A group of coordinate transformations which preserve the metric of Weinhold

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Recently Weinhold described a natural metric on the state space of an equilibrium thermodynamic system. We describe the coordinate transformations which preserve both the first law of thermodynamics and this metric.

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I. INTRODUCTION

We consider an n degree of freedom thermodynamic system whose extensive variables are $x_1,\ldots,x_n$, and conjugate intensities are $\partial E/\partial x_i = y_i$, where E is the internal energy. Weinhold[1] pointed out that the second derivative matrix

$$\left[\frac{\partial^2 E}{\partial x_i\,\partial x_j}\right] = [\eta_{ij}] = \eta, \tag{1}$$

being symmetric and positive definite, may be used to define a metric structure on the set of equilibrium states of a thermodynamic system. Distances measured by η have been interpreted as changes of velocities characteristic of the type of path.[2,3] He examined the group of coordinate transformations in the state space of $X = (x_1,\ldots,x_n)$ which preserved η, and found that this group was isomorphic to Gl(n), the group of all invertible linear transformations. Hermann[4] pointed out that a fuller view of the mathematical structure of equilibrium thermodynamics may be found in *phase-energy space* $(X,Y,E) = (x_1,\ldots,x_n, y_1,\ldots,y_n, E)$. Below, we solve the problem of finding the group of coordinate transformations in phase-energy space which preserve η.

Following Hermann, we identify the state space of an n-degree of freedom thermodynamic system with a surface of maximal dimension in phase-energy space which is a solution of the Pfaffian equation

$$\omega = dE - \sum_{i=1}^{n} y_i\, dx_i = 0 \tag{2}$$

expressing the first law of thermodynamics, where ω is the differential form defined by (2). The general theory[3] states that this will be an n-dimensional surface, which may be coordinatized by $x_1,\ldots,x_n$. When E is restricted to such a surface, it becomes a function of $x_1,\ldots,x_n$ alone. The most natural condition is the invariance of the first law. We will call coordinates (U,V,P) admissible provided

$$dE - \sum_{i=1}^{n} y_i\, dx_i = 0 \quad \text{iff} \quad dP - \sum_{i=1}^{n} v_i\, du_i = 0. \tag{3}$$

This condition is equivalent to

$$dE - \sum_{i=1}^{n} y_i\, dx_i = \alpha\left(dP - \sum_{i=1}^{n} v_i\, du_i\right) \tag{4}$$

for some function α. An obvious stronger requirement is (4) with $\alpha = 1$. If this is satisfied, we say that the form of the first law is preserved. Such transformations are called contact transformations,[4] and they form an infinite-dimensional group.

We will also require the invariance of the Weinhold metric

$$\eta = \sum_{i=1}^{n} dy_i\, dx_i, \tag{5}$$

where we used the same symbol η for this differential 2-form, since when η is restricted to a maximal surface, its matrix relative to the coordinates $(x_1,\ldots,x_n)$ is given by (1). We can see this as follows. In such a maximal surface $dE = \Sigma_{i=1}^{n} \times(\partial E/\partial x_i)dx_i$. Since $\omega = 0$ on the surface we have $dE = \Sigma_{i=1}^{n} y_i\, dx_i$. Since dx_i are independent on a maximal surface $y_i = \partial E/\partial x_i$. Thus

$$\eta = \sum_{i=1}^{n} dy_i\, dx_i = \sum_{i=1}^{n}\left(\sum_{j=1}^{n}\frac{\partial^2 E}{\partial x_i\,\partial x_j}dx_j\right)dx_i, \tag{6}$$

which gives the result. There are two important things to note here. The first is that $\partial^2 E/\partial x_i\,\partial x_j$ is only defined on a maximal surface and not on phase-energy space (E and x_i are independent coordinates on phase-energy space and thus $\partial^2 E/\partial x_i\,\partial x_j = 0$ in this setting). Since there are many maximal surfaces going through one point, it is not even clear that the $\partial^2 E/\partial x_i\,\partial x_j$ defined using one surface will be consistent with the metric defined using another surface. However, all these metrics are consistent because they agree with η which is defined on all of phase-energy space. We assume that η in (5) is the fundamental object, but caution the reader that η is *not* the only metric whose restriction gives $\partial^2 E/\partial x_i\,\partial x_j$ on each maximal surface. A quadratic form η_1 will have this restriction on each maximal surface if and only if it is of the form

$$\eta_1 = \eta + \omega\theta, \tag{7}$$

where θ is an arbitrary 1-form. Thus there are $(2n+1)$ free functions in the general metric that extends $\partial^2 E/\partial x_i\,\partial x_j$ to phase-energy space. Among these metrics, the choice with $\theta = 0$ seems the most natural. The only thing that is clear about the problem with general θ is that its solution is way

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beyond the techniques presented in this paper. Note that since θ has been fixed, the requirement of the invariance of η is a stronger requirement than the invariance of $\partial^2 E/\partial x_i\, \partial x_j$ alone.

The invariance of η amounts to the condition

$$\sum_{i=1}^{n} dy_i\, dx_i = \sum_{i=1}^{n} dv_i\, du_i. \tag{8}$$

We find two types of transformations that leave ω and η invariant. The first consists of transformations that are analogous to translations. They are of the form

$$F(X,Y,E) = (X + \mathbf{b}, Y + \mathbf{d}, E + \mathbf{d}\cdot X + \mathbf{e}), \tag{9}$$

where $\mathbf{b}$, $\mathbf{d} \in R^n$ and $\mathbf{e} \in R$. These pseudotranslations do not commute like real Euclidean translations, but they do form a group isomorphic to the n-dimensional Heisenberg group (H_n), a group[6,7] which is very close in structure to R^n. The second type of transformations are analogous to rotations. They fix the origin and are linear. Their matrices are of the form

$$\begin{pmatrix} A & 0 & 0 \\ 0 & (A^t)^{-1} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{10}$$

where A is any invertible $n \times n$ matrix. Thus these transformations form a group that is isomorphic to $\mathrm{Gl}(n)$. Just as the Euclidean group is the semidirect product of the rotations with the translations, we find the group of all transformations that fix ω and η is isomorphic to a semidirect product of $\mathrm{Gl}(n)$ with H_n. Thus the structure of this group is similar to the structure of the transformation group on R^n that leaves the standard Euclidean metric invariant.

In Sec. III we described those transformations which multiply ω and η by some constant factor. This allows more transformations. It is natural to allow the multiplication of ω by an arbitrary function as we described in the beginning of this chapter. However, a long and tedious computation using the ideas of Sec. II may be used to show that if a transformation fixes η and ω by a factor α, then α must be a constant. The suitability of letting η change by a factor is not so obvious. However, if the factor is constant, it may be interpreted as being only a change in energy scale. Thus these transformations are also given in Sec. III.

II. ABSOLUTE INVARIANCE

Letting X, Y, U, and V be n-component real vectors, we wish to find the group G of all coordinate transformations $f: R^{2n+1} \rightarrow R^{2n+1}$ such that

$$f(X,Y,E) = (U,V,P),$$

while

$$dE - \sum_{i=1}^{n} y_i\, dx_i = dP - \sum_{i=1}^{n} v_i\, du_i, \tag{11a}$$

$$\sum_{i=1}^{n} dy_i\, dx_i = \sum_{i=1}^{n} dv_i\, du_i, \tag{11b}$$

and [as a consequence of (11a)],

$$\sum_{i=1}^{n} dx_i \wedge dy_i = \sum_{i=1}^{n} du_i \wedge dv_i. \tag{11c}$$

It proves convenient to separate the problem into two parts by examining the subgroup $J = \{f \in G: f(0) = 0\}$ of transformations which fix the origin and

$$H = \{f \in G: f(X,Y,E) = (X + \mathbf{b},\ Y + \mathbf{d},\ E + \mathbf{d}\cdot X + \mathbf{e}),\ \mathbf{b}, \mathbf{d} \in R^n, \mathbf{e} \in R\} \tag{12}$$

of "translations." Elements of H involve arbitrary translations in the X and Y variables, but the invariance of (11a) requires the additional term $\mathbf{d} \cdot X$ in P. The fact that J and H are subgroups of G is easily verified.

Lemma 1: An arbitrary $f \in G$ may be written as the product of $j \in J$ and $h \in H$.

Proof: Consider $f \in G$ and suppose $f(0) = (\mathbf{b}_0, \mathbf{d}_0, \mathbf{e}_0)$. Then choosing h such that $h(X,Y,E) = (X - \mathbf{b}_0,\ Y - \mathbf{d}_0,\ E - \mathbf{d}_0\cdot X - \mathbf{e}_0 + \mathbf{b}_0\mathbf{d}_0)$, we find $h \circ f$ fixes the origin and hence equals j for some $j \in J$. But then $f = h^{-1} \circ j$, where

$$h^{-1}(X,Y,E) = (X + \mathbf{b}_0,\ Y + \mathbf{d}_0,\ E + \mathbf{d}_0\cdot X + \mathbf{e}_0) \in H. \tag{13}$$

Note further that the only element of H which fixes the origin is the identity. We see below that H is normal. These facts are enough to guarantee that G is the semidirect product of J and H.

Theorem 1: H is isomorphic to the $(2n + 1)$-dimensional Heisenberg group[6,7] $\mathrm{H}(n)$.

Proof: Clear by the correspondence

$$H \stackrel{\mathrm{def}}{=} T_{(\mathbf{b},\mathbf{d},\mathbf{e})} \sim \begin{pmatrix} 1 & 0 & \cdot & \cdot & \cdot & \cdot \\ b_1 & 1 & 0 & \cdot & \cdot & \cdot \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ b_n & 0 & \cdot & \cdot & 1 & 0 \\ e & d_1 & \cdot & \cdot & d_n & 1 \end{pmatrix}. \tag{14}$$

Theorem 2: The subgroup J of elements of G which fix the origin is isomorphic to

$$\mathrm{O}(n,n) \cap \mathrm{Sp}(n) \cong \mathrm{Gl}(n).$$

The key here is to note that by (11a) the $(2n + 1)$th component P of $j(X,Y,E)$ is determined once the $2n$ components U and V are specified, while in terms of these $2n$ components the restriction of j must preserve a nondegenerate quadratic form $\tilde{\eta}$ of type (n,n) and a symplectic form $\widetilde{d\omega}$. Hence j must be in both $\mathrm{O}(n,n)$ and $\mathrm{Sp}(n)$. For a proof of the second isomorphism indicated in the theorem as

$$\mathrm{O}(n,n) \cap \mathrm{Sp}(n) \cong \mathrm{Gl}(n). \tag{15}$$

see Helgason.[8]

Proof of Theorem 2: Define $\pi: R^{2n+1} \rightarrow R^{2n}$ and $I_{\mathbf{e}}: R^{2n} \rightarrow R^{2n+1}$ for each $\mathbf{e} \in R$ by

$$\pi(X,Y,E) = (X,Y) \tag{16}$$

and

$$I_{\mathbf{e}}(X,Y) = (X,Y,\mathbf{e}). \tag{17}$$

Then $\tilde{\eta} = \pi^*(\eta)$ and $\widetilde{d\omega} = \pi^*(d\omega)$ define nondegenerate quadratic and symplectic forms on R^{2n}. For $j \in J$ and $\mathbf{e} \in T$, define

$$j_{\mathbf{e}} = \pi \circ j \circ I_{\mathbf{e}} \tag{18}$$

which maps $R^{2n} \rightarrow R^{2n}$ and leaves $\tilde{\eta}$ and $\widetilde{d\omega}$ invariant. Note that $j_{\mathbf{e}}$ is the action of j on the X and Y variables with E held constant equal to $\mathbf{e}$. Since $j_{\mathbf{e}}$ preserves $\tilde{\eta}$ and fixes the origin, it is in $O(n,n)$ and is in particular linear.[9] Since j_e also preserves $\widetilde{d\omega}$, it must also be in $\mathrm{Sp}(n)$. Thus

$$j_e(X,Y) = (AX,(A^t)^{-1}Y) \tag{19}$$

for some $A\in \mathrm{Gl}(n)$, where $A = A(\mathbf{e})$ may depend on $\mathbf{e}$. Then

$$j(X,Y,E) = (AX,(A^t)^{-1}Y,P(X,Y,E)), \tag{20}$$

i.e., J fixes hyperplanes of constant E. To see that A is independent of E we let $A = [a_{ij}]$ and $A^{-1} = [b_{ij}]$ and use the invariance of η to get

$$\begin{aligned}\sum_{i=1}^n dx_i\, dy_i &= \sum_{i=1}^n d\left(\sum_{j=1}^n a_{ij}x_j\right)d\left(\sum_{k=1}^n b_{ki}y_k\right)\\ &= \sum_{i=1}^n dx_i\, dy_i + \sum_{i,j,k=1}^n x_j b_{ki}\frac{da_{ij}}{dE}dE\, dy_k\\ &\quad + \sum_{i,j,k=1}^n y_k a_{ij}\frac{db_{ki}}{dE}\, dE\, dx_j\\ &\quad + \sum_{i,j,k=1}^n x_j y_k \frac{da_{ij}}{dE}\,\frac{db_{ki}}{dE} dE\, dE \end{aligned}\tag{21}$$

which, by the linear dependence of the differential forms in the expansion, implies the equality of corresponding coefficients. In particular,

$$\sum_{i,j=1}^n x_j b_{ki}\frac{da_{ij}}{dE} = 0, \quad k = 1,\dots,n \tag{22}$$

for arbitrary $(x_1,\dots,x_n)$. Thus

$$\sum_{i=1}^n b_{ki}\frac{da_{ij}}{dE} = 0, \quad k,j = 1,\dots,n \tag{23}$$

and, since $[b_{ki}]$ is invertible,

$$\frac{da_{ij}}{dE} = 0, \quad i,j = 1,\dots,n. \tag{24}$$

Substituting (24) into (11a) gives

$$dE = dP \tag{25}$$

and, since $j(0) = 0$,

$$E = P. \tag{26}$$

The correspondence between

$$J \overset{\text{def}}{=} L_A = \begin{pmatrix} A & 0 & 0\\ 0 & (A^t)^{-1} & 0\\ 0 & 0 & 1\end{pmatrix}\in J \tag{27}$$

and

$A\in \mathrm{Gl}(n)\cong O(n,n)\cap \mathrm{Sp}(n)$ is now clear.

Lemma 2: H is normal in G.

Proof: For $j = L_A \in J$ and $h = T_{(\mathbf{b},\mathbf{d},\mathbf{e})}\in H$, we compute

$$\begin{aligned} j\circ h\circ j^{-1}(X,Y,E) &= j\circ h\,(A^{-1}X,A^t Y,E)\\ &= j(A^{-1}X + \mathbf{b},A^t Y + \mathbf{d},E\\ &\quad + \mathbf{d}\cdot A^{-1}X + \mathbf{e})\\ &= (X + A\mathbf{b}, Y + (A^t)^{-1}\mathbf{d},\\ &\quad E + (A^t)^{-1}\mathbf{d}\cdot X + \mathbf{e})\\ &= h'(X,Y,E), \end{aligned}\tag{28}$$

where $h' = T_{(A\mathbf{b},(A^t)^{-1}\mathbf{d},\mathbf{e})}\in H$. This can be written as

$$L_A T_{(\mathbf{b},\mathbf{d},\mathbf{e})} L_A{}^{-1} = T_{L_A(\mathbf{b},\mathbf{d},\mathbf{e})}. \tag{29}$$

The above results prove the following theorem.

Theorem 3: $G\cong J\otimes_\alpha H\cong \mathrm{Gl}(n)\otimes_\alpha \mathrm{H}(n)$.

III. RELATIVE INVARIANCE

We now allow η and ω to change by constant scale factors. This extra degreee of freedom adds two generators. Without this freedom, η fixes our unit of energy, though diagonal matrices in $\mathrm{Gl}(n)$ allow scaling of the other quantities for changes of units. Changes of energy units give one generator, while a complete Legendre transform on all variables gives the other generator. Accordingly, we seek the group $\widehat{G}$ of all coordinate transformations $f(X,Y,E) = (U,V,P)$ such that

$$dE - \sum_{i=1}^n y_i\, dx_i = \left(dP - \sum_{i=1} v_i\, du_i\right)\alpha \tag{30a}$$

and

$$\sum_{i=1}^n dx_i\, dy_i = \left(\sum_{i=1}^n du_i\, dv_i\right)\beta \tag{30b}$$

for some nonzero $\alpha,\beta\in R$. Again, by taking exterior derivatives in (30a), we get

$$\sum_{i=1}^n dx_i \wedge dy_i = \left(\sum_{i=1}^n du_i\wedge dv_i\right)\alpha. \tag{30c}$$

Note that $G\subseteq \widehat{G}$ consists of those elements of $\widehat{G}$ with $\alpha = \beta = 1$. Note that the correspondence $f^s \rightarrow (\alpha,\beta)$, sending $f\in\widehat{G}$ to the pair of scale factors of f, defines a homomorphism of $\widehat{G}$ to $R^*\otimes R^*$ with kernel G showing that G is a normal subgroup of $\widehat{G}$.

Lemma 3: For all $f\in\widehat{G}$, $|\alpha| = |\beta|$.

Proof: For $f\in\widehat{G}$, again define

$$f_e = \pi f I_e \tag{31}$$

and note that

$$f_e{}^*(\tilde{\eta}) = (1/\beta)\tilde{\eta} \tag{32}$$

and

$$f_e{}^*(\widetilde{d\omega}) = (1/\alpha)\widetilde{d\omega}. \tag{33}$$

Recalling that a quadratic form Q transforms under f_e to $f_e{}^*(Q) = Df_e Q(Df_e)^t$, where Df_e is the Jacobian matrix of f_e, we get, by looking at (32) and (33) in any coordinates and taking determinants,

$$(\det Df_e)^2(\det \tilde{\eta}) = \det((1/\beta)\tilde{\eta}) = (1/\beta^{2n})(\det \tilde{\eta}), \tag{34}$$

$$(\det Df_e)^2(\det \widetilde{d\omega}) = \det((1/\alpha)\widetilde{d\omega}) = (1/\alpha^{2n})(\det \widetilde{d\omega}). \tag{35}$$

Since $\det(\tilde{\eta})$ and $\det(\widetilde{d\omega})$ are nonzero, this gives

$$\alpha^{2n} = 1/(\det Df_e)^2 = \beta^{2n}, \tag{36}$$

i.e., $|\alpha| = |\beta|$ as desired.

We now find the generators of $\widehat{G}$ which are not in G. For $a\in R^*$, a nonzero real number, let

$$U_a(X,Y,E) = (X,aY,aE). \tag{37}$$

Note that $U_a\in\widehat{G}$ and $(\alpha)U_a = \beta(U_a) = 1/a$. Let U be the one-parameter subgroup of $\widehat{G}$ generated by the U_a, $a\in R^*$. Since the only element in U with $\alpha = \beta = 1$ is the identity,

$U \cap G$ contains only the identity element. U and G generate a subgroup

$$M = \{f \in \hat{G} : \alpha(f) = \beta(f)\}. \quad (38)$$

U and G are clearly contained in M. On the other hand, for $f_0 \in M$ with $\alpha(f_0) = \beta(f_0) = \alpha_0$, $U_{\alpha_0} \cdot f_0 \in G$ since

$$\alpha(U_{\alpha_0} \cdot f_0) = \alpha(U_{\alpha_0})\alpha(f_0) = 1, \quad (39a)$$

$$\beta(U_{\alpha_0} \cdot f_0) = \beta(U_{\alpha_0})\beta(f_0) = 1. \quad (39b)$$

The commutation relations

$$U_a L_A = L_A U_a, \quad (40)$$

$$U_a T_{(\mathbf{b},\mathbf{d},\mathbf{e})} = T_{(\mathbf{b},a\mathbf{d},a\mathbf{e})} U_a \quad (41)$$

follow easily by applying each side to (X,Y,E). We have established that

$$M \cong U \otimes_\beta G \cong R^* \otimes_\beta (\mathrm{Gl}(n) \otimes_\alpha \mathrm{H}(n)). \quad (42)$$

The commutation relations (29), (40), and (41) show that U_a and L_A commute, while the translations are normal in M. Thus we may also write

$$M = (R^* \otimes \mathrm{Gl}(n)) \otimes_\epsilon \mathrm{H}(n). \quad (43)$$

Note that this expression involves a direct product. The fact that M is normal in $\hat{G}$ follows by composing the homorphism $s: \hat{G} \to R^* \otimes R^*$ with the homomorphism

$$t(\alpha,\beta) = (\mathrm{sgn}(\alpha), \mathrm{sgn}(\beta)) \quad (44)$$

of $R^* \otimes R^*$ onto $Z_2 \otimes Z_2$ and noting that M is the kernel of $t \circ s$.

For our final generator, we define

$$\tau(X,Y,E) = (Y,X,X\cdot Y - E). \quad (45)$$

Note that $\tau^2 = 1$ and that τ is a Legendre transformation[10] exchanging all conjugate variables.

$$\tau^*(\omega) = d(X\cdot Y - E) - X\cdot dY$$
$$= -dE + Y\cdot dx = -\omega, \quad (46)$$

$$\tau^*(\eta) = \eta. \quad (47)$$

Thus $\tau \in \hat{G}$ with $\alpha(\tau) = -1$ and $\beta(\tau) = 1$. τ generates a two element subgroup whose intersection with M is the identity since $\tau \notin M$. If f is an arbitrary element of $\hat{G}$, then either $f \in M$ or $\alpha(f) = -\beta(f)$ by Lemma 3. Then $\tau f \in M$, since

$$\alpha(\tau f) = \alpha(\tau)\alpha(f) = -\alpha(f) = \beta(f) = \beta(\tau)\beta(f) = \beta(\tau f). \quad (48)$$

We have proved the following theorem.

Theorem 4:

$$\hat{G} \cong Z_2 \otimes_\gamma (R^* \otimes_\beta (\mathrm{Gl}(n) \otimes_\alpha \mathrm{H}(n)))$$
$$\cong Z_2 \otimes_\gamma ((R^* \otimes \mathrm{Gl}(n)) \otimes_\epsilon \mathrm{H}(n)).$$

The fact that the last product is only semidirect follows from the remaining commutation relations:

$$T_{(\mathbf{b},\mathbf{d},\mathbf{e})} \tau = \tau T_{\tau(\mathbf{b},\mathbf{d},\mathbf{e})}, \quad (49)$$

$$L_A \tau = \tau L_{(A^t)^{-1}}, \quad (50)$$

$$U_a \tau = \tau U_a L_{aI}. \quad (51)$$

The connected component of the identity N which is a normal subgroup of $\hat{G}$ is easily obtained from Theorem 4 by taking products of the connected components of the factors.

$$N \cong R \otimes_{\beta'} (\mathrm{Gl}^+(n) \otimes_\alpha \mathrm{H}(n))$$
$$\cong ((R \otimes \mathrm{Gl}^+(n)) \otimes_\epsilon \mathrm{H}(n)), \quad (52)$$

where we have used $(R, +)$ instead of the isomorphic group $(R^+_\lambda, \cdot)$. The generators τ, U_{-1}, and L_A together with N generate $\hat{G}$, where $A \in \mathrm{Gl}(n)$, $\det(A) = -1$, and $A^2 = I$. Since

$$\tau U_{-1} \tau U_{-1} = L_{-I}, \quad (53)$$

however, these generators do not generate a subgroup disjoint from N except for the identity unless $U_{-I} \notin N$. For n odd, this is the case since then $-I \notin \mathrm{Gl}^+(n)$ and we get $\hat{G} = D_4 \otimes_\lambda N$, where D_4 is the diheral group $Z_2 \otimes_\mu Z_4$ of symmetries of the square.[11] For n even, $-I \in \mathrm{Gl}^+(n)$ and no decomposition of the above form is possible. We have, in this case only, that

$$\hat{G}/N = Z_2 \otimes Z_2 \otimes Z_2. \quad (54)$$

IV. INTERPRETATIONS AND CONCLUSIONS

We have found that the group of coordinate transformations in the phase space of a thermodynamic system having

$$\omega = dE - Y\,dX \quad (55)$$

and

$$\eta = dX\cdot dY \quad (56)$$

as relative invariants is $\hat{G} \cong Z_2 \otimes_\gamma (R^* \otimes_\beta (\mathrm{Gl}(n) \otimes_\alpha \mathrm{H}(n)))$ with generators $T_{(b,d,e)}$, L_A, U_a, and τ, and commutation relations

$$L_A T_{(\mathbf{b},\mathbf{d},\mathbf{e})} = T_{L_A(\mathbf{b},\mathbf{d},\mathbf{e})} L_A, \quad (57)$$

$$U_a L_A = L_A U_a, \quad (58)$$

$$U_a T_{(\mathbf{b},\mathbf{d},\mathbf{e})} = T_{(\mathbf{b},a\mathbf{d},a\mathbf{e})} U_a, \quad (59)$$

$$T_{(\mathbf{b},\mathbf{d},\mathbf{e})} \tau = \tau T_{(\mathbf{d},\mathbf{b},\mathbf{d}\cdot\mathbf{b}-\mathbf{e})}, \quad (60)$$

$$L_A \tau = \tau L_A, \quad (61)$$

$$U_a \tau = \tau U_a L_{aI}. \quad (62)$$

If we require that ω and η be absolute invariants, the appropriate group shrinks to $G \cong \mathrm{Gl}(n) \otimes_\alpha \mathrm{H}(n)$ with generators L_A and $T_{(\mathbf{b},\mathbf{d},\mathbf{e})}$, and commutation relation (57).

For ω, relative invariance is physically a more reasonable requirement than absolute invariance, since $\omega = 0$ and $\alpha\omega = 0$ define the same solution surface. On the other hand, absolute invariance seems more reasonable for η, though relative invariance may be interpreted as a change of units of energy (see below). If we require absolute invariance of η and relative invariance of ω, then by Lemma 3, $\alpha = \pm 1$. The group becomes $\tilde{G} = Z_2 \otimes_\gamma (\mathrm{Gl}(n) \otimes_\alpha \mathrm{H}(n))$. $\tilde{G}$ is generated by τ, L_A, and $T_{(\mathbf{b},\mathbf{d},\mathbf{e})}$, i.e., the generators of $\hat{G}$ excluding U_a.

If we require the invariance of the origin, i.e., $f(0) = 0$, the generators $T_{(\mathbf{b},\mathbf{d},\mathbf{e})}$ are eliminated, and we are left with $Z_2 \otimes_\alpha (R^* \otimes_\beta \mathrm{Gl}(n))$ for relative invariance—relations (58), (61), and (62)—or with $\mathrm{Gl}(n)$ for absolute invariance.

We advance the following interpretations for the generators:

τ: τ corresponds to a classical Legendre transformation. As discussed in Sec. II, its interpretation[10,12] is to describe the state of a system using states of its environment, i.e., using Y instead of X.

U_a: U_a multiplies both E and Y by the constant factor a. This is exactly the effect of a change in the unit of energy.

L_a: Applying L_a may prove convenient when dealing with a chemical system. We can choose the coordinates AX to involve reaction coordinates and mole numbers of independent components. Using AX and the corresponding intensities $(A')^{-1}Y$ (affinities) can simplify analysis.[13]

$T_{(\mathbf{b},\mathbf{d},\mathbf{e})}$: This generator is difficult to interpret. The potential $P = E + \mathbf{d}X + \mathbf{e}$, which results from the action of $T_{(\mathbf{b},\mathbf{d},\mathbf{e})}$ on (X,Y,E), gives one clue. Note first that

$$T_{(\mathbf{b},\mathbf{d},\mathbf{e})} = T_{(\mathbf{b},0,\mathbf{e})} T_{(0,\mathbf{d},0)}. \tag{63}$$

For translations of the form $T_{(0,\mathbf{d},0)}$, if we interpret the Y variables as intensities representing the environment,[12] then replacing Y by $Y + \mathbf{d}$, i.e., placing the same system into an environment with intensities $Y + \mathbf{d}$, gives rise to the extra internal energy $\mathbf{d}\cdot X$. The translation $T_{(\mathbf{b},0,\mathbf{e})}$ corresponds then to changing the zero of our intensities. Note that $\mathbf{b}$ does not show up in the potential so an interpretation analogous to the one for $T_{(0,\mathbf{d},0)}$ is not possible. One is tempted to rule out transformations of the form $T_{(\mathbf{b},0,\mathbf{e})}$ by requiring that the origin in the subspace (X,E) remain invariant. However, since

$$\tau T_{(0,d,0)} \tau = T_{(d,0,0)}, \tag{64}$$

allowing translations in Y requires that we allow translations in X. Since $T_{(0,\mathbf{d},0)}$ moves the zero of E, we cannot require the invariance of $X = 0$ or $E = 0$ without requiring $Y = 0$. It is possible to rule out translation altogether by requiring the invariance of the origin in (X,Y,E). As mentioned above, this gives the group $G^* \cong Z_2 \otimes_\gamma (R^* \otimes \mathrm{Gl}(n))$.

Note that none of the group generators, and hence no element of $\widehat{G}$, mix the X and Y variables. More precisely, if $f \in \widehat{G}$ sends (X,Y,E) to $(U,V,P) = f(X,Y,E)$, then there are exactly n variables (U or V) which depend only on X and exactly n variables (V or U) which depend only on Y. In general, P may depend on all $(2n + 1)$ variables (X,Y,E). If X and Y are initially extensive and intensive, there will again be $(n + 1)$ extensive and n intensive variables after the action of any $f \in \widehat{G}$. Even when no such initial division into extensive and intensive variables can be made, e.g., when considering surface effects, the interpretation of the two sets of variables as parameters of state and parameters of environment remains valid.[12] Our conclusion then is that $f \in G$ does not mix parameters of the system and parameters of the environment except in the potential function P whose extrema determine the coexisting states of the system with the environment.

Finally, we note that $\widehat{G}$ does not contain most of the classical Legendre transforms: namely, those which exchange only some of the conjugate pairs of variables. For example,

$$g(x_1,x_2,y_1,y_2,E) = (y_1,x_2,x_1,y_2,x_1y_1 - E) \tag{65}$$

preserves η but not ω since

$$d(x_1y_1 - E) - x_1\,dy_1 - x_2\,dx_2 \neq (dE - y_1\,dx_1 - x_2\,dx_2)\alpha \tag{66}$$

for any $\alpha \in R^*$. We can regain the invariance of ω by using instead

$$g(x_1,x_2,y_1,y_2,E) = (y_1,x_2,-x_1,y_2,E - x_1y_1), \tag{67}$$

which is more familiar from standard treatments.[10] In this case, however, η is not invariant since

$$dx_1\,dy_1 + dx_2\,dy_2 \neq (-dx_1\,dy_1 + dx_2\,dy_2)\beta \tag{68}$$

for any $\beta \in R^*$.

Suppose, however, that we are interested only in processes for which one of the x_i (respectively y_i) remains constant. Along the corresponding subsurface of phase-energy space, we can take the differential form dx_i (dy_i) to be zero and ask for the invariance of ω and η with such zeros dropped out. If one chooses the right potential, then it is possible to eliminate the pair of variables x_i, y_i from consideration.

Case A: $x_i =$ const. In this case, x_i and y_i both drop out of ω and η on setting $dx_i = 0$. The problem thereby reduces to a problem with one less degree of freedom. This is implicit in the standard neglect of degress of freedom (e.g., magnetic) which "don't participate in a given process."

Case B: $y_i =$ const. In this case, x_i and y_i do not drop out of ω. However, if we apply $\tau(X,Y,E) = (Y,X,X\cdot Y - E)$, we get Case A with the potential $X\cdot Y - E$. We can then throw away x_i and y_i, since they disappear from $\tau^*(\omega)$ and $\tau^*(\eta)$. Let $\hat{\tau}$ be the Legrendre involution on the space $(\widehat{X},\widehat{Y},P)$ with $\hat{\tau}(\widehat{X},\widehat{Y},P) = (\widehat{Y},\widehat{X},\widehat{X}\cdot\widehat{Y} - P)$, where $\widehat{X} = (x,\ldots,x_{i-1}, x_{i+1},\ldots,x_n)$, $\widehat{Y} = (y_1,\ldots,y_{i-1},y_{i+1},\ldots,y_n)$. Applying $\hat{\tau}$, we regain the familiar form:

$$\hat{\tau}(\widehat{Y},\widehat{X},X\cdot Y - E) = (\widehat{X},\widehat{Y},E - x_iy_i); \tag{69}$$

the partial Legrende transform of E on the ith variable. The fact that thermodynamic analyses standardly employ such potentials for processes in which some $y_i =$ const fits in nicely with the above formalism.

In conclusion, we contrast the above group to previous group theoretic investigations in equilibrium thermodynamics. Koenig[14] and others,[15–17] while considering transformations associated with the Born diagram[10] have discussed contact transformations which also satisfy

$$E + G = H + A, \tag{70}$$

where E,G,H,A are the four classical thermodynamic potentials. The resulting group is generated by permutations of the variables induced by classical Legrende transformations. In light of work on generalizations of the thermodynamic Legrende transformation,[4,12] it appears that the invariance of (70) may be too strict a requirement.

Tisza,[18] observing that the matrix $\partial^2 E/\partial x_i\,\partial x_j$ is related to the stability of the system, studied coordinate transformations that leave the determinant and all principal minors of this matrix invariant.

As the first referee pointed out, it would be desirable to see a group theoretic investigation which required the invariance of the first two laws. Weinhold interprets the positive definiteness of η for stable systems to be the state space version of the second law. Thus all our transformations leave the second law invariant (τ changes the sign to negative definite). Preliminary evidence[2,3] seems to indicate, however, that not just the sign, but the magnitude of η, may be physically significant and will perhaps yield a strengthened form of the second law.

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[1]F. Weinhold, J. Chem. Phys. **63**, 2479, 2484, 2488, 2496 (1975); **65**, 559 (1976).

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

[3]P. Salamon, and R. S. Berry, "Weinhold Length and Dissipated Availability," Phys. Rev. Lett. (to be published).

[4]R. Hermann, *Geometry, Physics, and Systems* (Marcel Dekker, New York, 1973).

[5]R. L. Bishop and S. I. Goldberg, *Tensor Analysis on Manifolds* (Macmillan, New York, 1968), p. 272.

[6]R. Howe, Bull. Am. Math. Soc. **3**, 779 (1980).

[7]K. B. Wolf, in *Group Theory and Its Applications*, Vol. III, edited by E. M. Loebl (Academic, New York, 1981), p. 189.

[8]S. Helgason, *Differential Geometry and Symmetric Spaces* (Academic, New York, 1962).

[9]S. Kobayashi and K. Nomizu, *Foundations of Differential Geometry* (Wiley, New York, 1963), p. 238.

[10]See, for example, H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

[11]This copy of D_4 in $\widehat{G}$ bears no relation to the transformations of Koenig[14] which derive from partial Legendre transforms corresponding to the symmetries of the Born square.

[12]P. Salamon, Ph.D. thesis (University of Chicago, 1978); P. Salamon, B. Andresen, and R. S. Berry, Phys. Rev. A **15**, 2094 (1977).

[13]I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans, London, 1954).

[14]F. Koenig, J. Chem. Phys. **3**, 39 (1935); **56**, 4556 (1972).

[15]J. A. Prins, J. Chem. Phys. **16**, 65 (1948).

[16]F. Buckley, J. Res. Natl. Bur. Stand. **33**, 213 (1944).

[17]W. D. Hayes, Quart. Appl. Math. **4**, 227 (1945).

[18]L. Tisza, *Generalized Thermodynamics* (M.I.T., Cambridge, MA, 1966).