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Geometry of the ideal gas

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The manifold of equilibrium states for a fixed number of moles of ideal gas, when provided with a Riemannian metric based on the second derivatives of internal energy (studied by F. Weinhold), is found to have zero intrinsic curvature, in fact to be isometric to the Riemann surface of the natural logarithmic function. This and three other closely related flat spaces associated with an ideal gas are studied by means of explicit isometries.

I. INTRODUCTION

Recently a number of efforts[1–8] have been directed toward clarifying the physical content of a geometric notion which arises naturally from the mathematical formalism of thermodynamic theory. To provide the most natural setting for this notion, we regard the collection of equilibrium states of a thermodynamic system as a differentiable manifold: the Gibbs surface. The notion of interest then takes the form of a Riemannian metric or measure of length on this manifold.[9]

There are actually two different though closely related metric structures associated with two ways of parametrizing the collection of thermodynamic states. In one case we use the extensive variables $U,V,N_1,N_2,\ldots$ with an equation of state $S=S(U,V,\ldots)$ for the entropy of the system. Here U is the internal energy, V is the volume, and N_i are the mole numbers of the various chemical species. We will call this the entropy view. On the other hand, we may formulate an energy view by regarding the entropy S as one of the parameters and $U=U(S,V,\ldots)$ as the dependent variable. In the former case the second derivative form, $-D^2S$, defines the metric, in the latter case the metric is D^2U.

It is important to realize that these two structures are not equivalent. We have shown elsewhere[1] that they are conformally related, i.e.,

$$D^2U=-T\,D^2S\ , \tag{1.1}$$

where T is the temperature. This relation is intimately connected with the following relation between the availability dissipated, ΔA_u, and the entropy produced, ΔS_u, during a process where a system spontaneously equilibrates to a reservoir at temperature T:

$$\Delta A_u=-T\,\Delta S_u\ . \tag{1.2}$$

The connection between (1.1) and (1.2) suggests that the geometric notions may well have something to tell us about the irreversibilities of processes, and it is by way of (1.2) that the subtly different physical interpretations of the two structures may be seen.

Indeed, Salamon and Berry have shown[2] that the availability dissipated in a thermodynamic process is at least the square of the thermodynamic length of the process (defined in terms of the metric D^2U) times a mean relaxation time divided by the total time of the process [see the inequalities (3.15)]. The analogous statement holds for entropy produced in a process if the length is measured by D^2S[1].

The second-order Taylor coefficients, D^2S, have long been important in what is known as the Gaussian approximation to conventional thermodynamic fluctuation theory. Ruppeiner[3,4] has chosen to take the metric structure defined by D^2S as fundamental to a new thermodynamic fluctuation theory. He has shown that the curvature defined by D^2S is proportional to the correlation length. He has also used D^2S to incorporate local correlations into thermodynamic fluctuation theory, thereby extending the realm of such theory to volumes smaller than the correlation volume.

In this paper we examine the geometries of the ideal gas as defined by D^2S and D^2U. The first finding is that all four of the geometries naturally associated with the ideal gas (see Sec. III) are locally flat, i.e, they have zero curvature. In view of Ruppeiner's theorem connecting the curvature defined by D^2S with the correlation length, this finding is not surprising. The local flatness, however, enables us to find rectilinear coordinates for these geometries. In these coordinates, straight lines are the shortest paths between states and distances may be computed in terms of the usual Euclidean distance formula. In Sec. III we will make some qualifications of these statements due to the global structure of these geometries [see in particular Eqs. (3.14)].

II. SUBSPACES WITH POSITIVE DEFINITE METRIC

We start with some preliminary remarks to indicate why the forms D^2U and $-D^2S$, which we propose to use as Riemannian metrics, should be restricted to systems of fixed size.

Let us limit our remarks to the energy view, where the fundamental relation is given by $U=U(X_1,X_2,\dots,X_m)$. The hypersurface of states in $\mathbf{R}^{m+1}$ of $(m+1)$-tuples $(U,X_1,\dots X_m)$ can be seen to be a cone by virtue of the homogeneous first-order property of $U(X_1,\dots,X_m)$. That is, if $(U,X_1,\dots,X_m)$ lies on the hypersurface, so does $(aU,aX_1,\dots,aX_m)$ for any positive a. Now, each point on a cone is parabolic, and, thus the second fundamental form, which is D^2U in this case, is degenerate at each point. It has a null direction which corresponds to scaling the system.[7]

An instructive but less direct way to see this is by way of the Gibbs-Duhem relation

$$0=\sum_i X_i\,dY_i\ , \tag{2.1}$$

where $Y_i=\partial U/\partial X_i$. Write $dY_i=\sum_j[D^2U]_{ij}dX_j$ and substitute above to get

$$0=\sum_i\sum_j X_i[D^2U]_{ij}dX_j\ .$$

Now, since the dX_i's may be chosen at will, we must have

$$\sum_i X_i[D^2U]_{ij}=0\ \text{ for all } j\ . \tag{2.2}$$

This is a statement that the rows of the matrix D^2U are linearly dependent.

As can be seen from (2.2), the quadratic form is degenerate along a null process, i.e., a process along which all of the extensive variables change by the same factor. Such a null process has a geometrical interpretation as a generator of the cone of states. This degeneracy is generally avoided by restricting consideration to a cross section of the cone obtained by fixing the value of one of the extensive variables. For the ideal gas we will study two cases: fixed volume V, and fixed mole number N. Once we restrict our attention to such lower dimensional slices of the equilibrium manifold, the degeneracy in the metric disappears, i.e., we have eliminated the degenerate direction.

The positivity of the forms D^2U and $-D^2S$ in such a scaled system is well known[6] and embodies the principles of minimum energy and maximum entropy.

III. THE IDEAL GAS

In this section we will enumerate four distinct families of Riemannian manifolds whose underlying spaces are cross sections of the cone of states of the ideal gas. We will show that *each of these manifolds is isometric to a well-known flat Riemannian manifold.* In each case we will exhibit the isometries explicitly. This will provide an essentially unique global coordinate system in which the geometry of the manifold is laid bare and at the same time will provide a direct verification of flatness.

The cone of states, C, of the ideal gas is the collection of all 4-tuples $(x_1,x_2,x_3,x_4)=(U,S,V,N)$ in $\mathbf{R}^4_+$ satisfying some fundamental equation for the ideal gas, either $U=U(S,V,N)$ or $S=S(U,V,N)$. We will take the following two families of cross sections of this cone as underlying spaces for the manifolds to be studied. They are characterized, respectively, by constant mole number and constant volume.

(i) $\mathscr{N}=\{(x_1,x_2,x_3,x_4)\in C\mid x_4=N\}$.
(ii) $\mathscr{V}=\{(x_1,x_2,x_3,x_4)\in C\mid x_3=V\}$.

On each of these manifolds we will place two different metric (Riemannian) structures, $-D^2S$ and D^2U, to generate four families of Riemannian manifolds S_N, U_N, S_V, and U_V, where the subscript N or V denotes the variable held constant on the underlying space and the S or U signifies the metric structure imposed.

In each case, the structure will be introduced by way of a particular coordinate system. The cone of states inherits two natural coordinate systems from the ambient space in which it is imbedded. In the entropy view the coordinates are (U,V,N) and in the energy view they are (S,V,N). For the various cross sections the natural coordinates are as follows:

$$S_N\colon\ (U,V)\ , \tag{3.1a}$$

$$S_V\colon\ (U,N)\ , \tag{3.1b}$$

$$U_N\colon\ (S,V)\ , \tag{3.1c}$$

$$U_V\colon\ (S,N)\ . \tag{3.1d}$$

In the following, frequent use will be made of the first law of thermodynamics,

$$dU=T\,dS-P\,dV\ , \tag{3.2a}$$

and of the equations of state

$$\begin{gathered} PV=RNT,\quad U=C_VNT\ ,\\ R=C_P-C_V,\quad TS+\mu N=C_PNT\ . \end{gathered} \tag{3.2b}$$

In each case, the Riemannian structure is defined by identifying the matrix representation of the metric bilinear form in the coordinate systems (3.1) with the matrix of second derivatives of the entropy S, or of the energy U, with respect to these coordinates.

In particular, the metric form for S_N and S_V, respectively, in coordinates (3.1) can be readily calculated as second derivatives of S,

$$\begin{aligned} -D^2S(U,V)&=-\begin{bmatrix} \dfrac{\partial^2S}{\partial U^2} & \dfrac{\partial^2S}{\partial U\partial V}\\[2ex] \dfrac{\partial^2S}{\partial V\partial U} & \dfrac{\partial^2S}{\partial V^2}\end{bmatrix}\\ &=\begin{bmatrix} \dfrac{C_VN}{U^2} & 0\\[2ex] 0 & \dfrac{RN}{V^2}\end{bmatrix}, \end{aligned} \tag{3.3}$$

$$\begin{aligned} -D^2S(U,N)&=-\begin{bmatrix} \dfrac{\partial^2S}{\partial U^2} & \dfrac{\partial^2S}{\partial U\partial N}\\[2ex] \dfrac{\partial^2S}{\partial N\partial U} & \dfrac{\partial^2S}{\partial N^2}\end{bmatrix}\\ &=\begin{bmatrix} \dfrac{C_VN}{U^2} & -\dfrac{C_V}{U}\\[2ex] -\dfrac{C_V}{U} & \dfrac{C_P}{N}\end{bmatrix}, \end{aligned} \tag{3.4}$$

where the notation on the left in (3.3) and (3.4) is chosen to express the coordinate system in which the matrix represents the form D^2S.

Now, by immediately making use of the relation (1.1), we may also write for U_N and U_V, respectively,

$$D^2U(U,V)=\begin{bmatrix} \frac{1}{U} & 0 \\ 0 & \frac{RU}{C_V V^2} \end{bmatrix}, \tag{3.5}$$

$$D^2U(U,N)=\begin{bmatrix} \frac{1}{U} & -\frac{1}{N} \\ -\frac{1}{N} & \frac{C_P U}{C_V N^2} \end{bmatrix}. \tag{3.6}$$

It is important to note that the entries in the matrices in (3.5) and (3.6) are not second derivatives of U, i.e., that the coordinate systems are not those enumerated in (3.1). Indeed, other coordinate systems may be far more suitable to the intrinsic geometries we wish to study, so it is important to recall how a coordinate change is effected.

The matrix representation of the metric, $\overline{M}$, in a coordinate system, $\overline{X}=(\overline{X}_1,\overline{X}_2)$, may be found from the representation, M, in coordinate system, $X=(X_1,X_2)$ by

$$\overline{M}=J^tMJ\ , \tag{3.7}$$

where J and J^t are the Jacobian matrix $\partial(X_1,X_2)/\partial(\overline{X}_1,\overline{X}_2)$ and its transpose.

As we will soon see, the diagonal forms (3.3) and (3.5) are particularly convenient, so we are motivated to search for coordinate changes in S_V and U_V which will diagonalize their forms. The appropriate coordinates for S_V are (T,N) and those for U_V are $(U,\overline{S})$, where $\overline{S}=S/N$, the molar entropy. The Jacobian matrices necessary to effect these changes in (3.4) and (3.6) by way of (3.7) are, for S_V and U_V, respectively,

$$\left[\frac{\partial(U,N)}{\partial(T,N)}\right]=\begin{bmatrix} C_VN & C_VT \\ 0 & 1 \end{bmatrix}, \tag{3.8a}$$

$$\left[\frac{\partial(U,N)}{\partial(U,\overline{S})}\right]=\begin{bmatrix} 1 & 0 \\ \frac{1}{C_PT} & -\frac{N}{C_p} \end{bmatrix}, \tag{3.8b}$$

and the results are, for S_V and U_V, respectively,

$$-D^2S(T,N)=\begin{bmatrix} \frac{C_VN}{T^2} & 0 \\ 0 & \frac{R}{N} \end{bmatrix}, \tag{3.9}$$

$$D^2U(U,\overline{S})=\begin{bmatrix} \frac{R}{C_PU} & 0 \\ 0 & \frac{U}{C_PC_V} \end{bmatrix}. \tag{3.10}$$

It is instructive to write (3.3), (3.5), (3.9), and (3.10) as equations for the classical line element ds^2 on the manifold (for S_N, U_N, S_V, and U_V, respectively)

$$ds^2=\frac{C_VN}{U^2}dU^2+\frac{RN}{V^2}dV^2\ , \tag{3.11a}$$

$$ds^2=\frac{1}{U}dU^2+\frac{RU}{C_VV^2}dV^2\ , \tag{3.11b}$$

$$ds^2=\frac{C_VN}{T^2}dT^2+\frac{R}{N}dN^2\ , \tag{3.11c}$$

$$ds^2=\frac{R}{C_PU}dU^2+\frac{U}{C_PC_V}d\overline{S}^{\,2}\ . \tag{3.11d}$$

The first takes the form

$$ds^2=dx^2+dy^2$$

under the variable change (for S_N)

$$x=\sqrt{C_VN}\ln U,\quad y=\sqrt{RN}\ln V\ , \tag{3.12a}$$

whereupon (3.12a) is seen to effect an isometry between S_N and the Euclidean plane.

The last three all take the form

$$ds^2=dr^2+r^2d\theta^2$$

under the variable changes below (for U_N, S_V, and U_V, respectively)

$$r=2\sqrt{U},\quad \theta=\tfrac{1}{2}\sqrt{R/C_V}\ln V\ , \tag{3.12b}$$

$$r=2\sqrt{RN},\quad \theta=\tfrac{1}{2}\sqrt{C_V/R}\ln T\ , \tag{3.12c}$$

$$r=2\sqrt{RU/C_P},\quad \theta=\tfrac{1}{2}\sqrt{1/RC_V}\,\overline{S}\ . \tag{3.12d}$$

Equations (3.12b) and (3.12c) are seen to effect local isometries of U_N and S_V into the plane and global isometries onto the Riemann surface of the natural logarithmic function (see Fig. 1). Because of the requirement $\overline{S}>0$ in (3.13d), U_V is isometric to a submanifold of this Riemann surface: its upper half corresponding to $\theta>0$.

Figure 1 suggests the topology of the spaces S_V and U_N by showing the portion corresponding to $-2\pi\leq\theta\leq2\pi$

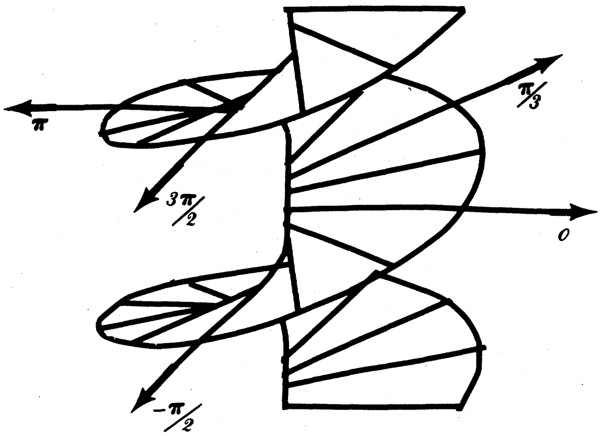

FIG. 1. The Riemann surface of the natural logarithmic function. The portion shown is for $-2\pi\leq\theta\leq2\pi$ and $0<r\leq1$. This surface is isometric to the spaces S_V and U_N. Its upper half ($\theta>0$) is isometric to the space U_V.

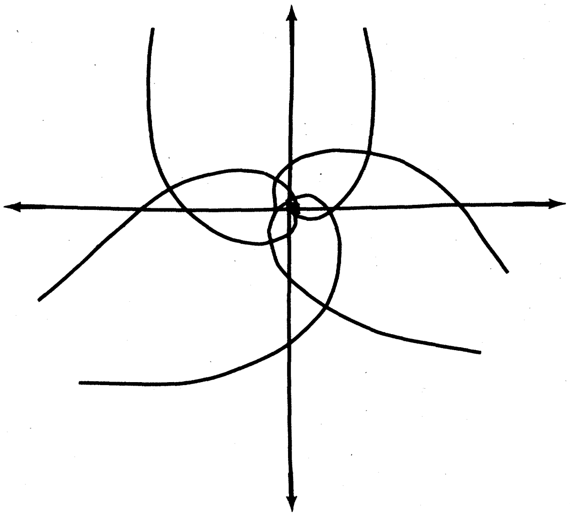

FIG. 2. Orthogonal families of equiangular spirals representing (p):$(\bar{S})$ in S_V, (S):(p) in U_N, and (T):(N) in U_V. The orthogonal families (μ):(S) in U_V are also similar.

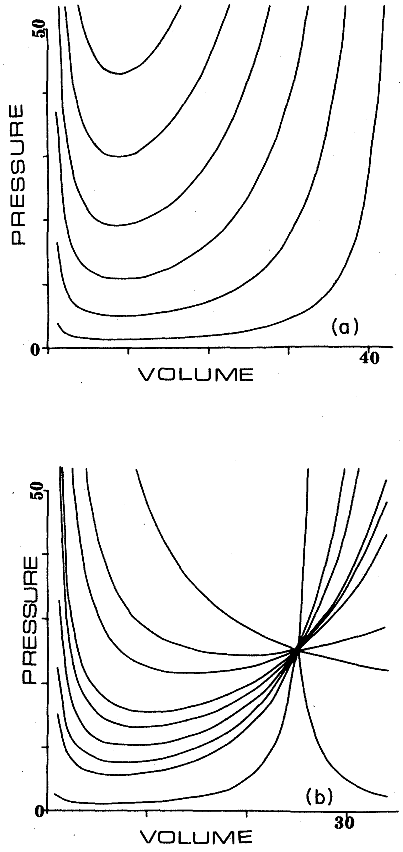

FIG. 3. pV plots of a family of parallel lines (a) and a family of lines through a point (b) for the geometry U_N.

and $0 < r \leq 1$. Selected values of θ are shown as extended rays. In U_V the lower half, $\theta \leq 0$, is truncated. The "polar axis" in the figure is identified to a single boundary point outside of the manifold. This point seems to play the role of absolute zero in the space U_N.

Certain familiar processes have simple forms and relationships in these geometries. Let (q) represent the family of processes in which the quantity q is held constant. For example, (S) and (p) are (reversible) adiabats and isobars, respectively. The following relation first proved by Weinhold[6] shows how to generate many pairs of orthogonal families.

Let X_1, X_2 be the natural (extensive) coordinates on the manifold as given by (3.1) and let Y_1, Y_2 be the corresponding intensive variables, i.e., $\partial U/\partial X_i$ or $\partial S/\partial X_i$, $i = 1,2$. Then it is true that (X_1):(Y_2) and (X_2):(Y_1) are pairs of orthogonal families.[10]

For our geometries, these orthogonal pairs may be tabulated as follows. Here μ is the chemical potential and $\rho = N/V$ is the molar density.

S_N: (V):(T) and (U):(ρ) .

S_V: (T):(N) and (p):$(\bar{S})$.

U_N: (V):(T) and (S):(p) .

U_V: (T):(N) and (μ):(S) .

S_N is particularly simple in that (V) and (ρ) are the horizontal lines and (T) and (U) are the vertical lines.

S_V and U_N are similar. In both geometries the first pair are, respectively, the radial lines and the circular arcs centered at the pole. The second pair are equiangular spirals of the form

$$r = Ke^{a\theta} , \tag{3.13}$$

where $a = -\sqrt{R/C_V}$ for the first family and $a = \sqrt{C_V/R}$ for the second. Figure 2 shows curves from this pair of orthogonal families for a monatomic gas.

In U_V, the first pair are also spirals of the above form, where, however, $a = -\sqrt{C_V/R}$ for the first family and $a = \sqrt{R/C_V}$ for the second. The behavior of the second pair is more complicated and need not concern us.

For the U_N geometry, pV plots are shown for a family of parallel lines [Fig. 3(a)] and a family of straight lines through a given point [Fig. 3(b)].

A consequence of the relations between the geometries U_N, S_V, U_V and the Riemann surface of the natural log function concerns the length of a shortest path connecting two states. If the angular separation between the two states is $\theta_{12} < \pi$, then the shortest path is a straight line. If the angular separation is $\theta_{12} > \pi$ then the shortest curve proceeds via the singularity at $r = 0$. As a consequence of this we get the distance formula

$$d((X_1,Y_1),(X_2,Y_2)) = \begin{cases} [(X_1 - X_2)^2 + (Y_1 - Y_2)^2]^{1/2}, & \theta_{12} < \pi \\ (X_1^2 + Y_1^2)^{1/2} + (X_2^2 + Y_2^2)^{1/2}, & \theta_{12} \geq \pi . \end{cases} \tag{3.14}$$

One application of this geometry is in connection with the bounds[1,2] on the entropy produced ΔS_u and the availability dissipated ΔA_u in a process which proceeds by means of states of local thermodynamic equilibrium from one equilibrium state to another. These bounds are given by

$$\Delta S_u \geq d_s^2 \epsilon/\tau \tag{3.15a}$$

and

$$\Delta A_u \geq d_u^2 \epsilon/\tau\ , \tag{3.15b}$$

where d_s and d_u are the distances measured by $D^2 S$ and $D^2 U$, respectively, ϵ is a mean relaxation time, and τ is the total time of the process. The values of d_s and d_u are thus useful in bounding the irreversibility of a process.

The short history of applications of the metric structure involves repeated instances of noting a similarity in some formula. Ruppeiner began by noting a similarity between correlation length and curvature[3] several years prior to proving that they are proportional. Similarly, the relationship between dissipation for the metric structure was first hinted at by the recognition of the formula for the length of adiabats of the ideal gas. This formula gives the change in flow velocity of the gas in the rarefaction fan of a shock wave. It seems likely therefore that the geometry described above will lead to further discoveries concerning thermodynamic length and its applications.

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[1] P. Salamon, J. Nulton, and E. Ihrig, J. Chem. Phys. **80**, 436 (1984). The principal theorem of this paper was first found by R. Gilmore (unpublished).

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

[3] G. Ruppeiner, Phys. Rev. A **27**, 1116 (1983); **24**, 488 (1981); **20**, 1608 (1979).

[4] G. Ruppeiner, Phys. Rev. Lett. **50**, 287 (1983).

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

[6] F. Weinhold, J. Chem. Phys. **63**, 2479 (1975); **63**, 2484 (1975); **63**, 2488 (1975); **63**, 2496 (1975); Acc. Chem. Res. **9**, 236 (1976).

[7] F. Weinhold, J. Chem. Phys. **65**, 559 (1976).

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

[9] All results in this paper are predicated on the assumption that the matrix of second-order Taylor coefficients can be used to define a physically significant metric structure on the set of equilibrium states of a thermodynamic system. This is true also of the papers in Refs. 1—7. A fundamentally different geometry results if, following Gilmore (Ref. 8), one lets the equilibrium surface $S = f(U, V, \ldots)$ inherit the metric induced from a Euclidean metric on the ambient R^{n+1}.

[10] This was first proved in a context equivalent to U_N, but is true in all the geometries. It is also independent of the equations of state of the system.