

Metric geometry of equilibrium thermodynamics. II. Scaling, homogeneity, and generalized Gibbs–Duhem relations

F. Weinhold

Department of Chemistry, Stanford University, Stanford, California 94305
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It is shown that the classical Gibbs–Duhem relation can be regarded, in the abstract metric framework proposed recently, as expressing the obvious geometric impossibility of finding $r + 1$ linearly independent vectors in an r -dimensional space. Certain connections between generalized Gibbs–Duhem relations and permissible scaling hypotheses for thermodynamic potentials are noted.

I. INTRODUCTION

In the preceding paper,¹ to be referred to as I, it was observed that the formalism of equilibrium thermodynamics exhibits a certain underlying geometric structure. It was shown that characteristic thermodynamic principles—empirical “laws” of universal experience—could be brought into correspondence with mathematical axioms of an abstract metric space. As a result, the thermodynamics of a given equilibrium state came to be formally associated with the geometry of an abstract Euclidean vector space. The present paper addresses certain additional features which such an abstract vector geometry must exhibit as a consequence of phase homogeneity, scale invariance, the extensive character of certain thermodynamic variables, and related aspects of a thermodynamic description.

Let us first recall that the construction of a thermodynamic metric space \mathfrak{M}_r of dimension r was carried out in Paper I on the basis of the following few thermodynamic principles:

(i) The Gibbs phase rule, e.g., the observation that equilibrium states are describable in terms of some small determinate number r of independent state variables.

(ii) The role of potentials, e.g., the observation that an equilibrium state can be mathematically characterized in terms of low-order derivatives of a thermodynamic potential (“fundamental equation”) U .

(iii) The first law, e.g., the observation that the potential U has an exact differential.

(iv) The second law, e.g., the observation that the potential U achieves an extremal value at equilibrium.

In a rough sense, it may be said that observation (i) led to the dimensionality of the proposed metric space \mathfrak{M}_r , while (ii), (iii), and (iv) led, respectively, to the distributive, symmetric, and positive character of the proposed scalar product in \mathfrak{M}_r . Clear distinction was drawn between the “extensivities” X_i , which served as arguments of the potential U ,

$$U = U(X_1, X_2, \dots, X_{r+1}), \quad (1)$$

and the conjugate “field”² variables,

$$R_i = \partial U / \partial X_i, \quad (2)$$

whose first differentials came to be associated with elements $|\mathcal{R}_i\rangle$ of the abstract vector space,

$$dR_i \leftrightarrow |\mathcal{R}_i\rangle \in \mathfrak{M}_r. \quad (3)$$

However, no direct account was taken of the extensive character of the X_i and of U (which will again be identified as internal energy), nor of the scale invariance³ and phase homogeneity which is observed (or assumed) to characterize macroscopic thermodynamic systems.⁴

In the classical treatments of thermodynamics, the extensive character of energy U , entropy S , volume V , mole numbers N_i , etc., is usually acknowledged at the outset. Thus, contributions to each X_i from various portions of the system are assumed to be simply additive, and total X_i is taken to be directly proportional to the overall scale of the system, i.e., to total mass or volume. These assumptions are usually expressed in terms of the first-order homogeneity of the energy function,

$$U(\lambda X_1, \lambda X_2, \dots, \lambda X_{r+1}) = \lambda U(X_1, X_2, \dots, X_{r+1}), \quad (4)$$

or the zero-order homogeneity of the field functions,

$$R_i(\lambda X_1, \lambda X_2, \dots, \lambda X_{r+1}) = R_i(X_1, X_2, \dots, X_{r+1}), \quad (5)$$

for all $\lambda > 0$. Such equations lead in a familiar fashion,⁵ through application of Euler’s theorem on homogeneous forms, to the *Gibbs–Duhem equation*,

$$0 = \sum_{i=1}^{r+1} X_i dR_i = \sum_{i=1}^{r+1} \xi_i dR_i, \quad (6)$$

which plays a key role in the Gibbsian analysis. (As in Paper I, ξ_i will be used to represent the numerical value assumed by the variable X_i in the state in question, and we shall again speak of the “point” ξ which labels this state, etc.) Homogeneity and additivity assumptions of the form (4) or (5) are thus deeply embedded in the classical formalism, though in real systems their validity might certainly be questioned, for example, in the limit of very small scale.⁶

In an abstract geometric representation, on the other hand, homogeneity assumptions play only a secondary role, but equations related to the Gibbs–Duhem equation (6) arise quite naturally and directly, as we shall subsequently describe. It will be shown that the metric framework permits one to significantly weaken assumptions (4) or (5) without significantly altering the basic formal structure. Certain general connections between the dimensional requirements of a metric space and possible scaling assumptions on a thermodynamic potential can thereby be clarified.

II. DIMENSIONALITY, LINEAR DEPENDENCE, AND GENERALIZED GIBBS-DUHEM RELATIONS

In the geometric representation, an equilibrium system consisting of c independent chemical components and ν phases is associated with an abstract geometric "image" in a metric space \mathfrak{M}_r of dimension r ,

$$r = c - \nu + 2. \tag{7}$$

Scalar products among the vector elements $|\mathcal{R}_i\rangle$ of this space are evaluated in terms of thermodynamic "response functions,"⁷

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle = \partial R_i / \partial X_j, \tag{8}$$

for the equilibrium state in question. While the vectors arise through the associations (3) and (8) in a somewhat abstract manner, they are isomorphic to vectors of an ordinary Euclidean space,⁸ and thus exhibit certain elementary properties which are characteristic of such spaces, and which we now briefly recall.⁹

If some collection of n such Euclidean vectors is chosen, the dimensionality of the manifold spanned by these vectors can be determined from the rank of the associated Gram matrix $\mathbf{G}^{(n)}$,

$$\dim \{ |\mathcal{R}_i\rangle, i = 1, 2, \dots, n \} = \text{rank}(\mathbf{G}^{(n)}), \tag{9}$$

whose elements are scalar products among the $|\mathcal{R}_i\rangle$,

$$(\mathbf{G}^{(n)})_{ij} = \langle \mathcal{R}_i | \mathcal{R}_j \rangle, \quad i, j = 1, 2, \dots, n. \tag{10}$$

The associated Gramian determinant $G^{(n)}$,

$$G^{(n)} = \det | \mathbf{G}^{(n)} |, \tag{11}$$

measures the (squared) volume of the parallelepiped generated by the $|\mathcal{R}_i\rangle$, and is thus a measure of their degree of linear dependence or independence. Thus, the Gramian vanishes,

$$G^{(n)} = 0, \tag{12}$$

if and only if the number n of vectors exceeds the dimension of the manifold,

$$n > \text{rank}(\mathbf{G}^{(n)}), \tag{13}$$

and it is therefore possible to find coefficients η_i , not all zero, such that

$$\sum_{i=1}^n \eta_i |\mathcal{R}_i\rangle = 0. \tag{14}$$

If Eq. (14) is multiplied successively by $\langle \mathcal{R}_j |$, $j = 1, 2, \dots, n$, one obtains a set of linear equations which can be written in matrix form as

$$\mathbf{G}^{(n)} \boldsymbol{\eta} = 0, \tag{15}$$

so that the vector $\boldsymbol{\eta} = \{\eta_i\}$ of coefficients in (14) is seen to form a null eigenvector of the singular matrix $\mathbf{G}^{(n)}$. The intrinsic dimensionality r of the full space \mathfrak{M}_r furthermore imposes the condition

$$\text{rank}(\mathbf{G}^{(n)}) \leq r = \dim(\mathfrak{M}_r) \tag{16}$$

for every n . If $n > r$, $\mathbf{G}^{(n)}$ must therefore have at least $n - r$ vanishing eigenvalues and corresponding null eigenvectors satisfying (15).

In the thermodynamic context, elements of \mathfrak{M}_r arise [through the association (3)] as partial derivatives of the potential U of Eq. (1). Although the r field vectors $|\mathcal{R}_i\rangle$ (temperature, pressure, etc.) arising from a "scaled" U (e.g., with constant scale factor X_{r+1}) may be considered sufficient to span the space \mathfrak{M}_r , one can introduce as well the additional field variable R_{r+1} (a chemical potential, if X_{r+1} is a mass variable),

$$R_{r+1} = \partial U / \partial X_{r+1}, \tag{17}$$

and corresponding field vector $|\mathcal{R}_{r+1}\rangle$ in a completely analogous manner. The corresponding Gram matrix $\mathbf{G}^{(r+1)}$ associated with the manifold of $r+1$ field vectors,

$$(\mathbf{G}^{(r+1)})_{ij} = \langle \mathcal{R}_i | \mathcal{R}_j \rangle, \quad i, j = 1, 2, \dots, r+1, \tag{18}$$

must however satisfy condition (16),

$$\text{rank}(\mathbf{G}^{(r+1)}) = r \tag{19}$$

so that necessarily

$$G^{(r+1)} = \det | \mathbf{G}^{(r+1)} | = 0, \tag{20}$$

$$\mathbf{G}^{(r+1)} \boldsymbol{\eta} = 0, \tag{21}$$

$$\sum_{i=1}^{r+1} \eta_i |\mathcal{R}_i\rangle = 0, \tag{22}$$

in view of (12)–(15). Equations (20)–(22) are essentially equivalent statements expressing the obvious impossibility of having $r+1$ linearly independent vectors in an r -dimensional space.

The vanishing of the Gram determinant $G^{(r+1)}$, Eq. (20), may be regarded as a *generalized Gibbs–Duhem relation*. The equivalent equation (22) could be immediately recognized as the ordinary Gibbs–Duhem equation (6) if one recalls the association (3) and sets

$$\eta_i = \xi_i, \quad i = 1, 2, \dots, r+1. \tag{23}$$

We can therefore anticipate that the special identification (23) will follow when we introduce the specific homogeneity assumption (4) or (5) into the metric formalism, as the Gibbs–Duhem equation itself follows from such an assumption in the usual formalism. But an equation having the *general form* of the Gibbs–Duhem equation must hold more generally, since it is a simple consequence of dimensional considerations in the metric framework.

III. GIBBS-DUHEM EQUATION

To obtain the Gibbs–Duhem equation in its usual form, e.g.,

$$\sum_{i=1}^{r+1} \xi_i |\mathcal{R}_i\rangle = 0, \tag{24}$$

we should evaluate the additional elements of the augmented Gram matrix $\mathbf{G}^{(r+1)}$,

$$\begin{aligned} (\mathbf{G}^{(r+1)})_{i,r+1} &= \langle \mathcal{R}_i | \mathcal{R}_{r+1} \rangle \\ &= \left(\frac{\partial R_i}{\partial X_{r+1}} \right)_{x_1 \dots x_r}, \quad i = 1, 2, \dots, r+1, \end{aligned} \tag{25}$$

on the basis of the supposed homogeneity relations (4) or (5). If we set

$$\lambda = X_{r+1}^{-1}, \tag{26a}$$

$$Y_i = \lambda X_i, \quad i = 1, 2, \dots, r \tag{26b}$$

Eq. (5) says that

$$R_i(X_1, X_2, \dots, X_{r+1}) = R_i(Y_1, Y_2, \dots, Y_r, 1), \tag{27}$$

and hence, by the chain rule,

$$\frac{\partial R_i}{\partial X_{r+1}} = \sum_{j=1}^r \frac{\partial R_i}{\partial Y_j} \frac{\partial Y_j}{\partial X_{r+1}}. \tag{28}$$

Noting that

$$\left(\frac{\partial Y_j}{\partial X_{r+1}} \right)_{X_1 \dots X_r} = -Y_j / X_{r+1}, \tag{29a}$$

$$Y_j \frac{\partial R_i}{\partial Y_j} = X_j \frac{\partial R_i}{\partial X_j} \tag{29b}$$

for each $j = 1, 2, \dots, r$, we can put Eq. (28) in the form

$$\begin{aligned} \langle R_i | R_{r+1} \rangle &= -X_{r+1}^{-1} \sum_{j=1}^r X_j \langle R_i | R_j \rangle \\ &= -\xi_{r+1}^{-1} \sum_{j=1}^r (\mathbf{G}^{(r+1)})_{ij} \xi_j, \quad i = 1, 2, \dots, r+1 \end{aligned} \tag{30}$$

which is merely a way of rewriting the matrix equation

$$\mathbf{G}^{(r+1)} \boldsymbol{\xi} = 0. \tag{31}$$

Equation (31), when compared with (21), verifies that the Gibbs–Duhem relation, (23) or (24), is the explicit form taken by the general equations (20)–(22) when the potential U and fields R_i scale in the simple manner of (4) and (5).

IV. GENERALIZED HOMOGENEITY CONDITIONS

Let us return to the general equations (20)–(22) in the absence of any specific scaling assumptions. If we define the ratios $n_i, i = 1, 2, \dots, r+1$, such that

$$n_i = \eta_i / X_i = \eta_i / \xi_i \text{ at } \boldsymbol{\xi}, \tag{32}$$

then Eq. (21) can be rewritten in the form

$$\frac{\partial R_i}{\partial X_{r+1}} = \sum_{j=1}^r \left(-\frac{n_j}{n_{r+1}} \frac{X_j}{X_{r+1}} \right) \frac{\partial R_i}{\partial X_j} \text{ at } \boldsymbol{\xi}, \tag{33}$$

so long as $n_{r+1} \neq 0$. If now Y_j are r new variables,

$$Y_j = f_j(X_{r+1}) X_j, \quad j = 1, 2, \dots, r \tag{34}$$

related to the old X_j by some (as yet unspecified) function $f_j = f_j(X_{r+1})$ of the proposed scale factor, then, for each $j = 1, 2, \dots, r$,

$$X_j \left(\frac{\partial R_i}{\partial X_j} \right)_{X_1 \dots X_{j-1} X_{j+1} \dots X_{r+1}} = Y_j \left(\frac{\partial R_i}{\partial Y_j} \right)_{Y_1 \dots Y_{j-1} Y_{j+1} \dots Y_r}, \tag{35}$$

and Eq. (33) can be rewritten as

$$\frac{\partial R_i}{\partial X_{r+1}} = \sum_{j=1}^r \left(-\frac{n_j}{n_{r+1}} \frac{Y_j}{X_{r+1}} \right) \frac{\partial R_i}{\partial Y_j} = \sum_{j=1}^r \frac{\partial Y_j}{\partial X_{r+1}} \frac{\partial R_i}{\partial Y_j} \text{ at } \boldsymbol{\xi}, \tag{36}$$

provided that Y_j has been chosen to satisfy

$$\left(\frac{\partial Y_j}{\partial X_{r+1}} \right)_{X_1 \dots X_r} = -\frac{n_j}{n_{r+1}} \frac{Y_j}{X_{r+1}}, \quad j = 1, 2, \dots, r. \tag{37}$$

Now Eq. (36) is apparently the chain rule for a function having the special property (for $c_0 = \text{constant}$)

$$R_i(X_1, X_2, \dots, X_{r+1}) = R_i(Y_1, Y_2, \dots, Y_r, c_0) \text{ at } \boldsymbol{\xi}, \tag{38}$$

in some asymptotic sense about point $\boldsymbol{\xi}$. The functions f_j which lead to (37) and (38) must satisfy

$$\left(\frac{\partial \ln Y_j}{\partial \ln X_{r+1}} \right)_{X_1 \dots X_r} = \frac{d \ln f_j}{d \ln X_{r+1}} = \frac{-n_j}{n_{r+1}}, \tag{39}$$

and therefore have the form

$$f_j = c_j X_{r+1}^{-n_j/n_{r+1}}, \quad c_j = \text{constant}. \tag{40}$$

Equation (38) can therefore be written as

$$R_i(X_1, X_2, \dots, X_{r+1}) = R_i(\lambda^{n_1} X_1, \lambda^{n_2} X_2, \dots, \lambda^{n_{r+1}} X_{r+1}), \tag{41}$$

provided we define

$$\lambda^{n_{r+1}} = c_0 / X_{r+1}, \tag{42a}$$

$$c_j = c_0^{n_j/n_{r+1}}. \tag{42b}$$

Functions having the property (41) are called *generalized homogeneous functions* (of “scale-invariant” type).¹⁰ These represent a considerably broader class than do the ordinary homogeneous functions, to which they reduce in the special case

$$n_1 = n_2 = \dots = n_{r+1} = 1. \tag{43}$$

Of course, in this same case the starting equation (21) becomes equivalent to the ordinary Gibbs–Duhem equation (24).

Thus, equations of the form (20)–(22), which arise from elementary dimensional considerations, can be recast into forms which correspond to (e.g., appear to result from) thermodynamic potentials which are generalized homogeneous functions, or behave asymptotically as such in the neighborhood of the given equilibrium state. Generalized Gibbs–Duhem relations, or linear dependence conditions, might therefore be associated with more general scaling assumptions than the ordinary homogeneity condition (4) or (5).¹¹ However, it seems a significant advantage of the metric formalism that Gibbs–Duhem-like relations, expressing the interdependence of thermodynamic field variables, arise without reference to any specific scaling assumptions on the thermodynamic potential.

V. CONCLUSION

The foregoing analysis has suggested a generalized form of Gibbs–Duhem relation which can be regarded as expressing, from the abstract geometric point of view, the obvious impossibility of finding $r+1$ linearly independent vectors in an r -dimensional space. The precise form taken by such relations depends on the scaling behavior which is observed (or assumed) to characterize the thermodynamic potential U in the neighborhood of the given equilibrium state. If U scales in the usual manner as an ordinary homogeneous function, the linear dependence condition becomes the Gibbs–Duhem equation in its usual form. Moreover, the assumption that the Gibbs–Duhem relation takes its ordi-

nary form implies that U could not scale except in the ordinary way. However, the generalized Gibbs–Duhem relation, or linear dependence condition, was shown in the absence of any subsidiary assumptions to correspond to a form of generalized homogeneous behavior of the thermodynamic potential. The foregoing treatment therefore points to a close connection between simple geometric considerations of dimensionality, on the one hand, and possible scaling hypotheses¹² for thermodynamic potential functions, on the other.

The natural role played by Gibbs–Duhem relations in the metric framework suggests that other features of equilibrium thermodynamics might be perceived or analyzed as elementary geometric consequences of the underlying metric structure. Additional implications of this structure will be explored in forthcoming papers.

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¹F. Weinhold, *J. Chem. Phys.* **63**, 2479 (1975) (preceding paper).

²R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A* **2**, 1047

(1970).

³Some indirect account was taken, however, by assigning the “scale factor” X_{r+1} a fixed numerical value throughout Paper I.

⁴See, e.g., L. Tisza, *Generalized Thermodynamics* (MIT, Cambridge, 1966), p. 44.

⁵See, e.g., H. B. Callen, *Thermodynamics* (Wiley, New York, 1960), pp. 47–50.

⁶See, e.g., Tisza, Ref. 4, pp. 44 and 123; J. W. Gibbs, *Collected Works* (Longmans, Green, and Co., New York, 1928), Vol. I, pp. 74–77.

⁷For this terminology, cf. H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University, New York, 1971), p. 28.

⁸See Ref. 1, 30.

⁹For definitions and theorems cited in the following paragraph, see, e.g., L. Mirsky, *An Introduction to Linear Algebra* (Oxford University, New York, 1955), pp. 48ff, 137, and 149ff; G. E. Shilov, *An Introduction to the Theory of Linear Spaces* (Prentice Hall, Englewood Cliffs, 1961), pp. 167ff.

¹⁰See, e.g., A. Hankey and H. E. Stanley, *Phys. Rev. B* **6**, 3515 (1972), and references therein.

¹¹Note that the simple homogeneity property (4) or (5) is invariant to linear transformations among the X_i (such as were used in Paper I), whereas a generalized homogeneity property such as (38) is not, but must be referred to some specific choice of these variables.

¹²See, e.g., B. Widom, *J. Chem. Phys.* **43**, 3898 (1965); L. P. Kadanoff, *Physics* **2**, 263 (1966); R. B. Griffiths, *Phys. Rev.* **158**, 176 (1967); A. Hankey and H. E. Stanley, *Int. J. Quantum Chem. Symp.* **5**, 593 (1971).