Metric geometry of equilibrium thermodynamics. III. Elementary formal structure of a vector-algebraic representation of equilibrium thermodynamics

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(Received 7 October 1974)

The thermodynamic geometry established in an earlier paper is taken as the basis for an abstract vector-algebraic representation of equilibrium thermodynamics. In this representation, thermodynamic field variables appear as abstract Euclidean vectors whose lengths and internal angles describe the equilibrium properties. A variety of thermodynamic indentities, stability conditions, and other relationships are derived and shown to have simple and natural geometric significance in the new framework. The geometric viewpoint is also found to suggest certain lines of development—such as the use of self-conjugate ("normal") field variables—with no obvious counterpart in the traditional differential formalisms. The formal ideas are illustrated throughout with elementary applications to properties of a simple homogeneous fluid.

I. INTRODUCTION

In Paper I,[1] it was found that the equilibrium thermodynamics of a given equilibrium state could be formally associated with the geometry of an abstract Euclidean vector space. In Paper II,[2] a geometric Gibbs–Duhem relation was discussed in connection with possible scaling hypotheses on thermodynamic potentials. It was suggested[1] that the abstract thermodynamic geometry could be made the basis for an alternative representation of equilibrium thermodynamics, which could augment or complement the classical formalism. A prominent feature of such a complementary representation is the natural emphasis on algebraic and geometric concepts (vector algebra of Euclidean spaces) instead of the analytic concepts (partial differential calculus of potential functions) of the traditional formalism. It is the purpose of the present paper to outline some principal formal features of a geometric representation, and to illustrate these briefly for the simple example of a homogeneous fluid.

II. THERMODYNAMIC VECTORS AND GEOMETRY

Let us recall[1] that a simple thermodynamic system of fixed scale which consists of c independent chemical components (in the sense of Gibbs[3]) and ν distinct phases is to be associated with a real metric space $\mathfrak{M}_r$ of dimension r,

$$r = c - \nu + 2. \tag{2.1}$$

In the classical Gibbsian formalism,[4] primary emphasis is laid on a *thermodynamic potential* (or "fundamental equation"), the internal energy U,

$$U = U(X_1, X_2, \ldots), \tag{2.2}$$

which is a function of a chosen set of *extensities* X_i [entropy S, volume V, mole numbers N_i ($i = 1, 2, \ldots, c$), or independent linear combinations thereof]. A specific thermodynamic state can then be identified by giving the numerical value ξ_i of each extensive variable X_i; as in Paper I, the "point" ξ (in a Cartesian phase space) will be taken as a convenient label for this state. Each extensive variable X_i is in turn associated with a conjugate *field*[5] function R_i,

$$R_i = (\partial U/\partial X_i)_{\mathbf{X}}, \tag{2.3}$$

such as temperature T, pressure P, etc. In writing such partial derivatives, we shall let subscripts such as $\mathbf{X}$ abbreviate the list of arguments held constant for the partial differentiation, e.g., each X_j for $j \neq i$.

In the geometric representation, the field functions R_i of Eq. (2.3) become of primary importance, inasmuch as they label the vector elements $|\mathcal{R}_i\rangle$ of the abstract space $\mathfrak{M}_r$ in accordance with the association

$$dR_i \leftrightarrow |\mathcal{R}_i\rangle = |\mathcal{R}_i(\xi)\rangle \in \mathfrak{M}_r. \tag{2.4}$$

As (2.4) implies, the full space $\mathfrak{M}_r = \mathfrak{M}_r(\xi)$, and thus each field vector $|\mathcal{R}_i\rangle = |\mathcal{R}_i(\xi)\rangle$, refers to the chosen equilibrium state ξ of interest. The metric space $\mathfrak{M}_r$ is invested with a *scalar product* $\langle\mathcal{R}_i|\mathcal{R}_j\rangle$ having the usual properties[6]:

$$\langle\mathcal{R}_i|\lambda\mathcal{R}_j + \mu\mathcal{R}_k\rangle = \lambda\langle\mathcal{R}_i|\mathcal{R}_j\rangle + \mu\langle\mathcal{R}_i|\mathcal{R}_k\rangle, \tag{2.5a}$$

$$\langle\mathcal{R}_i|\mathcal{R}_j\rangle = \langle\mathcal{R}_j|\mathcal{R}_i\rangle, \tag{2.5b}$$

$$\langle\mathcal{R}_i|\mathcal{R}_i\rangle \geq 0 \ (=0 \text{ only if } |\mathcal{R}_i\rangle = 0). \tag{2.5c}$$

In particular, for arbitrary field vectors $|\mathcal{R}_i\rangle$, $|\mathcal{R}_j\rangle$ and scalars λ, μ, it is meaningful to form the vector

$$|\lambda\mathcal{R}_i + \mu\mathcal{R}_j\rangle = \lambda|\mathcal{R}_i\rangle + \mu|\mathcal{R}_j\rangle, \tag{2.6}$$

which is required for the distributive property (2.5a). Contact with the classical formalism, and with experiment, is achieved by identifying each scalar product of $\mathfrak{M}_r$ with one of the thermodynamic *response functions*[7] (heat capacities, compressibilities, etc.) of the system by the prescription[8]

$$\langle\mathcal{R}_i|\mathcal{R}_j\rangle = (\partial R_i/\partial X_j)_{\mathbf{X}}, \tag{2.7}$$

where X_j is the variable conjugate to R_j in the sense of Eq. (2.3). With the identification (2.7), the abstract geometry of $\mathfrak{M}_r$ is known from the results of Paper I to be fully consistent with the equilibrium thermodynamics of the given system. In effect, "laws of thermodynamics" become "rules of geometry" [e.g., the axioms (2.5a)–(2.5c), which give $\mathfrak{M}_r$ its Euclidean character] in this abstract representation. Therefore, deductions which are geometrically valid in $\mathfrak{M}_r$ must, when interpreted through Eq. (2.7), lead to conclusions which are in all respects consistent with the laws of thermodynamics.[9]

The Euclidean character of $\mathfrak{M}_r$ permits one to associate with each abstract $|\mathcal{R}_i\rangle$ a "length" $|\mathcal{R}_i|$ in the usual manner,[6]

$$|\mathcal{R}_i| = \langle \mathcal{R}_i | \mathcal{R}_i \rangle^{1/2}. \tag{2.8}$$

Similarly, the "angle" θ_{ij} between abstract vectors $|\mathcal{R}_i\rangle$, $|\mathcal{R}_j\rangle$ is given by the usual formula,

$$\cos\theta_{ij} = \langle \mathcal{R}_i | \mathcal{R}_j \rangle / |\mathcal{R}_i| \cdot |\mathcal{R}_j|. \tag{2.9}$$

By virtue of (2.5a)–(2.5c), the lengths and angles thus defined exhibit all the expected Euclidean characteristics, including the *triangle inequality*

$$|\mathcal{R}_i - \mathcal{R}_j| \le |\mathcal{R}_i - \mathcal{R}_k| + |\mathcal{R}_k - \mathcal{R}_j|, \tag{2.10}$$

and the *Schwarz inequality*

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle \le |\mathcal{R}_i| \cdot |\mathcal{R}_j|. \tag{2.11}$$

We shall say that two vectors $|\mathcal{R}_i\rangle$, $|\mathcal{R}_j\rangle$ are *equal* if their "separation" $|\mathcal{R}_i - \mathcal{R}_j|$ vanishes, and that they are *orthogonal* if $\langle \mathcal{R}_i | \mathcal{R}_j \rangle = 0$. In short, the theorems, terminology, and working methods of Euclidean geometry can be carried over intact into this abstract thermodynamic domain.

With the help of Eq. (2.7) we may remark briefly on the general *physical* significance of the abstract lengths and angles: The length of $|\mathcal{R}_i\rangle$ measures the *responsiveness* of the system to a change in the associated extensive parameter X_i, e.g., the extent to which the system adjusts its value of R_i in response to a small change in X_i. (For example, the length of the temperature vector is related to the inverse heat capacity of the system, and that of the pressure vector to its inverse compressibility.) The angle θ_{ij} between vectors $|\mathcal{R}_i\rangle$ and $|\mathcal{R}_j\rangle$, on the other hand, measures the extent to which different responses are *coupled*, e.g., to what extent a small change in X_i will produce a response in R_j, and vice versa. (For example, the angle between the temperature and pressure vectors is related to the thermal expansion coefficient.) These metric parameters of $\mathfrak{M}_r$, unlike those of a phase space, therefore have an *intrinsic* thermodynamic significance, since they are uniquely associated with measured physical properties of the particular system under discussion. Note that lengths in $\mathfrak{M}_r$ depend on the physical units in which the associated responses are measured, but the "coupling" angles θ_{ij} do not.

It was noted in Paper II that the dimensionality of the subspace spanned by a chosen set of n vectors $|\mathcal{R}_i\rangle$ is given by the rank of the associated *Gram* (or *metric*) matrix $\mathbf{G}^{(n)}$, whose elements are scalar products among the $|\mathcal{R}_i\rangle$. Any Gram matrix $\mathbf{G}^{(r+1)}$ of $r+1$ vectors is therefore singular in this r-dimensional space, and the corresponding *Gramian* $G^{(r+1)}$ accordingly vanishes,

$$G^{(r+1)} = \det|\mathbf{G}^{(r+1)}| = 0. \tag{2.12}$$

Equation (2.12), which expresses the geometrical necessity of linear dependence among any $r+1$ vectors in an r-dimensional space, was recognized in Paper II as a generalized form of the *Gibbs–Duhem equation*, to which it directly reduces when the potential U scales in the usual manner with the extensities X_i.

When r reference fields R_i (with associated reference extensities X_i) have been selected which lead to a linearly independent set of field vectors $|\mathcal{R}_i\rangle$, the resulting Gram matrix $\mathbf{G}^{(r)}$ is nonsingular, and will be simply denoted as $\mathbf{G}$:[10]

$$(\mathbf{G})_{ij} = \langle \mathcal{R}_i | \mathcal{R}_j \rangle = (\partial R_i/\partial X_j)_{\mathbf{X}}, \quad i,j = 1, 2, \ldots, r \tag{2.13a}$$

$$\mathrm{rank}(\mathbf{G}) = r, \tag{2.13b}$$

$$G = \det|\mathbf{G}| \ne 0. \tag{2.13c}$$

The reference vectors $|\mathcal{R}_i\rangle$ span the r-dimensional space, and thus form a *basis* in $\mathfrak{M}_r$. A general element of this space, denoted $|\mathcal{R}_\alpha\rangle$, can then be represented in the form

$$|\mathcal{R}_\alpha\rangle = \sum_{i=1}^{r} \alpha_i |\mathcal{R}_i\rangle, \tag{2.14}$$

with "components" α_i which provide the unique label $\boldsymbol{\alpha}$ for the element in the set of (generally nonorthogonal) basis vectors $|\mathcal{R}_i\rangle$,

$$\alpha_i = (\partial R_\alpha/\partial R_i)_{\mathbf{R}}. \tag{2.15}$$

A general scalar product of vectors $|\mathcal{R}_\alpha\rangle$, $|\mathcal{R}_\beta\rangle$ then becomes, in view of (2.13a) and (2.14),

$$\langle \mathcal{R}_\alpha | \mathcal{R}_\beta \rangle = \boldsymbol{\alpha}^t \mathbf{G} \boldsymbol{\beta}, \tag{2.16}$$

where superscript t denotes the transpose. Thus, knowledge of the Gram matrix $\mathbf{G}$ for the reference fields $|\mathcal{R}_i\rangle$ is sufficient to determine all possible scalar products in $\mathfrak{M}_r$, and thereby to specify the thermodynamic geometry completely.

The Gram matrix is symmetric through property (2.5a),

$$\mathbf{G}^t = \mathbf{G}, \tag{2.17}$$

which natural symmetry can be recognized as summarizing the various *Maxwell relations*. Because of this symmetry, one can also see that no more than $r(r+1)/2$ elements of $\mathbf{G}$ are independent. This in turn establishes that no more than $r(r+1)/2$ independent response functions need be experimentally measured in order to characterize completely the thermodynamic geometry of the system. While such results can also be inferred from the classical formalism,[11] they have a particularly transparent basis in the metric space $\mathfrak{M}_r$.

III. CONJUGATE VARIABLES AND CONJUGATE VECTORS

Although the reference axes $|\mathcal{R}_i\rangle$ are in general nonorthogonal, one can easily construct an associated set of "*conjugate*" vectors $|\bar{\mathcal{R}}_i\rangle$ which are *biorthogonal* to the $|\mathcal{R}_i\rangle$,

$$\langle \bar{\mathcal{R}}_i | \mathcal{R}_j \rangle = \delta_{ij}. \tag{3.1}$$

Such vectors can be found whenever $\mathbf{G}$ is nonsingular, and take the explicit form

$$|\bar{\mathcal{R}}_i\rangle = \sum_{j=1}^{r} (\mathbf{G}^{-1})_{ij} |\mathcal{R}_j\rangle, \quad i = 1, 2, \ldots, r. \tag{3.2}$$

The conjugate vector $|\bar{\mathcal{R}}_i\rangle$ can be associated in the usual way, Eq. (2.4), with a corresponding thermodynamic variable $\bar{R}_i$; when this is done, the variable $\bar{R}_i$ will indeed be found to be "conjugate" to R_i in the sense of Eq. (2.3), *viz.*,

$$R_i = (\partial U/\partial \bar{R}_i)_{\bar{\mathbf{R}}}. \tag{3.3}$$

The variables $\bar{R}_i$ thus behave, in a differential sense, precisely as do the reference extensities X_i,[12]

$$d\bar{R}_i = dX_i, \quad i = 1, 2, \ldots, r \tag{3.4}$$

so that the symbols X_i and $\bar{R}_i$ are essentially interchangeable in any expressions involving changes of the extensive parameter. The conjugate vector $|\bar{\mathcal{R}}_i\rangle$ can therefore be thought of (and accordingly labeled) as corresponding to the extensive variable X_i,

$$dX_i \leftrightarrow |\mathcal{X}_i\rangle = |\bar{\mathcal{R}}_i\rangle, \quad i = 1, 2, \ldots, r \tag{3.5}$$

in much the same manner as $|\mathcal{R}_i\rangle$ is related to the corresponding field variable R_i in (2.4).

The biorthogonality relations (3.1) make clear the far-reaching symmetry between field vectors $|\mathcal{R}_i\rangle$ and their conjugates $|\bar{\mathcal{R}}_i\rangle$ in the geometric formalism. The formal symmetry is also seen in relations of the form

$$|\bar{\bar{\mathcal{R}}}_i\rangle = |\mathcal{R}_i\rangle, \tag{3.6}$$

which exhibits the *mutual* character of vector conjugacy. A general scalar product of two conjugate vectors becomes[13]

$$\langle \bar{\mathcal{R}}_i | \bar{\mathcal{R}}_j \rangle = (\partial X_i/\partial R_j)_{\mathbf{R}}, \tag{3.7}$$

paralleling (2.7). In the conjugate basis of $|\bar{\mathcal{R}}_i\rangle$'s, the roles of the conjugate variables X_i and R_i are evidently reversed, and one deals with response functions in which the fields R_i (rather than extensities X_i) play the role of independent variables.

Scalar products among conjugate vectors can also be evaluated from Eqs. (2.13a) and (3.2) in the form

$$\langle \bar{\mathcal{R}}_i | \bar{\mathcal{R}}_j \rangle = (\mathbf{G}^{-1}\mathbf{G}\mathbf{G}^{-1})_{ij} = (\mathbf{G}^{-1})_{ij}. \tag{3.8}$$

Taken together, Eqs. (3.7) and (3.8) lead to various thermodynamic identities connecting measured response functions. (A new set of simple, systematic procedures for deriving such thermodynamic identities by elementary geometric means will be given in the following paper (Paper IV.[14]). Equation (3.8) shows that the inverse matrix $\mathbf{G}^{-1}$ plays a role for conjugate vectors $|\bar{\mathcal{R}}_i\rangle$ which is analogous to that played by $\mathbf{G}$ itself for the field vectors $|\mathcal{R}_i\rangle$. For future reference, and in anticipation of Sec. IV, we may define the *conjugate* matrix $\bar{\mathbf{G}}$,

$$\bar{\mathbf{G}} = \mathbf{G}^{-1} = (\mathbf{G}^{-1})^t, \tag{3.9}$$

so that (3.8) becomes the obvious "conjugate" of Eq. (2.13a),

$$(\bar{\mathbf{G}})_{ij} = \langle \bar{\mathcal{R}}_i | \bar{\mathcal{R}}_j \rangle = (\partial X_i/\partial R_j)_{\mathbf{R}}, \quad i, j = 1, 2, \ldots, r. \tag{3.10}$$

Although $\mathfrak{M}_r$ was initially constructed from field variables R_i, introduction of the conjugate vectors $|\bar{\mathcal{R}}_i\rangle = |\mathcal{X}_i\rangle$ finally permits fields and conjugate extensities to be handled in a nearly symmetrical fashion in the geometric formalism. Nevertheless, a fundamental asymmetry persists in the formalism between these two types of variables.[15] For example, if X_{r+1} is a scale factor and R_{r+1} its conjugate field, it will be possible to find a vector $|\mathcal{R}_{r+1}\rangle$ representing R_{r+1} in $\mathfrak{M}_r$ (its expansion is given by the Gibbs–Duhem equation[2]), but there is obviously no corresponding vector representing X_{r+1}, since the inverse matrix which would be required in Eq. (3.2) for its construction does not exist, as shown by Eq. (2.12).

Example: Homogeneous Fluid

To give some of these ideas more concrete form, let us consider the elementary example of a homogeneous, one-component fluid system of fixed mass. In this case both c and ν are unity,

$$r = c - \nu + 2 = 2, \tag{3.11}$$

so the abstract space is two-dimensional. The internal energy U is a function of entropy S and volume V,

$$U = U(S, V), \tag{3.12}$$

characterizing, respectively, the thermal and mechanical properties of the system. The associated conjugate fields are the absolute temperature T and negative pressure $-P$,

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \quad -P = \left(\frac{\partial U}{\partial V}\right)_S. \tag{3.13}$$

Each of the fields and extensities is associated with a vector in $\mathfrak{M}_2$, as in (2.4) and (3.5),

$$T \leftrightarrow |\mathcal{T}\rangle, \quad P \leftrightarrow |\mathcal{P}\rangle,$$
$$S \leftrightarrow |\mathcal{S}\rangle, \quad V \leftrightarrow |\mathcal{V}\rangle. \tag{3.14}$$

Scalar products among these vectors are readily found from Eqs. (2.13a), (3.1), and (3.10), and are tabulated in Table I. The entries of Table I are written in terms of commonly measured properties, such as the *heat capacities* C_P and C_V,

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P, \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \tag{3.15}$$

the (isothermal and adiabatic) *compressibilities* β_T and β_S,

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \quad \beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S, \tag{3.16}$$

the *thermal expansion coefficient* α_P,

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \tag{3.17}$$

and the *heat of pressure variation* (at constant volume) Γ_V,

$$\Gamma_V = T(\partial S/\partial P)_V. \tag{3.18}$$

As pointed out below Eq. (2.17), only $2(2+1)/2 = 3$ of the above properties could be independent. Particular numerical values assumed by three such properties in the state of interest must be provided by experimental measurements (or by some microscopic model), and will serve to identify the particular substance under consideration.

From Eq. (2.8) and Table I, the lengths of the various vectors are seen to be

$$|\mathcal{T}| = (T/C_V)^{1/2}, \quad |\mathcal{P}| = (V\beta_S)^{-1/2},$$
$$|\mathcal{S}| = (C_P/T)^{1/2}, \quad |\mathcal{V}| = (V\beta_T)^{1/2}. \tag{3.19}$$

TABLE I. "Standard" scalar products.

	$\lvert\mathcal{T}\rangle$	$\lvert-\mathcal{P}\rangle$	$\lvert\mathcal{S}\rangle$	$\lvert\mathcal{V}\rangle$
$\lvert\mathcal{T}\rangle$	T/C_V	$-T/\Gamma_V$	1	0
$\lvert-\mathcal{P}\rangle$	$-T/\Gamma_V$	$1/V\beta_S$	0	1
$\lvert\mathcal{S}\rangle$	1	0	C_P/T	$V\alpha_P$
$\lvert\mathcal{V}\rangle$	0	1	$V\alpha_P$	$V\beta_T$

Similarly, Eq. (2.9) gives the angles separating the thermodynamic vectors; two such characteristic angles are θ_{SV}, separating $\lvert\mathcal{S}\rangle$ and $\lvert\mathcal{V}\rangle$,

$$\cos\theta_{SV} = \alpha_P (TV/C_P\beta_T)^{1/2}, \tag{3.20}$$

and θ_{ST}, separating $\lvert\mathcal{S}\rangle$ and $\lvert\mathcal{T}\rangle$,

$$\cos\theta_{ST} = (C_V/C_P)^{1/2}. \tag{3.21}$$

For example, Eq. (3.21) shows that the conjugate entropy and temperature vectors are separated by an angle of about 39° for a monatomic ideal gas (for which $C_V/C_P = 3/5$),

$$\theta_{ST}^{(\mathrm{ideal})} = \cos^{-1}(3/5)^{1/2} \approx 39.2^\circ. \tag{3.22}$$

Since $\lvert\mathcal{S}\rangle$ is orthogonal to $\lvert-\mathcal{P}\rangle$, and $\lvert\mathcal{T}\rangle$ is orthogonal to $\lvert\mathcal{V}\rangle$ by Eq. (3.1), it is easy to recognize geometrically that the conjugate vectors $\lvert-\mathcal{P}\rangle$, $\lvert\mathcal{V}\rangle$ must be separated by the same angle as were $\lvert\mathcal{S}\rangle$ and $\lvert\mathcal{T}\rangle$, or by its supplementary angle,

$$\cos^2\theta_{-P,V} = \cos^2\theta_{ST}, \tag{3.23}$$

which is the identity

$$C_P/C_V = \beta_T/\beta_S. \tag{3.24}$$

Other familiar identities connecting the properties (3.15)–(3.18) can be read off similarly from the elementary geometry of these vectors.

Finally, we can use Eq. (3.8) to obtain a group of such identities simultaneously. From Table I, the Gram matrix $\mathbf{G}$ and its inverse are:

$$\mathbf{G} = \begin{pmatrix} \langle\mathcal{T}\vert\mathcal{T}\rangle & \langle\mathcal{T}\vert-\mathcal{P}\rangle \\ \langle-\mathcal{P}\vert\mathcal{T}\rangle & \langle-\mathcal{P}\vert-\mathcal{P}\rangle \end{pmatrix} = \begin{pmatrix} T/C_V & -T/\Gamma_V \\ -T/\Gamma_V & 1/V\beta_S \end{pmatrix}, \tag{3.25a}$$

$$\mathbf{G}^{-1} = \begin{pmatrix} \langle\mathcal{S}\vert\mathcal{S}\rangle & \langle\mathcal{S}\vert\mathcal{V}\rangle \\ \langle\mathcal{V}\vert\mathcal{S}\rangle & \langle\mathcal{V}\vert\mathcal{V}\rangle \end{pmatrix} = \begin{pmatrix} C_P/T & V\alpha_P \\ V\alpha_P & V\beta_T \end{pmatrix}. \tag{3.25b}$$

If we invert the 2×2 matrix of Eq. (3.25b),

$$(\mathbf{G}^{-1})^{-1} = \mathbf{G} = G\begin{pmatrix} V\beta_T & -V\alpha_P \\ -V\alpha_P & C_P/T \end{pmatrix}, \tag{3.26}$$

and compare element-by-element with Eq. (3.25a), we read off the equations

$$G = \frac{T/C_V}{V\beta_T} = \frac{T/\Gamma_V}{V\alpha_P} = \frac{1/V\beta_S}{C_P/T}, \tag{3.27}$$

from which follow the identities

$$C_V\beta_T = \alpha_P\Gamma_V = C_P\beta_S = T/VG, \tag{3.28}$$

where $G = \det\lvert\mathbf{G}\rvert$ is the Gramian. Generally speaking, it is clear that the three independent equations in (3.28) would be sufficient to express any of the six properties C_P, C_V, β_T, β_S, α_P, Γ_V in terms of any chosen set of *three* independent responses, as we were led to expect from the "$r(r+1)/2$ rule."

IV. GENERAL TRANSFORMATION THEORY IN $\mathcal{M}_r$

While the discussion has thus far been largely confined to a specific set of reference fields and extensities, equations such as (2.14) make clear the possibility of treating more general types of thermodynamic variations. Transformations among thermodynamic variables will correspond to ordinary vector transformations in Euclidean space, and are therefore treated simply and systematically in the geometric formalism.

An application of Eq. (2.14) has already been seen in Eq. (3.2), where a specified linear combination of field variations was found to be associated with variations of an extensive coordinate. Such linear combinations of field variables would also be necessary to represent variations along a coexistence curve, or, indeed, along any path in phase space which is not parallel to one of the axes. An additional incentive to incorporate these more general variations is based on purely experimental considerations; as remarked in Paper I, the variables which are practically under an experimenter's control may involve simultaneous changes of two or more "reference" variables, and would thus require representation in the more general form of Eq. (2.14). It is therefore desirable that general expressions be available which allow easy transformation from one "coordinate system" to another.

To develop such transformation properties of $\mathcal{M}_r$, we now consider the simultaneous transformations of the r reference fields R_i which are generated by some arbitrary (but nonsingular) real $r\times r$ matrix $\mathbf{A}$,

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12}\cdots & a_{1r} \\ a_{21} & a_{22}\cdots & a_{2r} \\ \vdots & \vdots & \vdots \\ a_{r1} & a_{r2}\cdots & a_{rr} \end{pmatrix} \quad (\det\lvert\mathbf{A}\rvert \neq 0), \tag{4.1}$$

whose ith row will be denoted $\mathbf{a}_i$,

$$(\mathbf{A})_{ij} = (\mathbf{a}_i)_j. \tag{4.2}$$

The transformed field variables generated by this matrix are denoted $R_{\mathbf{a}_i}$ [cf. Eq. (2.14)], and take the form

$$R_{\mathbf{a}_i} = \sum_{j=1}^{r} (\mathbf{a}_i)_j R_j, \quad i = 1, 2, \ldots, r. \tag{4.3}$$

The reference fields R_i and transformed fields $R_{\mathbf{a}_i}$ may be gathered into column vectors $\mathbf{R}$ and $\mathbf{R}_\mathbf{A}$, respectively,

$$\mathbf{R} = \begin{pmatrix} R_1 \\ R_2 \\ \vdots \\ R_r \end{pmatrix}, \quad \mathbf{R}_\mathbf{A} = \begin{pmatrix} R_{\mathbf{a}_1} \\ R_{\mathbf{a}_2} \\ \vdots \\ R_{\mathbf{a}_r} \end{pmatrix}, \tag{4.4}$$

in such a manner that the overall transformation takes the form

$$\mathbf{R}_\mathbf{A} = \mathbf{A}\mathbf{R}. \tag{4.5}$$

In this notation, for example, Eqs. (3.2) become [using Eq. (3.9)]

$$\overline{\mathbf{R}} = \overline{\mathbf{G}}\mathbf{R}, \tag{4.6a}$$

that is,

$$\overline{\mathbf{R}} = \mathbf{R}_{\overline{\mathbf{G}}}, \tag{4.6b}$$

where $\overline{\mathbf{R}}$ is a column vector of the conjugate variables $\overline{\mathbf{R}}_i$,

$$\overline{\mathbf{R}} = \begin{pmatrix} \overline{R}_1 \\ \overline{R}_2 \\ \vdots \\ \overline{R}_r \end{pmatrix}. \tag{4.7}$$

Given a set $\mathbf{R}_\mathbf{A}$ of transformed field variables, we should naturally seek expressions for the corresponding *conjugate* variables $\overline{R}_{\mathbf{A}_i}$, which satisfy

$$R_{\mathbf{A}_i} = \left(\frac{\partial U}{\partial \overline{R}_{\mathbf{A}_i}}\right)_{\overline{\mathbf{R}}_\mathbf{A}}, \quad i = 1, 2, \ldots, r. \tag{4.8}$$

The considerations which led to Eqs. (3.2) and (4.6) now give

$$\overline{\mathbf{R}}_\mathbf{A} = \overline{\mathbf{G}}_\mathbf{A}\mathbf{R}_\mathbf{A}, \tag{4.9}$$

where $\overline{\mathbf{R}}_\mathbf{A}$ is the column vector of the $\overline{R}_{\mathbf{A}_i}$'s and $\mathbf{G}_\mathbf{A}$ is the Gram matrix for the transformed field variables,

$$(\mathbf{G}_\mathbf{A})_{ij} = \langle \mathcal{R}_{\mathbf{A}_i} | \mathcal{R}_{\mathbf{A}_j} \rangle, \quad i, j = 1, 2, \ldots, r. \tag{4.10}$$

Equation (2.16) shows that this transformed Gram matrix is simply

$$\mathbf{G}_\mathbf{A} = \mathbf{A}\mathbf{G}\mathbf{A}^t. \tag{4.11}$$

If we now introduce the *conjugate* (inverse transpose) matrix $\overline{\mathbf{A}}$ [cf. Eq. (13) of Paper I],

$$\overline{\mathbf{A}} \equiv (\mathbf{A}^{-1})^t = (\mathbf{A}^t)^{-1}, \tag{4.12}$$

and employ Eq. (4.6a), we obtain Eq. (4.9) in the form

$$\overline{\mathbf{R}}_\mathbf{A} = \overline{\mathbf{A}}\overline{\mathbf{R}}, \tag{4.13}$$

which is apparently the "conjugate" of Eq. (4.5). The conjugacy relation (4.12) for matrices is readily seen to have the properties [cf. Eq. (3.6)]

$$\overline{\overline{\mathbf{A}}} = \mathbf{A}, \tag{4.14}$$

$$\overline{(\mathbf{A}\mathbf{B})} = \overline{\mathbf{A}}\,\overline{\mathbf{B}}. \tag{4.15}$$

Property (4.15) then permits one to easily rewrite equations in their "conjugate" form; for example, Eq. (4.11) becomes

$$\overline{\mathbf{G}}_\mathbf{A} = \overline{\mathbf{A}}\,\overline{\mathbf{G}}\,\overline{\mathbf{A}}^t, \tag{4.16}$$

and so forth. For completeness, we remark finally that scalar products among the transformed variables become completely analogous to the corresponding Eqs. (2.13a), (3.1), and (3.7) when expressed in terms of the ordinary differential formalism, *viz.*,

$$\langle \mathcal{R}_{\mathbf{A}_i} | \mathcal{R}_{\mathbf{A}_j} \rangle = \left(\frac{\partial R_{\mathbf{A}_i}}{\partial \overline{R}_{\mathbf{A}_j}}\right)_{\overline{\mathbf{R}}_\mathbf{A}} = (\mathbf{G}_\mathbf{A})_{ij}, \tag{4.17a}$$

$$\langle \overline{\mathcal{R}}_{\mathbf{A}_i} | \overline{\mathcal{R}}_{\mathbf{A}_j} \rangle = \left(\frac{\partial \overline{R}_{\mathbf{A}_i}}{\partial R_{\mathbf{A}_j}}\right)_{\mathbf{R}_\mathbf{A}} = (\overline{\mathbf{G}}_\mathbf{A})_{ij}, \tag{4.17b}$$

$$\langle \overline{\mathcal{R}}_{\mathbf{A}_i} | \mathcal{R}_{\mathbf{A}_j} \rangle = \delta_{ij}. \tag{4.17c}$$

Example: Saturation Properties

We shall again illustrate these general ideas with the help of a specific example. Suppose that in place of the standard properties C_P and α_P (P = constant) we now wish to consider the analogous *saturation properties* C_σ and α_σ (see, e.g., Rowlinson[16]),

$$C_\sigma = T\left(\frac{\partial S}{\partial T}\right)_\sigma, \quad \alpha_\sigma = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_\sigma, \tag{4.18}$$

for a saturated fluid along its vapor-pressure curve (σ = constant). To deal with such properties, we shall wish to transform from the old reference fields

$$\begin{pmatrix} R_1 \\ R_2 \end{pmatrix} = \begin{pmatrix} T \\ -P \end{pmatrix} \tag{4.19a}$$

to a new set

$$\begin{pmatrix} R_1' \\ R_2' \end{pmatrix} = \begin{pmatrix} T \\ \sigma \end{pmatrix}, \tag{4.19b}$$

in which the "coexistence coordinate" σ is itself a variable. If $\mathbf{A}$ is the transformation from old fields to new,

$$\begin{pmatrix} R_1' \\ R_2' \end{pmatrix} = \mathbf{A}\begin{pmatrix} R_1 \\ R_2 \end{pmatrix}, \tag{4.20}$$

then the new Gram matrix $\mathbf{G}'$ is obtained from the old by Eq. (4.11),

$$\mathbf{G}' = \mathbf{A}\,\mathbf{G}\mathbf{A}^t. \tag{4.21}$$

Suppose γ_σ represents the slope of the coexistence curve in a conventional PT plot, so that, by definition,

$$(\partial P/\partial T)_\sigma = \gamma_\sigma. \tag{4.22}$$

The coexistence coordinate σ is therefore composed from the old fields T and $-P$ by the equation[17,18]

$$|\sigma\rangle = \gamma_\sigma |\mathcal{T}\rangle + |-\mathcal{P}\rangle, \tag{4.23}$$

and the transformation matrix $\mathbf{A}$ is therefore

$$\mathbf{A} = \begin{pmatrix} 1 & 0 \\ \gamma_\sigma & 1 \end{pmatrix}, \tag{4.24a}$$

with conjugate

$$\overline{\mathbf{A}} = \begin{pmatrix} 1 & -\gamma_\sigma \\ 0 & 1 \end{pmatrix}. \tag{4.24b}$$

The extensities X_1' and X_2' conjugate to R_1' and R_2' are accordingly, by Eq. (4.13),

$$\begin{pmatrix} \overline{T} \\ \overline{\sigma} \end{pmatrix} = \begin{pmatrix} X_1' \\ X_2' \end{pmatrix} = \overline{\mathbf{A}}\begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = \begin{pmatrix} S - \gamma_\sigma V \\ V \end{pmatrix}. \tag{4.25}$$

Of course, γ_σ is merely a numerical constant for the particular thermodynamic state under consideration.

Since the properties (4.18) of interest require derivatives with respect to fields T and σ, we shall look for the inverse Gram matrix $(\mathbf{G}')^{-1} = \bar{\mathbf{G}}'$, according to Eq. (4.17b):

$$\bar{\mathbf{G}}' = \begin{pmatrix} \left(\frac{\partial X_1'}{\partial R_1'}\right)_{R_2'} & \left(\frac{\partial X_2'}{\partial R_1'}\right)_{R_2'} \\ \left(\frac{\partial X_1'}{\partial R_2'}\right)_{R_1'} & \left(\frac{\partial X_2'}{\partial R_2'}\right)_{R_1'} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{C_\sigma}{T} - V\gamma_\sigma\alpha_\sigma & V\alpha_\sigma \\ V\alpha_\sigma & \left(\frac{\partial V}{\partial \sigma}\right)_T \end{pmatrix} . \tag{4.26}$$

However, $\bar{\mathbf{G}}'$ can also be written from Eq. (4.21) as

$$\bar{\mathbf{G}}' = \bar{\mathbf{A}}\,\bar{\mathbf{G}}\,\bar{\mathbf{A}}^t$$

$$= \begin{pmatrix} 1 & -\gamma_\sigma \\ 0 & 1 \end{pmatrix} \begin{pmatrix} C_P/T & V\alpha_P \\ V\alpha_P & V\beta_T \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -\gamma_\sigma & 1 \end{pmatrix}$$

$$= \begin{pmatrix} \frac{C_P}{T} - 2V\gamma_\sigma\alpha_P + V\gamma_\sigma^2\beta_T & V\alpha_P - V\gamma_\sigma\beta_T \\ V\alpha_P - V\gamma_\sigma\beta_T & V\beta_T \end{pmatrix} . \tag{4.27}$$

Element-by-element comparison of Eqs. (4.26) and (4.27) then gives the desired identities,

$$\alpha_\sigma = \alpha_P - \gamma_\sigma\beta_T, \tag{4.28a}$$

$$C_\sigma = C_P - TV\gamma_\sigma\alpha_P, \tag{4.28b}$$

$$(\partial V/\partial\sigma)_T = V\beta_T. \tag{4.28c}$$

Equation (4.28a) and (4.28b) are, of course, well known,[16] but their derivation here illustrates rather general and systematic algebraic procedures which may be expected to retain their effectiveness when more traditional manipulations would be excessively cumbersome.

V. NORMAL FIELDS

Since the field vectors $|\mathcal{R}_{\ast_i}\rangle$ are in general neither orthogonal nor normalized, it is of interest to identify that particular choice of $\mathbf{A}$ for which these vectors become an *orthonormal* set. Such orthonormal field vectors will be called the *normal fields*[19] and denoted $|\mathcal{E}_i\rangle$, with associated normal field variable E_i. The desired transformation therefore takes the form

$$|\mathcal{E}_i\rangle = \sum_{j=1}^{r} (\mathbf{A})_{ij}\,|\mathcal{R}_j\rangle, \quad i = 1, 2, \ldots, r \tag{5.1}$$

where, by definition,

$$\langle\mathcal{E}_i|\mathcal{E}_j\rangle = \delta_{ij}. \tag{5.2}$$

We note first that the matrix $\mathbf{A}$ leading to normal fields (5.1) is not uniquely defined, for if $\mathbf{O}$ is any *orthogonal* matrix, satisfying

$$\mathbf{O}^t = \mathbf{O}^{-1}, \tag{5.3}$$

then the substitution

$$\mathbf{A} \rightarrow \mathbf{O}\mathbf{A} \tag{5.4}$$

in Eq. (5.1) leaves the orthonormality property (5.2) unaffected. When Eqs. (5.1) are inverted for the reference fields $|\mathcal{R}_i\rangle$,

$$|\mathcal{R}_i\rangle = \sum_{j=1}^{r} (\mathbf{A}^{-1})_{ij}\,|\mathcal{E}_j\rangle, \quad i = 1, 2, \ldots, r \tag{5.5}$$

it is apparent that substitution (5.4) cannot affect any scalar products $\langle\mathcal{R}_i|\mathcal{R}_j\rangle$ (which are the only observables in this formalism), and hence should not be ascribed any physical significance. The orthogonal matrix $\mathbf{O}$ can therefore be chosen for convenience (e.g., to simplify $\mathbf{A}$) without essential loss of generality; it merely reflects the usual freedom to arbitrarily rotate Cartesian axes in an ordinary Euclidean space.

The defining property (5.2) establishes, in conjunction with Eq. (3.1), that the normal fields are *self-conjugate*,

$$|\mathcal{E}_i\rangle = |\bar{\mathcal{E}}_i\rangle \tag{5.6a}$$

$$E_i = (\partial U/\partial E_i)_{\mathbf{E}}, \quad i = 1, 2, \ldots, r \tag{5.6b}$$

that is, they represent the particular choice of variables $\{R_{\ast_i}\}$ for which $R_{\ast_i}$ and $\bar{R}_{\ast_i}$ coincide for each i,

$$\mathbf{R}_{\mathbf{A}} = \bar{\mathbf{R}}_{\mathbf{A}}. \tag{5.7}$$

Equation (4.9) shows that the desired matrix $\mathbf{A}$ must therefore satisfy

$$\bar{\mathbf{G}}_{\mathbf{A}} = \mathbf{I}, \tag{5.8}$$

or, from Eq. (4.16),

$$\mathbf{A}^t\mathbf{A} = \mathbf{G}^{-1}, \tag{5.9}$$

where again the invariance to substitution (5.4) is manifest.

Let us now introduce the orthogonal matrix $\mathbf{Q}$, with rows $\mathbf{q}_i$,

$$(\mathbf{Q})_{ij} = (\mathbf{q}_i)_j \quad (\mathbf{Q}^t = \mathbf{Q}^{-1}), \tag{5.10}$$

which transforms the (real symmetric) Gram matrix $\mathbf{G}$ to its diagonal matrix of eigenvalues $\boldsymbol{\kappa}$,

$$\mathbf{Q}\mathbf{G}\mathbf{Q}^t = \boldsymbol{\kappa}, \tag{5.11a}$$

$$(\boldsymbol{\kappa})_{ij} = \kappa_i\delta_{ij}, \quad i, j = 1, 2, \ldots, r. \tag{5.11b}$$

It follows from Eqs. (5.11) that

$$\mathbf{G}^{-1} = (\mathbf{Q}^t\boldsymbol{\kappa}\mathbf{Q})^{-1} = (\boldsymbol{\kappa}^{-1/2}\mathbf{Q})^t(\boldsymbol{\kappa}^{-1/2}\mathbf{Q}), \tag{5.12}$$

where the (diagonal) square root matrix $\boldsymbol{\kappa}^{-1/2}$ is

$$(\boldsymbol{\kappa}^{-1/2})_{ij} = \kappa_i^{-1/2}\delta_{ij}, \tag{5.13}$$

and where (say) the positive square root of each real positive κ_i is to be taken. Equations (5.9) and (5.12) evidently have the solution

$$\mathbf{A} = \boldsymbol{\kappa}^{-1/2}\mathbf{Q}, \tag{5.14}$$

which is unique up to the arbitrary orthogonal transformation discussed in (5.4). In terms of the eigenvalues κ_i and eigenvectors $\mathbf{q}_i$ of the Gram matrix $\mathbf{G}$,

$$\mathbf{G}\mathbf{q}_i = \kappa_i\mathbf{q}_i, \quad i = 1, 2, \ldots, r \tag{5.15}$$

the normal field vectors are therefore

$$|\mathcal{E}_i\rangle = \sum_{j=1}^{r} \kappa_i^{-1/2}(\mathbf{q}_i)_j\,|\mathcal{R}_j\rangle, \quad i = 1, 2, \ldots, r. \tag{5.16}$$

Each reference field $|\mathcal{R}_i\rangle$ can in turn be expanded in terms of the normal fields $|\mathcal{E}_j\rangle$ to give

$$|\mathcal{R}_i\rangle = \sum_{j=1}^{r} \kappa_j^{1/2} (\mathbf{q}_j)_i \, |\mathcal{E}_j\rangle, \tag{5.17a}$$

$$|\overline{\mathcal{R}}_i\rangle = \sum_{j=1}^{r} \kappa_j^{-1/2} (\mathbf{q}_j)_i \, |\mathcal{E}_j\rangle, \quad i = 1, 2, \ldots, r. \tag{5.17b}$$

Equations (5.17) provide useful starting points for obtaining explicit representations of the abstract $|\mathcal{R}_i\rangle$ and $|\overline{\mathcal{R}}_i\rangle$ as ordinary column vectors. It will often be convenient, for example, to represent the normal fields $|\mathcal{E}_i\rangle$ as the unit column vectors,

$$|\mathcal{E}_1\rangle = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad |\mathcal{E}_2\rangle = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix}, \quad \ldots, \quad |\mathcal{E}_r\rangle = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix}, \tag{5.18}$$

so that each $|\mathcal{R}_i\rangle$ and $|\overline{\mathcal{R}}_i\rangle$ takes on a corresponding representation whose vector elements depend explicitly on κ_j's and $\mathbf{q}_j$'s in a prescribed manner.

VI. STABILITY CONDITIONS

The second law of thermodynamics is known to imply certain rigorous inequalities among thermodynamic properties, such as

$$C_P \geq C_V, \tag{6.1}$$

$$C_P \beta_T \geq TV\alpha_P^2, \tag{6.2}$$

etc. Such *stability conditions* serve to ensure the maximization of entropy at constant energy (or minimization of energy at constant entropy) which is embodied in the second law. It is well know, for example, that the theoretical "van der Waals gas" cannot everywhere satisfy such stability conditions, and to this extent is incompatible with basic laws of thermodynamics. Inequalities such as (6.1) and (6.2) can thus serve as a useful check on microscopic models of fluids, on proposed functional forms for equations of state, or on the experimental data themselves for consistency with broad thermodynamic principles. The magnetic analog of inequality (6.2), for example, has played an important role (expressed in the form of "Rushbrooke's inequality" for critical exponents[20]) in recent theoretical and experimental studies on critical phenomena.[21]

In the geometric representation, where laws of thermodynamics appear only as "rules of geometry," all such stability conditions arise merely as instances of the *Schwarz inequality* in the vector space $\mathfrak{M}_r$.

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle^2 \leq \langle \mathcal{R}_i | \mathcal{R}_i \rangle \langle \mathcal{R}_j | \mathcal{R}_j \rangle. \tag{6.3a}$$

The Schwarz inequality (6.3a) can equivalently be expressed as the condition

$$\langle \mathcal{R}_{\boldsymbol{\alpha}} | \mathcal{R}_{\boldsymbol{\alpha}} \rangle \geq 0, \quad \text{all } \boldsymbol{\alpha} \tag{6.3b}$$

or again as the elementary geometric proposition

$$-1 \leq \cos\theta_{ij} \leq 1 \quad (\cos\theta_{ii} = 1), \tag{6.3c}$$

in terms of the "angles" θ_{ij} defined in Eq. (2.9).

For example, when inequality (6.3c) is applied to the angle θ_{ST} between the entropy and temperature vectors [cf. Eq. (3.21)],

$$-1 \leq \cos\theta_{ST} = (C_V/C_P)^{1/2} \leq 1, \tag{6.4}$$

one obtains directly the stability condition (6.1). Similarly, application of (6.3c) to the angle θ_{SV} of Eq. (3.20) leads directly to inequality (6.2). If we apply (6.3b) successively to the vectors $|\mathcal{T}\rangle$, $|\mathcal{P}\rangle$, $|\mathcal{S}\rangle$, and $|\mathcal{V}\rangle$, the results are (since $T > 0$, $V > 0$)

$$C_V \geq 0, \;\; \beta_S \geq 0, \;\; C_P \geq 0, \;\; \beta_T \geq 0, \tag{6.5}$$

which are again well known consequences of the second law. Stability conditions which are not so well known can be obtained by easy analogy. For example, if we consider the angle between the vectors $|\overline{\mathcal{T}}\rangle$ and $|\bar{\sigma}\rangle$ of Eq. (4.25), the result is

$$C_\sigma \geq TV\alpha_\sigma(\gamma_\sigma + \alpha_\sigma/\beta_T), \tag{6.6}$$

and so forth.

Of course, no more than a few of the stability conditions given above are independent, since in principle one could use identities like Eqs. (3.28) or (4.28) to deduce some of these inequalities in terms of others. It is easy to recognize from the form (6.3b) that exactly r such inequalities will suffice in general, since (6.3b) is the condition [cf. Eq. (2.16)] that the matrix $\mathbf{G}$ be positive semidefinite,[22]

$$\boldsymbol{\alpha}^t \mathbf{G} \boldsymbol{\alpha} \geq 0, \quad \text{all } \boldsymbol{\alpha} \tag{6.7a}$$

which in turn is equivalent to the non-negativity of its r eigenvalues κ_i,

$$\kappa_1 \geq 0, \;\; \kappa_2 \geq 0, \;\; \ldots, \;\; \kappa_r \geq 0. \tag{6.7b}$$

Of course, the r inequalities (6.7b) are only one of many possible minimal sets one might choose to express overall stability; for this reason, one may prefer to regard the Schwarz inequality itself, e.g., inequality (6.3c), as the more general and transparent expression of the constraints imposed by thermodynamic stability.

VII. CONCLUSION

The general outlines of an alternative representation of equilibrium thermodynamics have been sketched and illustrated in a simplified manner. In the present work we have sought principally to show how *known* thermodynamic identities, stability conditions, and other relationships arise in a unified way from the elementary geometry of the thermodynamic vectors, but the possibility for significant extension of the classical formalism appears at several junctures [as in the use of *normal* field variables, or in the geometric evaluation of general response functions, as described in the following paper (Paper IV)]. In respect to the convenience of its underlying vector-algebraic methods, the new representation appears to compare favorably with the traditional formalism of partial differential equations. The algebraic techniques of the present approach, for example, seem particularly susceptible to systematic application in complex multicomponent chemical systems, where portions of the traditional formalism become exceedingly cumbersome.

ACKNOWLEDGMENTS

The author extends sincere thanks to Professor Hans C. Andersen and Dr. Suzanne Hudson for encouragement and discussions.

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[1] F. Weinhold, J. Chem. Phys. **63**, 2479 (1975) (second preceding paper, hereafter referred to as Paper I).

[2] F. Weinhold, J. Chem. Phys. **63**, 2484 (1975) (preceding paper, hereafter referred to as Paper II).

[3] J. W. Gibbs, *Collected Works* (Longmans, Green, and Co., New York, 1928), Vol. I.

[4] See, e.g., H. B. Callen, *Thermodynamics* (Wiley, New York, 1960); L. Tisza, *Generalized Thermodynamics* (MIT, Cambridge, 1966).

[5] R. B. Griffiths and J. E. Wheeler, Phys. Rev. A **2**, 1047 (1970).

[6] For the general properties of Euclidean vector spaces, see, e.g., G. E. Shilov, *An Introduction to the Theory of Linear Spaces* (Prentice Hall, Englewood Cliffs, 1961). It may be noted that the entire formalism permits easy generalization to a *complex* space, but the elementary thermodynamics of simple systems does not appear to require this greater generality.

[7] We adopt the term "response functions" (rather loosely) for such general thermodynamic derivatives as in Eq. (2.7), as suggested, e.g., by H. E. Stanley, *An Introduction to Phase Transitions and Critical Phenomena* (Oxford University, New York, 1971), p. 28.

[8] Such partial derivatives are, of course, to be evaluated at the point $\mathbf{X}=\boldsymbol{\xi}$, corresponding to the particular state of interest, so that each $\langle\mathcal{R}_i|\mathcal{R}_j\rangle$ is simply a scalar.

[9] And, of course, with the classical formalism which is based on those laws.

[10] The central role of what we have here called the "Gram determinant," Eq. (2.13c), was already apparent to Gibbs (see Ref. 3, p. 111ff.), and such a determinant likewise appears prominently in the "neo-Gibbsian" formalism of Tisza and Callen (see Ref. 4).

[11] See, e.g., F. H. Crawford, Phys. Rev. **72**, 521A (1947).

[12] This can be confirmed by noting that Eqs. (3.2), in the form

$$dR_i=\sum_{j=1}^{r}(\mathbf{G})_{ij}\,d\bar{R}_j,\quad i=1,2,\ldots,r$$

have the same form as the equations resulting from differentiating $R_i=R_i(X_1,X_2,\ldots,X_r)$ directly,

$$dR_i=\sum_{j=1}^{r}\left(\frac{\partial R_i}{\partial X_j}\right)_{\mathbf{x}}dX_j,\quad i=1,2,\ldots,r$$

so that Eq. (3.4) will follow by construction.

[13] This could also be seen directly from the equations of Ref. 12.

[14] F. Weinhold, J. Chem. Phys. **62**, (1975) (following paper, hereafter referred to as Paper IV).

[15] This assymetry goes back essentially to the Gibbs phase rule, and is reflected in our initial choice of *fields* as basic elements of $\mathfrak{M}_r$. The reader may remark that the formal construction of a metric space in Paper I, which could be called the "(U,X_i,R_i) construction," might also have been attempted with a "(U_L,R_i,X_i) construction," in which roles of R_i and X_i are exchanged, and U is everywhere replaced by its Legendre transform U_L (essentially, a Gibbs free energy.) (As we shall see below, the second construction would merely identify $\mathbf{G}^{-1}$ rather than $\mathbf{G}$ as "Gram matrix" for the "space," and so could not lead to additional information, even if acceptable on other grounds.) The chosen (U,X_i,R_i) construction is, however, dictated on physical grounds, inasmuch as it is the number of independent *field* variables which is enumerated by the Gibbs phase rule, and which therefore comes to have dimensional significance. Hence, Gibbs' number r of "degrees of freedom" is to be associated with rank($\mathbf{G}$), the number of independent *field* variables, rather than with rank($\mathbf{G}^{-1}$), which cannot even be defined for certain states of interest.

[16] J. T. Rowlinson, *Liquids and Liquid Mixtures* (Academic, New York, 1959), Chap. 2.

[17] It can be seen that Eq. (4.22) determines the coefficients in Eq. (4.23) only up to a multiplicative constant. This has been chosen so that V (rather than a multiple thereof) becomes one of the conjugate variables in Eq. (4.25).

[18] We may remark parenthetically on certain dimensional questions which may be raised by vector equations such as (2.14) or (4.23). Because each vector $|\mathcal{R}_i\rangle$ apparently carries physical *units* (since its "length," Eq. (2.8), depends on the units in which the response function $\partial R_i/\partial X_i$ is measured), it might superficially appear that vector Eq. (2.14) is rendered meaningless on dimensional grounds. That this is incorrect can be seen in Eq. (2.15), where the coefficients α_i of such vectors will themselves be seen to "carry units" in a manner which removes any potential inconsistencies.
One can appreciate in Eq. (4.23) the intrinsic physical significance which the coexistence coordinate σ possesses (in a real physical phase diagram, for example), even though it involves simultaneous changes of coordinates having different units (so that its own "units" would be difficult to discuss); if $|\mathcal{T}\rangle$ and $|\mathcal{P}\rangle$ were measured in different units, the numerical value of the coefficient γ_σ would readjust to represent the same *physical* coordinate, so that no mathematical or physical inconsistency could result. As remarked in Sec. II, lengths in $\mathfrak{M}_r$ depend (consistently) on the units in which measured response functions are expressed, whereas internal angles are intrinsic invariants of the system.

[19] The term "normal" for these fields may be taken to suggest certain analogies with the "normal coordinates" (or "normal modes") in the theory of elastic vibrations. (One might also choose the term "principal field," to suggest the analogy with principal axes of a geometric figure.)

[20] G. S. Rushbrooke, J. Chem. Phys. 39, 842 (1963).

[21] See, e.g., Stanley, Ref. 7, and references therein.

[22] It is clear that $\mathbf{G}$ must actually be positive definite under the assumptions (2.13b) and (2.13c) on its rank, so that the stability inequalities could all be sharpened to strict inequalities. However, provision for possible equality in such expressions permits one to take account of more general cases when $\mathbf{G}$ may not be of full rank (e.g., at critical points).