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The geometry of thermodynamic potentials

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In this paper, the performance of a diagrammatic method based on geometric and algebraic considerations is illustrated. This method, based on the particular symmetry of a thermodynamic diagram, allows to obtain the most important thermodynamic expressions of a simple system. In fact, these thermodynamic expressions can be developed with the application of various geometric patterns to the proposed diagram. The particular symmetry of the thermodynamic diagram allows to develop a matrix formulation of the different geometric patterns. This matrix formalism requires that the thermodynamic parameters of the diagram be recast in a vectorial form.

1. Introduction

Recently, some studies of the application of pattern recognition to the problem of searching correlations among thermodynamic parameters have been reported [1–3]. Pattern recognition is a subfield of artificial intelligence and a large fraction of the effort in this area must be devoted to the recognition of appropriate geometric patterns from given relationships.

The purpose of this paper is to illustrate a geometric formalism that allows to derive the thermodynamic interrelationships of a simple system, which can also be encoded by the aid of a matrix formalism that is strictly related to the particular geometry of the thermodynamic diagram in table 1.

From the thermodynamic diagram 1 in tabe 1 (for details about this diagram we refer to [2] and references therein) a series of geometric patterns, N, P, M, F and b can be derived and used to obtain the most important thermodynamic expressions of simple systems. In fact, the various thermodynamic expressions result from the application of a series of operations of the geometric patterns in table 1, when they overlap diagram 1. The geometric form of the patterns are easy to remember as they trace the shape of a letter. This trace indicates the relation among the thermodynamic parameters and the sign of the variable is determined by the direction of the arrow of diagram 1.

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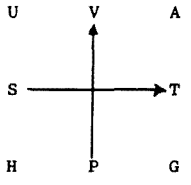
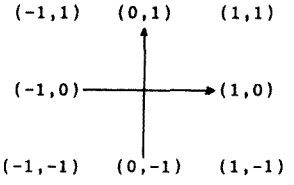
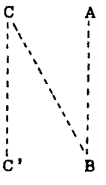
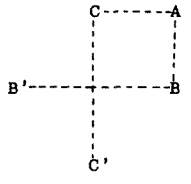
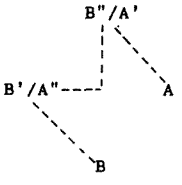
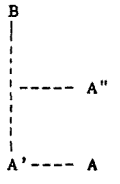
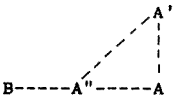
Table 1
The diagram for thermodynamic relationships (diagram 1), the vector diagram for thermodynamic relationships (diagram 2), and the geometric patterns N, P, M, F and b.

Diagram 1	Diagram 2	N
		

P	M	F	b
			

2. General formalism

In diagram 1 the thermodynamic parameters A, G, H, U, P, S, T and V represent Helmholtz free energy, Gibbs free energy, enthalpy, internal energy, pressure, entropy, temperature and volume [4]. The geometric formalism starts with the following series of rules, which after some practice are very easy to remember:

(a) Letters used to abbreviate thermodynamic parameters are placed at the corners (energy terms) and sides (non-energy terms) of the diagram (see diagram 1).

(b) To obtain an energy term from the variables in the diamond pattern, multiplication must occur between two variables along the same arrow.

(c) To generate the thermodynamic relationships, terms are used in alphabetical order and in unprimed, primed and twice primed order.

(d) When going from one term on an arrow to the other term on the same arrow, the sign is positive when the direction of tracing the letter approaches the arrowhead and negative when the same direction approaches the arrowtail.

The given geometric method is mainly based on the particular symmetry of the thermodynamic diagram, which can be used to derive a matrix formalism to obtain the different thermodynamic interrelationships if the parameters of the diagram are written in a vectorial form [3] as represented in diagram 2 of table 1. Here, parameters A, G, H, U, P, S, T and V are represented as two component (x, y) row matrices: $(1, 1)$, $(1, -1)$, $(-1, -1)$, $(-1, 0)$, $(0, -1)$, $(-1, 0)$, $(1, 0)$ and $(0, 1)$.

These thermodynamic vectors possess an interesting mathematical property: adjacent potentials (corner vectors) or adjacent variables (diamond vectors) in diagram 2 are orthogonal to each other, that is, multiplying a thermodynamic vector

by the Hermitian adjoint (here, transpose T) of another adjacent thermodynamic vector, the result is always zero, e.g.: $(-1,1)\cdot(1,1)^{\mathrm{T}}=0$ or $(-1,0)\cdot(0,1)^{\mathrm{T}}=0$ but, $(-1,1)\cdot(1,-1)^{\mathrm{T}}\neq 0$ or $(-1,0)\cdot(1,0)^{\mathrm{T}}\neq 0$. Thus, the only combinations between thermodynamic parameters of the diamond (P, S, T and V) allowed by this rule are the following energy-dimensioned combinations: S and T or P and V.

In order to obtain, by matrix formalism, the thermodynamic expressions we are interested in, the following matrices must be used:

$$C_4^+ = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \tag{1}$$

$$C_4^- = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \tag{2}$$

$$\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{3}$$

$$\sigma_y = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{4}$$

These matrices perform a 90° or a −90° rotation about the axis of diagram 2 of table 1 and a x- or y-reflection parallel to the x or y axis.

The following four nilpotent matrices are also needed to transform potentials lying over or under the x or y axis into a variable function lying on the axis:

$$L_x = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \tag{5}$$

$$L_{-x} = \begin{pmatrix} -1 & 0 \\ 0 & 0 \end{pmatrix}, \tag{6}$$

$$L_y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \tag{7}$$

$$L_{-y} = \begin{pmatrix} 0 & -1 \\ 0 & 0 \end{pmatrix}. \tag{8}$$

Before starting the different matrix operations, some consideration of the sign convention is necessary. A negative sign for a term in a thermodynamic expression is contributed only by vectors $(-1,0)$ and $(0,-1)$ when (s1) these vectors are not differentiated, excluding the constant parameter, (s2) they are the 2nd factor in a nondifferentiable energy-dimensioned term and (s3) they are a constant parameter in a wholly differentiable expression; otherwise the sign is always positive.

2.1. GEOMETRIC RELATIONS BETWEEN NEIGHBORING POTENTIALS

2.1.1. The N pattern

The relationships in this pattern when overlaid on diagram 1 (see table 1 and fig. 1) have the following form:

$$\mathrm{A} = \mathrm{B} - \mathrm{CC}' .$$

As from C to C′ we are moving towards the arrowtail, a minus sign is required before the third term of this equation.

By superimposing the dashed lines of the N pattern to diagram 1 and by substituting the alphabetical terms with the corresponding thermodynamic terms we obtain the following equation:

$$A = G - VP . \tag{9}$$

With successive 90° rotations of the superimposed N pattern and by substituting (90° substitution), we obtain

$$G = H - TS , \tag{10}$$

$$H = U + PV , \tag{11}$$

$$U = A + ST . \tag{12}$$

Rotating the N pattern around its CC′ axis by 180° (a 180° substitution, followed by a 90° substitution) we obtain the other four equivalent expressions, e.g.,

$$U = H - PV . \tag{13}$$

2.1.2. Matrix formalism for the neighboring potentials

Generating step: the matrix form of the well-known $H = U + PV$ relation, shown in eq. (14),

$$(-1,-1) = (-1,1) + (0,-1)(0,1) , \tag{14}$$

can be obtained by operating on potential $H \equiv (-1,-1)$ with the matrix succession, σ_x, L_y, L_{-y}, as shown in the following equation:

$$(-1,-1) = (-1,-1)\sigma_x + (-1,-1)L_y \cdot (-1,-1)L_{-y} . \tag{15}$$

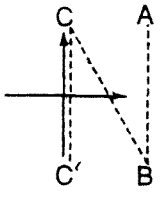


Fig. 1. Example of a superimposed pattern: the N pattern.

Operating on potential $(1,-1) \equiv G$ with matrix succession σ_y, L_x, L_{-x}, as shown in eq. (16), we obtain eq. (17), i.e., $G = H - TS$:

$$(1,-1) = (1,-1)\sigma_y + (1,-1)L_x \cdot (1,-1)L_{-x}\,, \tag{16}$$

$$(1,-1) = (-1,-1) - (1,0)(-1,0)\,, \tag{17}$$

while with the former matrix succession we can obtain $G = A + PV$.

The generating step converts the starting vector into a neighboring vector and, then, adds to it the product of the projections of these two vectors on the corresponding x or y axis; the σ operation could be substituted by a C_4. As further multiplication between two row vectors is not possible, matrix operations stop at this level. The operations $\sigma_{x,y}$, $L_{y,x}$, $L_{-y,-x}$ (the generator) could be used to generate the remaining thermodynamic relations, which can also be generated by the aid of the following propagating step.

The propagating step, formally easier than the generating step, operates on the terms of a well-known starting relation with rotation or reflection matrices only. Repeating this process with the terms of the newly obtained relation we can generate every thermodynamic expression. Operating, for example, on eq. (14), with C_4^+:

$$(14)C_4^+: \quad (-1,-1)C_4^+ = (-1,1)C_4^+ + (0,-1)C_4^+ \cdot (0,-1)C_4^+\,, \tag{18}$$

we obtain (after operations have been performed) eq. (19), that is, $U = A + ST$:

$$(-1,1) = (1,1) + (-1,0)(1,0)\,. \tag{19}$$

While operating with σ_y we can obtain $G = A + PV$:

$$(14)\sigma_y: \quad (1,-1) = (1,1) + (0,-1)(0,1)\,. \tag{20}$$

Now, operating on eq. (19) with C_4^+ we obtain eq. (21) ($A = G - VP$):

$$(19)C_4^+: \quad (1,1) = (1,-1) - (0,1)(0,-1)\,. \tag{21}$$

Thus, every expression, that holds between thermodynamic potentials, can be obtained. The negative signs in eqs. (17) and (21) are supported by the (s2) sign convention.

2.2. GEOMETRY OF THE DIFFERENTIAL FORMS OF THE POTENTIALS

2.2.1. The P pattern

The relationship for this geometric pattern when overlaid on diagram 1 (see table 1) is given by an equation of the following form:

$$\mathrm{dA} = -\mathrm{dB(B')} - \mathrm{dC(C')}\,.$$

See the preceding paragraph for the sign convention. With a substitution and rearranging (that is, $\mathrm{dB(B')} = \mathrm{B'dB}$) we obtain the following equation:

$$dA = -SdT - PdV\,. \tag{22}$$

With successive 90° substitutions we obtain the following equations:

$$dG = VdP - SdT\,, \tag{23}$$

$$dH = TdS + VdP\,, \tag{24}$$

$$dU = -PdV + TdS\,. \tag{25}$$

2.2.2. Matrix formalism for the differential forms of the potentials

Propagating step: starting with the matrix expression of the well-known differential form of potential U, $dU = TdS - PdV$, shown in eq. (26):

$$d(-1,1) = (1,0)d(-1,0) - (0,-1)d(0,1)\,, \tag{26}$$

and operating on the terms of this equation with C_4^+ or σ_y we obtain eq. (27) or (28) ($dA = -PdV - SdT$ or $dA = -SdT - PdV$) and operating on eq. (27) with C_4^+ we obtain eq. (29) ($dG = -SdT + VdP$) and so on.

$$(26)C_4^+: \quad d(1,1) = -(0,-1)d(0,1) - (-1,0)d(1,0)\,, \tag{27}$$

$$(26)\sigma_y: \quad d(1,1) = -(-1,0)d(1,0) - (0,-1)d(0,1)\,, \tag{28}$$

$$(27)C_4^+: \quad d(1,-1) = -(-1,0)d(1,0) + (0,1)d(0,-1)\,. \tag{29}$$

Equation (26) can also be derived by the aid of the following generating step performed on vector $(-1,1) \equiv U$:

$$d(-1,1) = (-1,1)L_{-x}d(-1,1)L_x + (-1,1)L_{-y}d(-1,1)L_y\,. \tag{30}$$

Applying generators L_{-x}, L_x, L_{-y}, L_y to vector $(1,-1) \equiv G$ (eq. (31)) we obtain eq. (32) ($dG = -SdT + VdP$):

$$d(1,-1) = (1,-1)L_{-x}d(1,-1)L_x + (1,-1)L_{-y}d(1,-1)L_y\,, \tag{31}$$

$$d(1,-1) = -(-1,0)d(1,0) + (0,1)d(0,-1)\,. \tag{32}$$

In the same manner we can generate all the other relations.

Negative signs in the right hand side of eqs. (27), (28), (29) and (32) are supported by the (s1) sign convention.

2.3. GEOMETRY OF THE MAXWELL RELATIONS

2.3.1. The M pattern

The relationships of this pattern when overlaid on diagram 1 are given by an equation of the following form:

$$-(\delta \mathrm{A}/\delta \mathrm{A}')_{\mathrm{A}''} = (\delta \mathrm{B}/\delta \mathrm{B}')_{\mathrm{B}''} .$$

The sign arises from the fact, that tracing from A to A″ we approach an arrowtail while from B to B″ the tracing approaches an arrowhead. With a substitution we obtain

$$-(\delta T/\delta V)_S = (\delta P/\delta S)_V . \tag{33}$$

With successive 90° substitutions we obtain eqs. (34)–(37):

$$-(\delta P/\delta T)_V = (\delta S/\delta V)_T , \tag{34}$$

$$(\delta S/\delta P)_T = -(\delta V/\delta T)_P , \tag{35}$$

$$-(\delta V/\delta S)_P = -(\delta T/\delta P)_S . \tag{36}$$

2.3.2. Matrix formalism for the Maxwell relations

The generator for the Maxwell relation is the matrix succession: C_4^-, σ_y, C_4^+, σ_y, C_4^- which applied to vector $(1,0) \equiv T$ (eq. (37)) generates eq. (38), i.e., $-(\delta T/\delta V)_S = (\delta P/\delta S)_V$,

$$(\delta(1,0)/\delta(1,0)C_4^-)_{(1,0)\sigma_y} = (\delta(1,0)C_4^+/\delta(1,0)\sigma_y)_{(1,0)C_4^-} , \tag{37}$$

$$-(\delta(1,0)/\delta(0,1))_{(-1,0)} = (\delta(0,-1)/\delta(-1,0))_{(0,1)} , \tag{38}$$

while by the aid of the propagating step we obtain, e.g., the following interrelations:

$$(38)C_4^+ : \quad (\delta(0,-1)/\delta(1,0))_{(0,1)} = (\delta(1,0)/\delta(0,1))_{(1,0)} , \tag{39}$$

$$(39)\sigma_x : \quad (\delta(-1,0)/\delta(0,-1))_{(1,0)} = -(\delta(0,1)/\delta(1,0))_{(0,-1)} , \tag{40}$$

i.e., $(\delta P/\delta T)_V = (\delta S/\delta V)_T$ and $(\delta S/\delta P)_T = -(\delta V/\delta T)_P$, respectively. The negative sign is given, here, by the (s3) sign convention.

2.4. GEOMETRIC RELATIONS FOR THE COEFFICIENTS

2.4.1. The F pattern

The form of the relationships of this pattern when overlaid to diagram 1 is given by

$$(\delta \mathrm{A}/\delta \mathrm{A}')_{\mathrm{A}''} = -\mathrm{B} .$$

As tracing from A′ to B we approach the arrowtail, one of the two terms (A′ or B) should be negative. With a substitution we obtain the following equation:

$$(\delta A/\delta T)_V = -S , \tag{41}$$

while with successive 90° substitutions we obtain the following equations:

$$(\delta G/\delta P)_T = V \quad (F \text{ upside down}), \tag{42}$$

$$(\delta H/\delta S)_P = T, \tag{43}$$

$$(\delta U/\delta V)_S = -P. \tag{44}$$

With a 180° substitution around the A″ axis, followed by a 90° substitution we obtain the other four interrelationships, such as

$$(\delta A/\delta V)_T = -P \quad (F \text{ rightside up}). \tag{45}$$

2.4.2. Matrix formalism for the coefficients

From eq. (26), after differentiation, we can derive eq. (46), that is, $(\delta U/\delta V)_S = -P$,

$$(\delta(-1,1)/\delta(0,1))_{(-1,0)} = -(0,-1), \tag{46}$$

and with the aid of the propagating step we can obtain, e.g. relations (47) and (48), that is, $(\delta A/\delta T)_V = -S$ and $(\delta G/\delta T)_P = -S$:

$$(46)C_4^+: \quad (\delta(1,1)/\delta(1,0))_{(0,1)} = -(-1,0), \tag{47}$$

$$(47)\sigma_x: \quad (\delta(1,-1)/\delta(1,0))_{(0,-1)} = -(-1,0). \tag{48}$$

The negative signs on the right side of these equations are supported by the (s1) sign convention.

Ignoring every vector of eq. (46) except $(-1,1) \equiv U$, we could have applied to the $(-1,1)$ vector in the denominator, constant parameter and coefficient the generating sequence L_y, L_x and L_{-y}, respectively and derived, in this manner, eq. (46).

It is noteworthy that the given sign convention, which could be based on x and y directions of diagram 1, has the advantage of avoiding continuous reference to any form of diagrams.

The power of this pattern recognition system can be underlined by the fact that it permits problem solving by geometric convention. For example, exercise 5.4 on page 119 of Atkins [4] asks to determine the equation for the temperature dependence of A (Helmholtz free energy) that corresponds to the well-known form of the Gibbs–Helmholtz equation

$$(\delta(G/T)/\delta(1/T))_P = H.$$

This exercise can be geometrically solved once the pattern relating the parameters of this equation has been recognized in diagram 1 of table 1. A closer examination of this diagram shows that superposing on it the last pattern of table 1 (a kind of b), every thermodynamic variable involved in the Gibbs–Helmholtz relation

will be encompassed in a specific order given by the alphabetical letters A, A′, A″ and B while the algebraic relationship for this geometry is:

$$\delta(\mathrm{A}/\mathrm{A}')/\delta(1/\mathrm{A}')_{\mathrm{A}''} = \mathrm{B}\,.$$

Thus, to find out the temperature dependence of potential A we just have to overlay the dashed lines of pattern b to diagram 1, to rotate it by 180° around the ST axis and substitute the alphabetical terms with the corresponding thermodynamic terms, in the same order, obtaining the right answer,

$$(\delta(A/T)/\delta(1/T))_V = U\,.$$

3. Conclusion

This diagrammatic method for thermodynamic relationships based on geometric and matrix operations not only represents a stimulating alternative view on a matter that usually leaves no space for imagination but also, being based on a minimal set of information is not too unwieldy, computationally and conceptually. The space covered by the thermodynamic diagram can be considered as a thermodynamic topological space in which neighborhood relations are important properties. In fact the geometry of these neighborhood relations determines the entire formalism which is unambiguous and straightforward. It should be noticed that while the propagating step of the matrix formalism is self-explanatory, the construction of the less obvious generating step can be generated with the help of diagram 1 and the rule that only allows S and T or P and V energy-dimensioned combinations of the diamond parameters (orthogonality rule).

This paper can be seen as a suggestion for the construction of a topological space that should allow to derive physical relationships of any order and complexity.

Acknowledgements

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