Inducing Weinhold's metric from Euclidean and Riemannian metrics

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We show that Weinhold's metric cannot be induced on the equation-of-state surface from a Euclidean metric in the ambient space of all extensive state variables, whereas it can be induced if the ambient space is assumed to have only a Riemannian metric. This metric, however, is not unique.

I. INTRODUCTION

In the preceding paper[1] the relationship between the thermodynamic geometry of Gibbs[2,3] and Gilmore,[4,5] on the one hand, and that obtained by using Weinhold's metric,[6] on the other,[7–9] has been clarified. We refer to that paper for definitions, notation, and general references. Here we want only to emphasize that Weinhold's metric is intrinsically defined on the n-dimensional manifold of equilibrium states whereas the geometrical structure introduced by Gibbs is extrinsically derived from this manifold, being imbedded as a convex surface in an $(n+1)$-dimensional linear space. Gilmore infused metric geometrical ideas into the Gibbsian framework by introducing Euclidean metrics which potential surfaces should inherit from the ambient space.

This procedure raises two questions: Can Weinhold's metric be induced on the equilibrium surface from a Euclidean metric on the ambient space, and, if not, will a Riemannian metric on the ambient space satisfy the requirement? The importance of trying to use a Euclidean metric derives from the fact that only such metrics will be compatible with the linear structure of Gibbs. Theorems 1 and 2 below show that Weinhold's metric cannot be induced from a Euclidean ambient metric although it can be induced in a nonunique fashion from a Riemannian ambient metric. These results have strong implications for any attempt to extend geometric concepts of thermodynamics based on Weinhold's geometry to nonequilibrium situations which are represented by points in $\mathbb{R}^{n+1}$ off the equilibrium surface.

II. INDUCING FROM A EUCLIDEAN METRIC

A Euclidean metric in $\mathbb{R}^{n+1} = \{(x^0,x^1,\dots,x^n) \mid x^0,x^1,\dots,x^n \text{ are real numbers}\}$ cannot induce Weinhold's metric D^2S on single-phase regions of the equation-of-state surface. This is the content of the following theorem.

Theorem 1. Let

$$\sum_{i,j=1}^{n} g_{ij}\,dx^i dx^j = \sum_{i=1}^{n} (dx^i)^2 + \sum_{i,j=1}^{n} (\partial S/\partial x^i)(\partial S/\partial x^j) dx^i dx^j \quad (1)$$

be the metric induced on the surface $(x^0=S, x^1,\dots,x^n)$ by a Euclidean metric in $\mathbb{R}^{n+1}$ and let

$$D^2S = \sum_{i,j=1}^{n} (\partial^2 S/\partial x^i \partial x^j) dx^i dx^j \quad (2)$$

be Weinhold's metric. Then for all functions S, we have that $g \neq D^2S$ on any piece—more precisely, open subset—of the equation-of-state surface.

Proof. We assume that $g = D^2S$ and work toward a contradiction. The assumption of equivalence requires that

$$\delta_{ij} + (\partial S/\partial x^i)(\partial S/\partial x^j) = (\partial^2 S/\partial x^i \partial x^j) \ . \quad (3)$$

In the present proof we assume that $(\partial S/\partial x^i) \neq 0$ for all i. In the Appendix we present a proof of the theorem for the case when $(\partial S/\partial x^i)$ is allowed to equal zero. We first consider this equation for $i \neq j$ and rearrange to

$$\frac{\partial}{\partial x^j}\left[\ln\left|\frac{\partial S}{\partial x^i}\right| - S\right] = 0 \ \text{ for all } j \neq i \ , \quad (4)$$

which means that

$$\ln(\partial S/\partial x^i) - S = \alpha_i \ , \quad (5)$$

where α_i is a function of x^i alone. This in turn implies that

$$e^{-S} = \sum_{i=1}^{n} \beta_i \ , \quad (6)$$

where each β_i is a function of x^i alone. We next consider $i=j$ in Eq. (3) which then takes the form

$$1+(\partial S/\partial x^i)^2=(\partial^2 S/\partial x^{i2}) . \tag{7}$$

From Eq. (6) we see that

$$\begin{aligned}(\partial S/\partial x^i)&=-e^S(\partial\beta_i/\partial x^i) ,\\ (\partial^2 S/\partial x^{i2})&=e^{2S}(\partial\beta_i/\partial x^i)^2-e^S(\partial^2\beta_i/\partial x^{i2}) ,\end{aligned} \tag{8}$$

and using this in Eq. (7) gives

$$\partial^2\beta_i/\partial x^{i2}=-e^{-S} . \tag{9}$$

Since this equation must hold for all i and since each $(\partial^2\beta_i/\partial x^{i2})$ can only depend on x^i, we conclude that S is constant. But in this case $D^2S=0$, while $g=\sum dx^{i2}$. Thus there is no function S for which $g=D^2S$. ■

The above theorem showed that the Weinhold geometry on any piece of the surface of equilibrium states will never equal a Euclidean geometry induced from the ambient space.

III. INDUCING FROM A RIEMANNIAN METRIC

The next theorem shows that it is possible, however, to define a *nonconstant* (non-Euclidean) 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 $\mathbb{R}^{n+1}$ equipped with this metric is non-Euclidean.

Theorem 2. Let

$$f=\sum_{i,j=1}^{n} f_{ij}\,dx^i dx^j \tag{10}$$

be a metric on $\mathbb{R}^n$. Then there exists a metric

$$h=\sum_{i,j=1}^{n+1} h_{ij}\,dy^i dy^j \tag{11}$$

on $\mathbb{R}^{n+1}$ such that $f=\Phi^*h$, where Φ is the map from $\mathbb{R}^n$ to $\mathbb{R}^{n+1}$ defined by $\Phi(X)=(X,S(X))$ and Φ^* is the associated map[10] sending forms on $\mathbb{R}^{n+1}$ to forms on $\mathbb{R}^n$.

Proof. We prove the existence of h by providing a recipe for its construction. First we choose a basis v_i of tangent vectors in $\mathbb{R}^{n+1}$ along the surface $(X,S(X))$. We choose $v_i=\Phi_*(\partial/\partial x^i)=\partial/\partial y^i$, $i=1,\ldots,n$, and $v_{n+1}=\partial/\partial y^{n+1}=\partial/\partial S$. While there are many ways to extend the basis to all of $\mathbb{R}^{n+1}$, we use the translations $\rho_t(y^1,\ldots,y^n,y^{n+1})=(y^1,\ldots,y^n,y^{n+1}+t)$. Then we let

$$v_i(y^1,\ldots,y^{n+1})=(\rho_{y^{n+1}-S(y^1,\ldots,y^n)})_* \times v_i(y^1,\ldots,y^n,S(y^1,\ldots,y^n)) . \tag{12}$$

Note that this gives global definitions for all $n+1$ independent v_i. Define $h(v_i,v_j)=f(\partial/\partial x^i,\partial/\partial x^j)$ for $i,j<n$ and $h(v_i,v_{n+1})=\delta_{i,n+1}$. Now note that

$$\begin{aligned}(\Phi^*h)(\partial/\partial x^i,\partial/\partial x^j)&=h(\Phi^*\partial/\partial x^i,\Phi^*\partial/\partial x^j)\\ &=f(\partial/\partial x^i,\partial/\partial x^j)\end{aligned} \tag{13}$$

so $\Phi^*h=f$. ■

IV. DISCUSSION

Extrinsic metrics h could serve to give extensions of Weinhold's metric off the equilibrium surface, thereby including nonequilibrium states. The statistical-mechanical metric[11] already does that, i.e., measures distance traversed in a process passing through nonequilibrium states. The question of choosing a particular metric in $\mathbb{R}^{n+1}$ which agrees with the second derivative metric on the surface then becomes a search for something universal about the geometry as equilibrium is approached. For a preliminary result in this direction, the reader is referred to Ref. 12 where it is shown that the addition of a constraint always shifts the equilibrium in an orthogonal direction.

The theorems show that if we try to extend Weinhold's metric to the space of $(x^0,x^1,\ldots,x^n)$ surrounding the equation-of-state surface, then this extension geometry is non-Euclidean. In particular, this means that one is forced to relinquish the natural linear structure of this ambient space. This structure provides the meaning of straight-line segment in terms of which the Gibbsian concept of convexity is defined.[2] The corresponding physical interpretation follows from the fact that the juxtaposition of two thermodynamic systems has a state which, in the coordinates of the extensive variables, is the sum of the two separated states. Accordingly, it is unfortunate that such linear structure does not have a clearer place in the representation of the equilibrium states as a semi-Riemannian manifold.

In fact, such linearity does play a role in the semi-Riemannian representation. It is reflected in the fact that one can use the second derivative of S in the usual extensive coordinates or in any linear combinations of these coordinates (which will, of course, again be extensive). In any of these coordinates, one will end up with the same metric tensor.[6] This is, of course, no longer the case if one allows nonlinear transformations for which the second derivative matrix and the metric matrix transform differently.

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APPENDIX

In this appendix we show that theorem 1 remains valid without the assumption that $\partial S/\partial x_i\neq 0$. Let

$U=\{X\in\mathbb{R}^n \mid \partial S/\partial x_i(X)\neq 0$ for $i=1,\ldots,n\}$. If U is not empty, then the calculations in the proof of theorem 1 presented in the text suffice to reach a contradiction. Thus U is empty and the manifold of concern is a union of the n sets $A_i=\{X\in\mathbb{R}^n \mid \partial S/\partial x_i(X)=0\}$. At least one of these sets must therefore have a nonempty interior by the Baire category theorem. If we restrict our attention to a point in the interior of A_i, we find $\partial^2 S/\partial x_i \partial x_j=0$ for all j. In particular, this is true for $i=j$ and Eq. (11) gives us $1+(\partial S/\partial x_i)^2=0$. This provides the desired contradiction.

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