since the equilibrium surface $U=U(S,V)$ is embedded in $\mathbb{R}^3$, but the Riemannian surface $[(S,V),U_{\alpha\beta}(S,V)]$ is not embedded at all. Nor have they discussed the curvature of the Riemannian space $[(S,V),U_{\alpha\beta}(S,V)]$. The calculation of the Gaussian sectional curvature $K(S,V)$ was carried out in Ref. 6. Two questions now arise:

(1) Can the Riemannian surface $[(S,V),U_{\alpha\beta}(S,V)]$ be embedded in a three-dimensional space $\mathbb{R}^3$?

(2) If so, can the embedded surface $z=z(S,V)$ be identified with the original equilibrium surface $U=U(S,V)$?

In answer to (1), a local embedding is always possible (result of Janet-Cartan).[3] If we assume the surface is orientable, a global embedding is also possible. To construct these surfaces, we observe that we have a well-defined first fundamental form $g_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$. Although there is no second fundamental form, there is information about one of the curvature invariants. We can introduce a family of real symmetric tensors $L_{\alpha\beta}(S,V)$ subject to the condition $\det L = K \det U_{\alpha\beta}$. Then, by the fundamental theorem of surface theory,[3,4] to each pair of fundamental forms $g_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$ and $L_{\alpha\beta}(S,V)$ there corresponds a unique (up to rigid displacements) embedded surface: $z=z(S,V)$. We now turn to question (2): Can any of these surfaces correspond to the original equilibrium surface? To resolve this question we look at the signature (number of positive eigenvalues minus number of negative eigenvalues) of the second fundamental form. For the equilibrium surface $U=U(S,V)$ both principal curvatures are positive, so the signature is $+2$. For the embedded Riemannian surfaces the principal curvatures are of the same sign at $(S,V)$ if $K(S,V)>0$ (signature is $+2$ or $-2$), but must be of opposite signs if $K(S,V)<0$ (signature is 0). Since the signature of the curvature of a surface at a point is an invariant,[5,10,11] the embedded surface $z=z(S,V)$ constructed from the fundamental theorem of surface theory cannot be identified with the equilibrium surface $U=U(S,V)$ unless they have identical signatures everywhere. To put it another way, if the curvature signature of $z=z(S,V)$ is not $+2$ everywhere, this surface is not everywhere convex, and therefore cannot be an equilibrium surface, since lack of convexity violates the second law of thermodynamics.[1,2] A necessary but not sufficient condition that $z=z(S,V)$ be identifiable with $U=U(S,V)$ is that $K(S,V)$, computed from $g_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$, be positive. These conditions are presented explicitly in Ref. 6, Eq. (5.3).

An alternative approach to the questions of length, curvature, and embedding was also proposed in Ref. 6, Sec. VI. In this approach the stability matrix $U_{\alpha\beta}(S,V)$ is identified with the second fundamental form $L_{\alpha\beta}(S,V)$ of the equilibrium surface $U=U(S,V)$. To determine the first fundamental form, we first introduce a notion of distance in $\mathbb{R}^3$, the space of thermodynamic variables [Ref. 6, Eq. (6)]. The metric on the surface $U=U(S,V)$ is then induced from this metric on $\mathbb{R}^3$, giving a first fundamental form $g'_{\alpha\beta}(S,V)$ [Ref. 6, Eq. (6.2)]. With this metric, the space $[(S,V),g'(S,V)]$ is a Riemannian space. The second fundamental form $L_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$ cannot be computed from $g'_{\alpha\beta}(S,V)$ but the Gaussian sectional curvature $K(S,V)$ can be. In Ref. 6, Eq. (6.5), we show that the scalar $K(S,V)$ so computed is equal to one of the invariants of $L_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$. This compatibility ensures that the surface embedded in $\mathbb{R}^3$, which is constructed from the Riemannian space $[(S,V),g'(S,V)]$ by the fundamental theorem of surface theory, can always be identified with the original equilibrium surface.

The dialogue contained in this and the preceding two papers[12,13] raises the following possibilities:

(1) The relation between the Riemann metric tensor $g_{\alpha\beta}(S,V)$ and the Gaussian curvature scalar $K(S,V)$ should be ignored. This amounts to rejecting Gauss's *theorema egregium.*

(2) First and second fundamental forms $g_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$ and $L_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$ can independently be introduced. This ignores the Gauss-Codazzi compatibility conditions relating the two fundamental forms.

(3) An arbitrary positive-definite metric [e.g., $g_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$] can be introduced on the thermodynamic variables $(S,V)$. The resulting Gaussian sectional curvature may indeed be negative. This appears to be the operating assumption of the two previous papers.[12,13] This approach ignores the uniqueness statement of the fundamental theorem of surface theory. That is, $z=z(S,V)$ constructed from $[(S,V),U_{\alpha\beta}(S,V)]$ by the fundamental theorem of surface theory cannot be identified with the original equilibrium surface $U=U(S,V)$ unless the former has positive Gaussian sectional curvature everywhere (a necessary but not sufficient condition).

(4) The Gaussian sectional curvature $K(S,V)$ constructed from the Riemannian metric tensor $g_{\alpha\beta}(S,V)=U_{\alpha\beta}(S,V)$ must be non-negative. This assumption leads to a "new class of thermodynamic inequalities" involving second and third partial derivatives of the thermodynamic potential $U(S,V)$ [Ref. 6, Eq. (5.3)].

(5) The matrix $U_{\alpha\beta}(S,V)$ should be adopted for what it is: a description of the curvature of the equilibrium surface. A reasonable notion of distance in the space $\mathbb{R}^3=(U,S,V)$ of thermodynamic variables then leads to an induced Riemannian metric which is fully compatible with the curvature properties of the equilibrium surface. This is the point of view presented in Ref. 6 (Sec. VI).

Each of the first three assumptions described in the preceding paragraph violates one or more of the fundamental results of classical differential geometry: Gauss's *theorema egregium*, the Gauss-Codazzi compatibility equations, or Bonnet's fundamental theorem of surface theory. These three choices are unacceptable, as they require abandoning the rigidity of classical differential geometry. The fourth assumption leads to a set of "new thermodynamic inequalities," which are not only unrecognized in thermodynamics, but which are also not satisfied by a standard thermodynamic model.[14] This leaves only the fifth approach, which is fully internally self-consistent, obeys the theorems of classical differential geometry, and which predicts no new thermodynamic inequalities.

In the case of $n>2$ independent extensive variables the differences between our two approaches become even more pronounced. In the approach which I have previously described,[6] the equilibrium surface is considered as embedded in $\mathbb{R}^{n+1}$. A metric is placed on $\mathbb{R}^{n+1}$ and a Riemannian metric is induced on the surface. Typical texts[3] show that the $n$-dimensional Riemannian space so constructed can be embedded in $\mathbb{R}^{n+1}$ and identified with the initial surface. In the approach proposed by others,[8,9,12,13] the Riemannian metric on the $n$-independent variables is not induced but imposed. The nontrivial theorems of Janet and Cartan[3,7] only guarantee that this Riemannian space can be locally embedded in $\mathbb{R}^t$, $t \geqslant n(n+1)/2$. These authors[8,9,12,13] claim that their surface can be embedded in $\mathbb{R}^{n+1}$. No proof of this is offered; indeed, not even a hint is given that this generally cannot be done.[3,7] Thus, previous authors fail to substantiate their claims in two ways: (1) that their $n$-dimensional Riemannian surface can exist in $\mathbb{R}^{n+1}$, and (2) that its curvature properties conform to those of the equilibrium surface.

Many claims have been made that the Riemannian surface $[(S,V),U_{\alpha\beta}(S,V)]$ can be identified with the equation of state surface $U=U(S,V)$ in $\mathbb{R}^3$, but no proofs of this equivalence have been offered.[8,9,12,13] It is not sufficient to claim this equivalence; a proof must be provided, following the standard procedures of differential geometry. The message of a preceding[6] and of the current work is that such a proof is not possible; that the two surfaces cannot in fact be identified. Any choice of Riemannian metric tensor to measure distances in the equilibrium surface must lead, through the Riemannian curvature tensor, to a Gaussian sectional curvature which is everywhere positive (semi)definite if that choice is not to violate the second law of thermodynamics. Both Ruppeiner and Horn fail to recognize this in their Comments.

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## APPENDIX

We here briefly discuss two other points raised by Horn. Since a potential (constrained energy) rather than the internal energy was used in Ref. 6, all first partial derivatives vanish at the equilibrium. Horn's Eq. (2.6) therefore involves only second partial derivatives when evaluated at the equilibrium. Horn's Eq. (3.11) is not dimensionally correct. When this equation is made dimensionally correct by the introduction of suitable scale factors [Ref. 6, (6.2)], the "error" he finds in Ref. 6 (6.5) disappears.


[1]O. Penrose, *Foundations of Statistical Mechanics* (Pergamon, New York, 1970).

[2]H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, New York, 1971).

[3]D. Laugwitz, *Differential and Riemannian Geometry* (Academic, New York, 1965).

[4]D. J. Struik, *Differential Geometry* (Addison-Wesley, Reading, MA, 1950).

[5]R. Gilmore, *Lie Groups, Lie Algebras and Some of Their Applications* (Wiley, New York, 1974); S. Helgason, *Differential Geometry and Symmetric Spaces* (Academic, New York, 1962).

[6]R. Gilmore, Phys. Rev. A **30**, 1994 (1984).

[7]This theorem states that every $n$-dimensional Riemannian manifold can be locally embedded in a Euclidean $t$-dimensional space if $t \geqslant n(n+1)/2$.

[8]G. Ruppeiner, Phys. Rev. A **29**, 1608 (1979).

[9]P. Salamon, B. Andresen, P. D. Gait, and R. S. Berry, J. Chem. Phys. **73**, 1001 (1983).

[10]M. Morse, Trans. Am. Math. Soc. **33**, 72 (1931).

[11]T. Poston and I. N. Stewart, *Catastrophe Theory and its Applications* (Pitman, London, 1978); R. Gilmore, *Catastrophe Theory for Scientists and Engineers* (Wiley, New York, 1981).

[12]G. Ruppeiner, Phys. Rev. A **32**, 3141 (1985) (this issue).

[13]K. Horn, Phys. Rev. A **32**, 3142 (1985) (preceding Comment).

[14]R. Gilmore and J. Xu (unpublished).