

Dimension of the Gibbs function topological manifold: 1. Graph representation of the thermodynamic equilibrium state

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Abstract This article shows that the Gibbs function topological manifold $G(p, T, x_1, x_2, \dots, x_C)$ at the thermodynamic equilibrium is always two-dimensional (2D). This means that the set of values G , regardless of the number of independent components C , creates a 2-D surface. Based on a state with zero degrees of freedom as a reference state, it was shown that the state of a thermodynamic equilibrium is represented by a graph on such a 2-D surface. In the equilibrium state, graph edges that connect points corresponding to individual degrees of freedom have a minimal length.

Keywords Graph theory · Thermodynamic equilibrium · Phase transitions

Mathematics Subject Classification 80A10 · 80A50

1 Introduction

The state of equilibrium in an isothermal–isobaric system is given by the values of pressure (p) and temperature (T) and by the chemical composition $x_1, x_2, \dots, \tilde{x}_C$, where x_i is the mole fraction of the i th component, with the tilde over one of the fractions indicating that for closed systems, the fraction is given by the values of other fractions: $\tilde{x}_C = 1 - (x_1 + x_2 + \dots + x_{C-1})$. The set of parameters that characterise the system shall henceforth be marked by the general symbol $\chi \equiv (p, T, x_1, x_2, \dots, \tilde{x}_C)$.

In memory of Marysia Ajzensztadt (1922–1942), the *Nightingale of the Warsaw Ghetto*.

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In a thermodynamic equilibrium, the values of these parameters lead to the minimum of the Gibbs function [1]:

$$G \equiv G(\chi) \equiv H(\chi) - TS(\chi) \quad (1)$$

where G , H , and S are, respectively, the molar Gibbs function, molar enthalpy, and molar entropy of the system. It can be shown that in multi-phase systems, the minimum G condition is met if the chemical potentials of each i th component are equal in all phases [1,2]:

$$\mu_i^{(k)} = \mu_i^{(k')} \equiv \mu_i \quad k, k' = 1, 2, \dots, P \quad (2)$$

where:

$$\mu_i = \left(\frac{\partial G}{\partial x_i} \right)_{p, T, x_j} \quad (3)$$

Conditions (2) lead to the relationship called the *Gibbs' phase rule* [1,2], which indicates the number of thermodynamic parameters, i.e., degrees of freedom (f), in a system in equilibrium between phases with C independent components and P thermodynamic phases. In a system that is not restrained in any way (e.g., by having several phases with the same composition), the rule is given by:

$$f = C - P + 2 \quad (4)$$

In special cases where there exist r aforementioned restraints, the '2' in Eq. (4) is replaced with '2-r'.

The phase rule (4) is identical to the equation derived from Euler's topological theorem on planar graphs [3]. The theorem states that the number of faces (F), edges (E), and vertices (V) in a connected planar graph drawn on a surface that is isomorphic with the surface of a two-dimensional sphere (2-S) is given by the equation:

$$F = E - V + 2 \quad (5)$$

Initially Euler formula (5) had usually interpreted in terms of polyhedra. Recently graph theory and topology indicate that (5) relates to a wider class of expressing mathematical objects, i.e. the planar graph on the surface of topologically isomorphic to the 2-D sphere without holes. This extension seems logical, if noted that Euler's formula also relates to e.g. a loop with one vertex or two vertices cycle.

The surprising similarity between equations from two relatively distinct areas of science has for almost 80 years motivated chemists to attempt to interpret thermodynamic equilibria through graph theory [4–12]. Assuming that the similarity between Eqs. (4) and (5) is not just a coincidence, or 'God's fancy', then the thesis becomes justified that a connected planar graph drawn on a surface that is isomorphic to 2-S can be ascribed to any given thermodynamic equilibrium. Not all researchers who have interpreted the similarity understood this relationship. For instance, authors of the most frequently quoted publication on graphs in the thermodynamics of equilibria [9] ascribe a planar graph not to individual equilibrium states but to all equilibrium

states of the same kind in general, i.e., to all areas and lines in a phase diagram. Such a proposal seems as nonsensical as a proposal to ascribe a single biometric passport to all citizens of a given country simply because they all belong to the group of beings that each possess one head, two arms, and two legs.

In our previous publications [12–14] on the graph representation of thermodynamic equilibria, we showed that a planar graph representing an equilibrium is nothing else than a graphical form of the Gibbs function (1). The value of this function can be interpreted as the (minimal) length of the path that connecting the graph vertices, which in turn are nothing else than the degrees of freedom in the system. The graph obtained in this manner is connected and includes no simple cycles; in other words, it constitutes a tree. Each degree of freedom of the graph is obtained by mapping the equilibrium state onto a certain reference state. A change in the thermodynamic state is represented by the change in the positions of graph vertices, which leads to the change in edge lengths. At certain positions of graph vertices, graph edges form closed areas (e.g., loops or cycles) on the surface. The forming of planar graphs with loops or cycles from tree graphs represents a thermodynamic transformation that involves the creation of a new phase.

The following issues remain unresolved so far:

1. What constitutes the 2-D surface on which the planar graph of a thermodynamic state is drawn?
2. What reference state (RS) should we choose that would allow the mapping of the thermodynamic state in question (i.e., a point in the space of thermodynamic parameters) onto such an RS to represent the set of degrees of freedom in the system (i.e., graph vertices) objectively, rather than subjectively?

We provide the answers to these questions and related questions further in this article. It seems that these answers will ultimately explain the connection between Gibbs' phase rule and Euler's formula for planar graphs. Thus, Nenad Trinajstić's statement from 1992 that 'The exact connection between the Euler formula and the Gibbs phase rule has not yet been established' [15] will finally be proven wrong.

2 Theory

A set of values of a function creates in the *arguments – values of a function* space a geometric shape referred to as a *topological manifold* [16]. The topological manifold for a function of n variables is usually an n -dimensional object immersed in a space with $n + 1$ dimensions (n x -axes and one y -axis).

The issue of topological manifolds of thermodynamic functions, especially with respect to their dimension, has gone unnoticed in thermodynamics thus far. The issue is implied in Carathéodory's [17, 18] approach to axiomatic thermodynamics. Carathéodory, when discussing differential equations in thermodynamics (Pfaffian equations), states that the equation:

$$dQ = \sum_{i=1}^n A_i(x_1, x_2, \dots, x_n) dx_i = 0 \quad (6)$$

is holonomic, i.e., there exists such a multiplier $\lambda(x_1, x_2, \dots, x_n)$ that transforms (6) into:

$$dS(x_1, x_2, \dots, x_n) = \lambda(x_1, x_2, \dots, x_n) \sum_{i=1}^n A_i(x_1, x_2, \dots, x_n) dx_i = 0 \quad (7)$$

where dS is an exact differential. Thus, the solutions of (7) take the form:

$$S(x_1, x_2, \dots, x_n) = \text{const} \quad (8)$$

where ‘const’ is any constant. Carathéodory terms equation (8) the *equation for the surface in space with $n+1$ dimensions* (n parameters plus 1 value of a function). However, it seems more justified to refer here to a topological manifold rather than a ‘surface’ [16]. The author makes no explicit statement about the dimension of such a manifold. Nonetheless, he suggests that the issue of dimension is important based on his theorem on the non-intersecting of adiabatically different surfaces [i.e., surfaces for which the value of ‘const’ in Eq. (8) differs].

Based on Eq. (1), one might expect that the dimension of the Gibbs function topological manifold for closed thermodynamic systems with C independent components would equal $C + 1$ ($C - 1$ concentrations plus p and T). Notice, however, that apart from restraints due to the closed character of the system:

$$\sum_{i=1}^C x_i = 1 \quad (9)$$

the Gibbs function is also affected by restraints derived from the Gibbs–Duhem theorem for isothermal–isobaric closed systems [19,20]:

$$\sum_{i=1}^C x_i d\mu_i = 0 \quad (10)$$

These constraints form $C - 1$ equations that can be written as:

$$\sum_{i=1}^C x_i \left(\frac{\partial \mu_i}{\partial x_j} \right) = 0 \quad j = 1, 2, \dots, C - 1 \quad (11)$$

If $C - 1$ constraints given by Eqs. (11) affect a Gibbs function with $C + 1$ degrees of freedom, then we may conclude that the actual dimension of this function’s topological manifold will equal $(C + 1) - (C - 1)$, i.e., 2. As a result, all values of G should be located on a 2-D surface regardless of how complex the closed thermodynamic system is. This conclusion, while elementary for unary systems, is not as obvious for system with two or more components. To illustrate: why should the values of the Gibbs function for the binary system $G(p, T, x_1, \bar{x}_2)$ form a 2-D surface immersed in a 5-D space (four x -axes and one y -axis) rather than a 4-D topological manifold immersed in a 5-D space? The qualitative answer to this question lies in the statement that the state of a system is defined by a set of parameters χ that must be determined

by the mean value of energy in the system, i.e., the internal energy (U), and by the mean value of information about the system, i.e., entropy (S). These two values may create a network of geodesic lines of the Gibbs function topological manifold; in such a case, the manifold will be 2-D regardless of the number of components in the system. Further in this article, we will not use a network of geodesic lines formed directly by U and S but rather a more natural network formed by X and Y , where:

$$X = X(\chi) \equiv H(\chi) \quad Y = Y(\chi) \equiv -T \cdot S(\chi) \tag{12}$$

Before we apply the network of geodesic lines defined in (12) to describe the Gibbs function topological manifold, let us briefly consider 2-D topological manifolds. It will be interesting to divide such manifolds into smooth manifolds and piecewise smooth manifolds. A characteristic feature of the latter is that the first derivative is discontinuous in at least one point of the manifold. The Gibbs function topological manifold is without a doubt complex, rather than smooth, because it is created by “gluing” together sections of smooth manifolds that correspond to individual phases $k = \alpha, \beta, \gamma, \dots$ of the system. The gluing takes place along the phase transformation line. It is unclear whether the phase transformation line constitutes a geodesic line of the manifold. We will address this issue in a further part of this work. It is worth noticing a particular property that distinguishes the two manifolds: while in the former, two points lie close to each other only if both geodesic coordinates of these points are almost equal in value, in the latter, two points may have vastly different values of coordinates and still lie close to each other (but only when, of course, these points are located close to the gluing line, i.e., the phase transformation line).

Another issue worth mentioning is the immersion of 2-D manifolds in a Euclidian space. The topological theorem on the immersion of smooth manifolds [16] states that every smooth manifold with the dimension D can be immersed in a Euclidian space with the dimension $2D + 1$. For instance, a curve, i.e., a 1-D manifold, will fit in a 2-D space, but a curve with knots, such as a 1-D manifold with any degree of complexity, requires a 3-D space to fit. Thus, the immersion theorem allows us to conclude that all topologically allowed thermodynamic states will only appear for systems with three or more independent components. This is because the dimension of a space drawn on the thermodynamic parameters of these systems equals 5 or more, and only such a space can contain any 2-D topological manifolds, including all manifolds that represent the Gibbs function.

For the k th phase of single-component systems, the Gibbs function (1) is represented by a network of geodesic lines given by (13):

$$G^{(k)}(X, Y) = X^{(k)} + Y^{(k)} \tag{13}$$

where $X^{(k)}, Y^{(k)}$ are the values of X and Y for the k th phase defined in (12). We shall use Eq. (14) to describe multi-component systems:

$$G^{(k)}(X, Y) = \sum_{i=1}^C x_i \mu_i^{(k)} \equiv \sum_{i=1}^C g_i^{(k)}(X, Y) \tag{14}$$

where $g_i^{(k)}$ may be termed the *weighed chemical potentials of the i th component*:

$$g_i^{(k)} = \left(\frac{\partial G^{(k)}}{\partial \ln x_i} \right)_{p,T,x_j} \quad (15)$$

A change in the Gibbs potential is given by the following differential:

$$dG^{(k)} = \begin{cases} dX^{(k)} + dY^{(k)} & C = 1 \\ \sum_{i=1}^C \left[\left(\frac{\partial g_i^{(k)}}{\partial X^{(k)}} \right) dX^{(k)} + \left(\frac{\partial g_i^{(k)}}{\partial Y^{(k)}} \right) dY^{(k)} \right] & C > 1 \end{cases} \quad (16)$$

Each thermodynamic equilibrium state defined by the values of thermodynamic parameters marked $\chi_0 \equiv (p_0, T_0, x_{10}, x_{20}, \dots, \tilde{x}_{C0})$ is represented by the point $R_0^{(k)} = (X_0^{(k)}, Y_0^{(k)})$ located on the $G^{(k)}$ surface. The distance between this point and $G = 0$ is the value of the Gibbs function in the k th phase of the system. In thermodynamics, the value of a function is usually provided not in relation to the zero of the function but in relation to the value of the function in a certain reference state.

If we define this reference state as $\chi^* \equiv (p^*, T^*, x_1^*, x_2^*, \dots, \tilde{x}_C^*)$, then the value of the Gibbs function will be given by:

$$\Delta G^{(k)} = G^{(k)}(\chi_0) - G^{(k)}(\chi^*) \quad (17)$$

The thermodynamic state χ_0 mapped onto the reference state χ^* allows the latter to be represented by the set $\chi_1, \chi_2, \dots, \chi_{C+1}$, where:

$$\begin{aligned} \chi_1 &= (p_0, T^*, x_1^*, x_2^*, \dots, \tilde{x}_C^*) \\ \chi_2 &= (p^*, T_0, x_1^*, x_2^*, \dots, \tilde{x}_C^*) \\ &\vdots \\ \chi_{C+1} &= (p^*, T^*, x_{10}, x_{20}^*, \dots, \tilde{x}_C^*) \end{aligned} \quad (18)$$

Figure 1 explains the mapping operation performed in two dimensions.

The set χ_i creates the set of points $R_i^{(k)}$ $i = 1, 2, \dots, C + 1$ on the surface of the Gibbs function manifold. These points represent the degrees of freedom in the system on this surface:

$$\begin{aligned} R_1^{(k)} &= (X^{(k)}(\chi_1), Y^{(k)}(\chi_1)) \\ R_2^{(k)} &= (X^{(k)}(\chi_2), Y^{(k)}(\chi_2)) \\ &\vdots \\ R_{C+1}^{(k)} &= (X^{(k)}(\chi_{C+1}), Y^{(k)}(\chi_{C+1})) \end{aligned} \quad (19)$$

It is worth noticing that, firstly, there are as many of these points as there are degrees of freedom in a one-phase equilibrium state, and secondly, each point $R_i^{(k)}$ represents one degree of freedom in the system rather than two, as one would expect from a point located on a 2-D space. The latter fact stems from the constraints induced by the reference state.

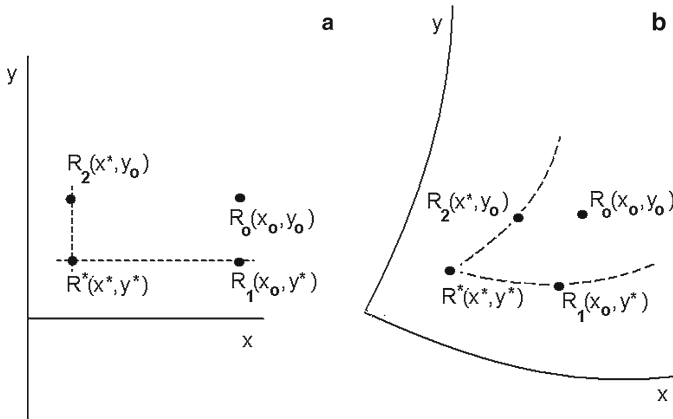


Fig. 1 Mapping of the point R_0 onto the reference point R^* in a two-dimensional space (x, y) . **a** An orthogonal coordinate and **b** a curvilinear coordinate system

2.1 One-phase systems

This part of the article will show that in an equilibrium state of one-phase systems, the value of the Gibbs function calculated relative to a certain reference state (17) is equal to the length of the minimal path connecting the individual degrees of freedom (19) on the surface of the $G^{(k)}$ function manifold.

Let us begin with unary systems with only two degrees of freedom: $R_1^{(k)}$, $R_2^{(k)}$. Equation (16) indicates that the value of the Gibbs function along the path connecting the two degrees of freedom equals:

$$\int_{R_1^{(k)} \cap R_2^{(k)}} \cdot dG^{(k)} = \int_{R_1^{(k)} \cap R_2^{(k)}} \cdot dX^{(k)} + \int_{R_1^{(k)} \cap R_2^{(k)}} \cdot dY^{(k)} \tag{20}$$

where $R_1^{(k)} \cap R_2^{(k)}$ is the arc connecting the points $R_1^{(k)}$, $R_2^{(k)}$.

In the equilibrium state, the change in the Gibbs potential (20) reaches the minimum. The value of this minimum depends only on the location of the points $R_1^{(k)}$, $R_2^{(k)}$:

$$\begin{aligned} \Delta G^{(k)}(R_1^{(k)}, R_2^{(k)}) &= \min \left(\int_{R_1^{(k)} \cap R_2^{(k)}} \cdot dG^{(k)} \right) = \left[X^{(k)}(R_2^{(k)}) - X^{(k)}(R_1^{(k)}) \right] \\ &\quad + \left[Y^{(k)}(R_2^{(k)}) - Y^{(k)}(R_1^{(k)}) \right] \\ &\equiv G^{(k)}(R_2^{(k)}) - G^{(k)}(R_1^{(k)}) \end{aligned} \tag{21}$$

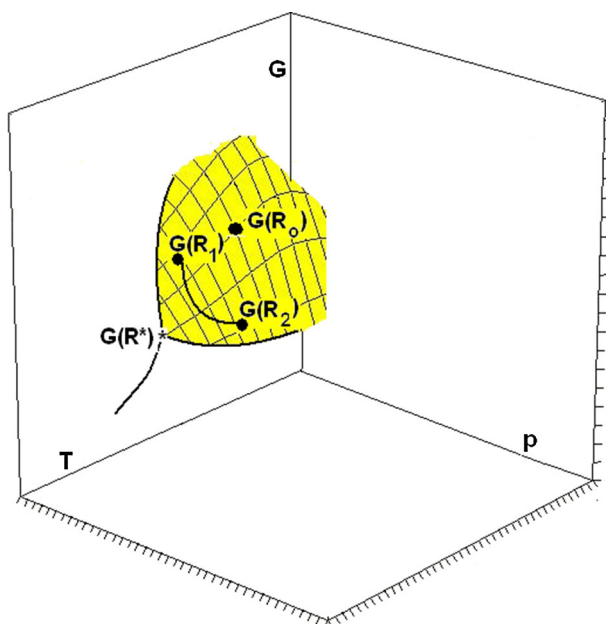


Fig. 2 For unary systems, the value of the Gibbs function in a state defined by the geodesic coordinates R_0 , measured relative to the reference state R^* : $\Delta G = G(R_0) - G(R^*)$ is equal to the length of the minimal path on the surface of the Gibbs function 2-D topological manifold connecting the degrees of freedom R_2 and R_1 . The section of the topological manifold in question is marked in yellow, the network of geodesic lines (X, Y) is marked with the *thin black line*, the minimal path connecting the degrees of freedom is marked with the *thick black line*, and the reference state, located at the bifurcation point of the phase transformation line, is marked with an *asterisk* (Color figure online)

It is easy to notice that the value of $\Delta G^{(k)}(R_1^{(k)}, R_2^{(k)})$ is exactly equal to the value of the Gibbs function in the χ_0 state measured in relation to the reference state (17):

$$\Delta G^{(k)}(R_1^{(k)}, R_2^{(k)}) = G^{(k)}(\chi_0) - G^{(k)}(\chi^*) \quad (22)$$

Equation (22) shows that the values of the Gibbs function are encoded in the geometry of the function's topological manifold. In particular, these values are equal to the length of the minimal path on the manifold surface connecting the two degrees of freedom in the system (Fig. 2). This leads to the natural conclusion that for one-phase unary systems, the values of the Gibbs function are represented by a graph with two vertices (Fig. 2) and edge length equal to the value of the Gibbs function. Each vertex represents one degree of freedom in the system.

What about one-phase multi-component systems? For binary systems, the answer is easy and unambiguous. The value of the Gibbs function is defined by the three degrees of freedom $R_1^{(k)}, R_2^{(k)}, R_3^{(k)}$ and is equal to the integral over the shortest path connecting these degrees of freedom. If we number the degrees of freedom in such a manner that the path consists of arcs connecting points 1–2 and 2–3, then

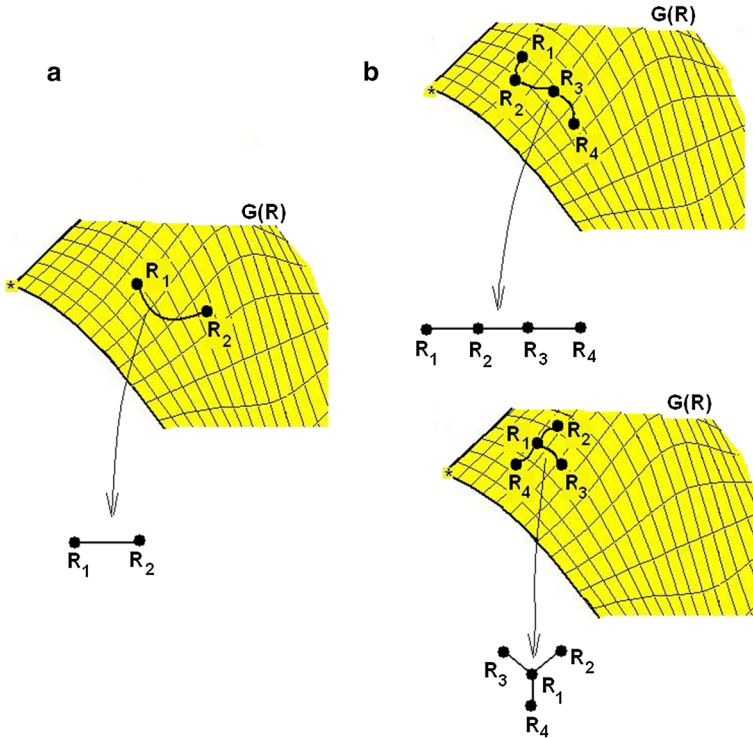


Fig. 3 In a state of equilibrium, the Gibbs potential measured relative to the reference state (marked with an *asterisk* in the figure) is equal to the length of the minimal path on the topological manifold connecting the individual degrees of freedom R_i in the system. **a** A state graph that represents the path for a one-phase system with $C = 1$, and **b** graphs for one-phase systems with $C = 3$

$$\Delta G^{(k)}(R_1^{(k)}, R_2^{(k)}, R_3^{(k)}) = \sum_{i=1}^2 \int_{R_i^{(k)} \cap R_{i+1}^{(k)}} \left[\left(\frac{\partial g_i^{(k)}}{\partial X^{(k)}} \right) dX^{(k)} + \left(\frac{\partial g_i^{(k)}}{\partial Y^{(k)}} \right) dY^{(k)} \right] \tag{23}$$

To facilitate calculations, let A denote the first component of the system [$i = 1$ in (23)] and B denote the second component. Then the integral in Eq. (23) leads to the relationship:

$$\Delta G^{(k)}(R_1^{(k)}, R_2^{(k)}, R_3^{(k)}) = g_A^{(k)}(R_1^{(k)}, R_2^{(k)}) + g_B^{(k)}(R_2^{(k)}, R_3^{(k)}) \tag{24}$$

This equation is represented by a graph, namely, a tree with two edges (Fig. 3a). The edges in this graph are the weighted chemical potentials of individual components of the system.

Topological interpretation of the Gibbs phase rule allows us to see only the topological aspects of the equilibrium. For the equilibrium involving $H_2(g)$, $N_2(g)$ and $NH_3(g)$ (i.e. the system with $C=2$, $P=1$ and $f=3$) the topological aspects of the

Table 1 State graphs for moderately complex systems, i.e., those with C no greater than 4. The description under Fig. 4 shows individual independent components and their corresponding lines. The values of the degrees of freedom can be found in column 1 of the table. Each state graph for systems with $C = 4$ that will be used in the further part of this publication is marked with an identifying symbols. Description of the components and the phase is the same as in Fig. 5.

$f \backslash C$	1	2	3	4
0				
1				1
2				6
3				12
4				
5				

equilibrium are represented by a simple graph, i.e. 2-vertices tree (see Table 1: graph in row3 and column3). Examples of graphs representing the states of equilibrium on the phase diagrams of simple chemical systems are given in my previous work [12].

The corresponding calculations for systems with three or more components and four or more degrees of freedom are more complicated due to the fact that for $f \geq 4$, there exists more than one way in which the edges can connect the degrees of freedom (graph vertices). These ways differ in the extent to which the tree branches out. For instance, for $C = 3$, the graphs that represent the value of the Gibbs function will represent Eqs. (25a) and (25b), which show how the Gibbs function may depend on the four degrees of freedom in the system:

$$\Delta G^{(k)} \left(R_1^{(k)}, R_2^{(k)}, R_3^{(k)}, R_4^{(k)} \right) = g_A^{(k)} \left(R_1^{(k)}, R_2^{(k)} \right) + g_B^{(k)} \left(R_2^{(k)}, R_3^{(k)} \right) + g_C^{(k)} \left(R_3^{(k)}, R_4^{(k)} \right) \tag{25a}$$

$$\Delta G^{(k)} \left(R_1^{(k)}, R_2^{(k)}, R_3^{(k)}, R_4^{(k)} \right) = g_A^{(k)} \left(R_1^{(k)}, R_2^{(k)} \right) + g_B^{(k)} \left(R_1^{(k)}, R_3^{(k)} \right) + g_C^{(k)} \left(R_1^{(k)}, R_4^{(k)} \right) \tag{25b}$$

Figure 3b shows graphs that represent the value of the Gibbs function for $C = 3$. With the increase in the number of components C , the number of states represented by a branching tree increases. For $C = 4$, the number, marked η , equals 2 (plus 1 non-branching graph); for $C = 5$, $\eta = 5$; for $C = 6$, $\eta = 10$; and for $C = 9$, $\eta = 105$ [21]. In our previous publication [12], we used the term *exotic states* to denote the thermodynamic states represented by such graphs, because these states appear only in complex systems with $C \geq 3$, which have yet to be researched in detail. The subsequent part of this article will discuss the numerous reasons why quasicrystals may constitute exotic states. Notice that exotic states begin to appear from $C = 3$, i.e., from the point where the dimension of a Euclidian space drawn on thermodynamic parameters reaches 5. As has been mentioned, the topological theorem on immersion allows any type of 2-D topological manifolds to be immersed (i.e., inserted without self-intersections) in such a space, including manifolds represented by the values of the Gibbs function.

In sum, the value of the Gibbs function for a one-phase equilibrium state is represented by a tree located on the 2-D surface of the topological manifold G . Weighted chemical potentials of individual components constitute graph edges. Degrees of freedom in the system, obtained by mapping the classically defined state (a point in a space drawn on thermodynamic parameters) onto a certain RS, constitute vertices that connect the individual edges in this state graph. This is why we shall now address the choice of the RS.

2.2 Reference state

Let us begin with unary systems. If the state of the system is identical to the RS: $\chi_0 \equiv \chi^*$, then such a state has no degrees of freedom, i.e., is an invariant state. Note that in unary systems, the RS involves the co-existence of three phases. Equations (4) and (5) indicate that such a state is represented by a planar graph with three faces, one edge, and no vertices. Such a graph seems peculiar at first, but if we consider the surface of the Gibbs function $G(p, T)$ for unary systems or the mapping of this surface on the p, T surface, we will notice that $G(p, T)$ consists of three sections of individual phases glued along the phase transformation line (Fig. 4a). The phase transformation line has a bifurcation point at the meeting point of the three sections, i.e., a point with zero variance. Thus, the state graph for the RS is the phase transformation line on the surface of the Gibbs function. The bifurcation point on this line is the RS, while the graph faces are the sections of the surface that correspond to individual phases of the system. Such an interpretation of the RS constitutes a tool that allows invariant states in complex systems to be classified. Figure 4b, c shows the types of invariant states

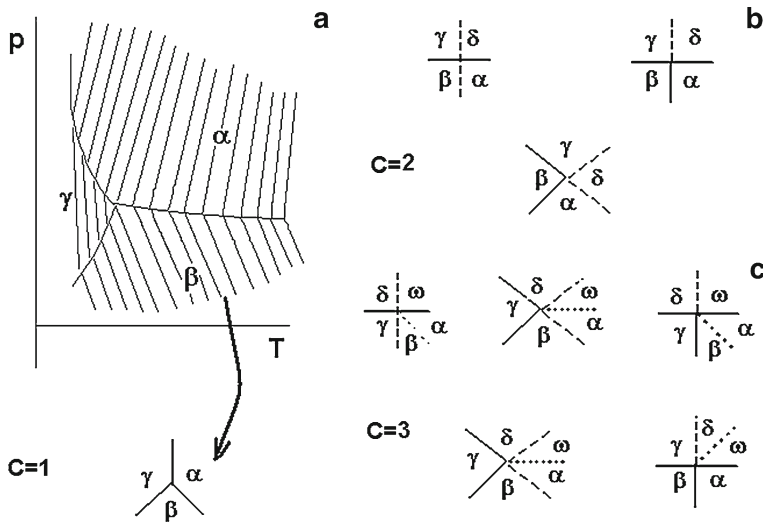


Fig. 4 Invariant state graphs for systems with $C = 1, 2,$ and 3 independent components. Component A is marked with a *continuous line*, component B is marked with a *dashed line*, component C is marked with a *dotted line*, and component D is marked with a *dashed-dotted line*. Individual phases are marked with *Greek letters*. The composition of a given phase is marked with the *lines* of individual components adjacent to the phase

for binary and ternary systems. Note that for topological reasons, the tool enables us to rule out the existence of certain equilibrium types at a point with zero degrees of freedom. For instance, in binary systems, four phases with both components, ((A,B), (A,B), (A,B), (A,B)), or two phases with one component each and two phases with both components, ((A), (B), (A,B), (A,B)) and ((A), (A), (A,B), (A,B)), may exist at such a point. However, equilibria such as the one that involves three phases with one component each and one phase with both components are forbidden.

An invariant state is the only characteristic point on the $G(\chi)$ surface, which is why choosing it at the RS seems objectively justified. Another characteristic element of the Gibbs function topological manifold is the phase transformation line, which seems to make choosing it as on the coordinate axes of the system justified. Of course, such a coordinate system will be curvilinear.

2.3 Two-phase systems

For unary systems, a two-phase state will be represented by a point located on the phase transformation line. Because the line also constitutes an axis of the coordinate system, the classically defined state will take the form $\chi_0 = (p^*, T_0)$ or $\chi_0 = (p_0, T^*)$. If we select the first form of the state, then according to (18), the mapping of this state onto the RS will lead to:

$$\begin{aligned}\chi_1 &= (p^*, T^*) \equiv \chi^* \\ \chi_2 &= (p^*, T_0)\end{aligned}\quad (26)$$

On the surface of the Gibbs function manifold $R_i^{(k)}$, the coordinates of these points will depend on which phase (either of two) we approach the phase transformation line from:

$$\begin{aligned} R_1^{(k)} &= \left(X^{(k)}(\chi_1), Y^{(k)}(\chi_1) \right) \equiv R^{(k)*} \\ R_2^{(k)} &= \left(X^{(k)}(\chi_2), Y^{(k)}(\chi_2) \right) \end{aligned} \tag{27}$$

where $k = \alpha, \beta$. Because the points $R_1^{(\alpha)}$ and $R_1^{(\beta)}$ are identical to the RS, only the points $R_2^{(\alpha)}$, $R_2^{(\beta)}$ will define the state of the system. Note, however, that these points overlap or are located close to each other despite having different coordinates. Such a behaviour on the part of points located on the phase transformation line in a piecewise smooth manifold has already been mentioned in this article. Now we shall explain the reasons for such behaviour. The condition for a two-phase equilibrium (28) states that the value of the Gibbs function is equal for both values of the geodesic coordinates $R_2^{(\alpha)}$, $R_2^{(\beta)}$, i.e., the same point on the Gibbs topological manifold corresponds to these two coordinates:

$$G \left(R_2^{(\alpha)} \right) = G \left(R_2^{(\beta)} \right) \tag{28}$$

where:

$$G \left(R_2^{(\alpha)} \right) = X^{(\alpha)}(\chi_2) + Y^{(\alpha)}(\chi_2); \quad G \left(R_2^{(\beta)} \right) = X^{(\beta)}(\chi_2) + Y^{(\beta)}(\chi_2) \tag{29}$$

This point is a vertex of the state graph and unambiguously defines the value of the Gibbs function in this equilibrium. The value is equal to the length of the graph edge. Figure 5 shows how such graphs are constructed. Figure 5a addresses the case where the phase transformation line is a geodesic line. In such a case, the graph will consist of two edges that, due to their proximity, combine into one edge that crosses the point $R_2^{(k)}$. Figure 5b addresses the case where the gluing line is not geodesic. Note that the graph in Fig. 5b conforms to that suggested by Euler’s formula (5), which indicates that a planar graph with one vertex and one edge must have two faces that, according to the phase rule (4), correspond to the individual phases in the system. It seems, therefore, that the phase transformation line is most likely not geodesic (albeit this issue should be thoroughly investigated in the future). In sum, the state of a two-phase, unary system is represented by a one-edge cycle, i.e., a loop with one vertex formed by gluing together the points $R_2^{(\alpha)}$ and $R_2^{(\beta)}$. Hence, graph theory describes a phase transformation in the following manner: if one of the degrees of freedom represented by a graph vertex, e.g., $R_2^{(\alpha)}$ is located on the gluing line of a Gibbs function topological manifold, then the edge connecting $R_2^{(\alpha)}$ and $R_2^{(\beta)}$ has a lower length (i.e., equal to zero) than the edge connecting $R_2^{(\alpha)}$ with, e.g., $R_1^{(\alpha)}$ in the original graph. Thus, the state represented by the graph $R_2^{(\alpha)}-R_1^{(\alpha)}$ becomes the state represented by the graph $R_2^{(\alpha)}-R_2^{(\beta)}$. Because in the latter graph the vertices overlap (they have undergone gluing), it will have one vertex less than the original graph and will, therefore, include a loop or a cycle.

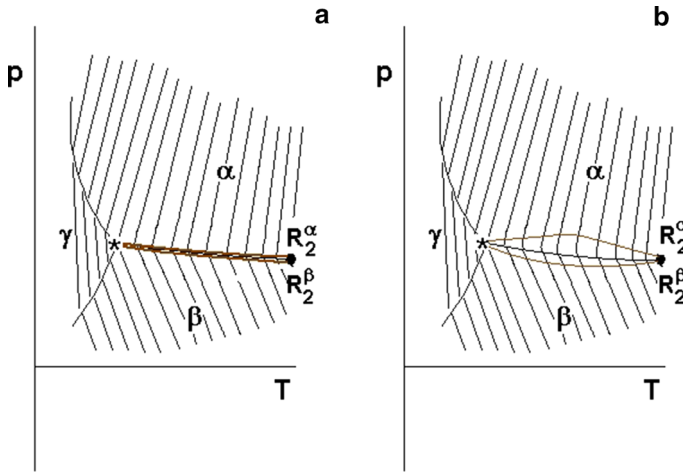


Fig. 5 A graph of a two-phase system with $C = 1$. Such a state forms if the degree of freedom R_2 is located on the phase transformation line. The state graph is created by gluing together the degrees of freedom $R_2^{(\alpha)}$, $R_2^{(\beta)}$ into the point R_2 connected with a line that crosses this point and the reference state. The graph in **a** corresponds to the situation in which the phase transformation line is a geodesic line. In such a case, the graph comprises two lines located very close to the phase transformation line on the sections of phases α and β . The graph in **b** corresponds to the situation where the phase transformation line is not a geodesic line. In such a case, the graph comprises a loop that crosses the point R_2 and the reference state. The graphs in **a**, **b** are marked with a *brown line* (Color figure online)

Before we review the types of state graphs in multi-phase systems, let us attempt to simplify the presentation of graphs with loops or cycles. The simplification will involve transposing such graphs from a piecewise smooth surface onto a smooth surface. As Fig. 5b shows, on a piecewise smooth surface, both phases are represented by the smooth sections of a topological manifold. The gluing line of the manifold (the phase transformation line) divides these sections. On the other hand, Eqs. (4) and (5) indicate that on a smooth surface, thermodynamic phases are represented by the interior and exterior face of the graph (a loop or a cycle). A smooth surface is easier to handle; moreover, it is easier to interpret topological properties of graphs located on such a surface. For the latter reason, we shall smooth (“flatten”) the piecewise smooth manifold by eliminating gluing lines. Obviously, we will first (prior to the smoothing) transpose each surface representing the phases of the system onto the exterior and interior face of the graph (a loop or a cycle) face. Figure 6 shows the simplification procedure based on the graph from Fig. 5b. As a closing remark, note that such a simplification operation for cyclic graphs is only meant to facilitate interpreting the findings of graph theory with respect to complex multi-phase systems.

2.4 Complex multi-phase systems

Let us begin with a summary: the values of the Gibbs function form a 2-D topological piecewise smooth manifold. By choosing an invariant state on the surface of this manifold as a reference state, we are able to present the thermodynamic state of the

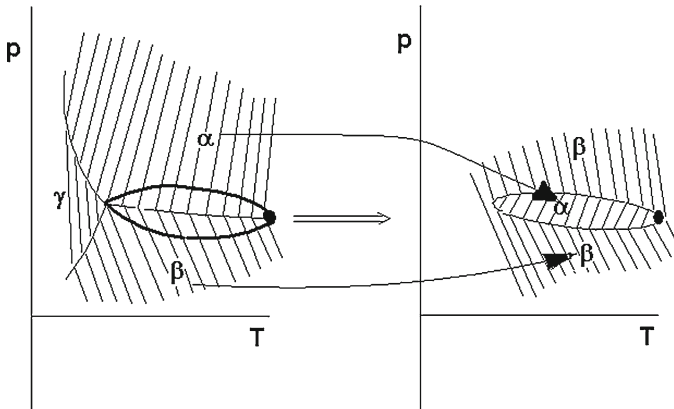


Fig. 6 Smoothing multi-phase state graphs involves transforming the state graph from a piecewise smooth topological manifold into a smooth manifold. The figure shows smoothing for unary systems ($C = 1$)

system using a set of points, i.e., the degrees of freedom in the system. The value of the Gibbs function for the equilibrium state is equal to the length of the shortest path connecting the individual degrees of freedom. This path forms a state graph that represents the thermodynamic equilibrium state. Each degree of freedom constitutes a graph vertex and the weighed chemical potential of each component, i.e., each component's contribution to the value of the Gibbs function, constitutes a graph edge. Finally, graph faces represent the individual phases of the system, with each phase's composition determined by the edges that form a given face.

Graph faces that represent phases of multi-phase systems form if a given degree (or degrees) of freedom and a given graph vertex (vertices) are located on the manifold gluing line (or lines). In such circumstances, two or more graph vertices become glued and a cycle (often a loop) is created within the graph. Table 1 shows a list of state graphs for systems with $C = 1, 2, 3, 4$ components. The table indicates that one-phase states represented by branching trees start to appear for $C = 3$ and that the number of such states increases with the increase in C . There are many more two-phase system types than one-phase system types. For instance, 2 two-phase types exist for $C = 2$ and four exist for $C = 3$, whereas as many as nine exist for $C = 4$. Nonetheless, all these types can always be divided into two classes. The first class includes equilibria in which both phases include all components of the system, and the second class includes equilibria in which one phase includes different components than the other.

The former class includes congruent equilibria¹, while the latter comprises only non-congruent equilibria. The first class is represented by only one state graph that

¹ about congruent and non-congruent processes in [19] we can read: if “the components form a compound stable up to the melting point” then “the compound melts at a constant temperature and the melt has the same stoichiometric composition; such compounds are said to have congruent melting points” and if “the components form a compound unstable at the melting point” then it “decomposes below its melting point, which on further heating forms a melt with a composition different from that corresponding to the stoichiometry of the compound. These compounds are said to have incongruent (non-congruent) melting point.”

always constitutes a cycle with C edges. The second class is represented by considerably more graphs that include loops as well as cycles. There are three such states for $C = 3$ and as many as eight for $C = 4$. It is worth noting that even though two-phase state graphs can form from one-phase state graphs by gluing the appropriate vertices of a one-phase tree, not all one-phase states allow us to create a given type of a two-phase state. Table 1 makes it easy to notice that, for instance, any of the four allowed two-phase states represented by the graphs in the table can be created from a normal state of a three-component system, but an exotic state of a three-phase system can only become 1 of 2 two-phase state types, represented by the last two graphs in the same table. Furthermore, as far as four-component exotic states are concerned, the state represented by graph a_1 can become any of the states except those represented by graphs b_0 and b_7 , and a_2 can become either b_3 or b_5 . On the other hand, one-phase normal states of such systems represented by a_0 can become all two-phase system types except those represented by graphs b_4 , b_5 , and b_8 . How do individual two-phase state types differ with respect to the graph-based representation of states? Providing a general answer is difficult. While systems with $C = 2$ differ in the composition of individual phases (in the state represented by the first graph in Table 1, both phases have the same qualitative composition, but in the state represented by the second graph, their composition is different), the same is not true for systems with $C \geq 3$. This, as can easily be noticed based on Table 1, is due to the fact that there always exist at least two graphs that correspond to particular states with no differences in phase composition. Do such types of degenerated equilibria have any property that would differentiate them? It seems that the answer can be found by investigating the transformation of such equilibria into simpler (i.e., with a smaller number of phases) or more complex ones (i.e., with a greater number of phases). For instance, the two-phase equilibrium with $C = 3$, represented by the ‘loop at the terminal vertex’ graph, cannot become a one-phase exotic state, while the state represented by the ‘loop at the central vertex’ graph cannot become a one-phase normal state. For very complex system compositions, such as systems with $C \gg 4$, the specifics of individual two-phase equilibria represented by different graph types are even more perplexing and require further investigation. Let us now briefly consider individual state graph types to points on the phase diagram. Ascribing these types poses no difficulty for systems with $C = 1$ or $C = 2$ and has been described in our previous publication [12]. Let us only remind the reader that, e.g., for a system with $C = 2$, the ‘cycle with two edges’ represents a point on the phase transformation line on the diagram showing a system with two components that are mixed in both phases, while the ‘loop glued to a tree with one edge’ graph represents a state on the phase transformation line on the diagram showing binary eutectic systems [12].

Equilibrium graphs with three or more phases can be created by gluing several vertices in equilibrium graph with fewer phases. The number of such graphs will increase up to a certain point and consequently, so will the number of equilibrium types with three or more phases. The equilibrium in systems with $C + 1$ phases will constitute a critical point. The state of such systems is determined by one degree of freedom. Furthermore, as Table 1 shows, there exists only one equilibrium type for such systems, represented by a graph composed of only C loops. Note also that the number of different thermodynamic equilibrium types increases if we take into account

not only graph topology, but also the chemistry of the system. For instance, a one-phase normal state of a three-component system represented by a three-edge non-branching tree will become three graphs that differ only in edge permutation once the chemistry of such a system is taken into account. If the number of degrees of freedom in the system decreases to zero (an invariant state), the number of equilibrium types will increase. However, it is the chemistry, not topology, of the system that is responsible for this increase. In graph theory, the influence of one chemical factor can most easily be taken into account by “painting” the gluing edges and lines of the manifold with different colours corresponding to different components in the system. Once such a method is used, it becomes apparent that there exist three equilibrium types for binary systems and five equilibrium types for invariant systems with $C = 3$.

3 Summary and conclusions

This article investigated the reasons for the similarity between the Gibbs’ phase rule (4) and Euler’s theorem (5) on planar graphs on isomorphic surfaces with the surface of a two-dimensional sphere (2-S). It was shown that the similarity is not coincidental but instead stems from the fact that for closed isothermal–isobaric systems, the Gibbs function topological manifold is a two-dimensional piecewise smooth surface (2-D). The locations of any points on this surface are determined by the values of two geodesic coordinates defined on the surface. This surface has, at a first glance, a peculiar property: the height of any point (that represents a state of the system) located in the smooth area of the manifold, measured relative to a reference point (i.e., an invariant state), is equal to the length of the minimal path connecting the degrees of freedom in the system, i.e., points on the surface that constitute a mapping of the state onto the reference state of the system. The equality between the height of the point on the surface and the length of the path introduces a graph-based representation of equilibrium states into phenomenological thermodynamics. In such a representation, an equilibrium state represented by a point on the surface of the Gibbs function is also represented by a tree graph in which the path connecting individual vertices is equal to the value of the Gibbs function. If one or more graph vertices are located on the gluing line of the topological manifold (the phase transformation line), then two or more graph vertices will become glued. The gluing of vertices creates cyclic components in the graph (loops or cycles). Such a graph represents a multi-phase equilibrium in the system. Thus, gluing vertices or breaking them apart may be interpreted as a graph-based description of phase transformations. A state graph with cycles can be transferred onto a smooth surface (from a piecewise smooth surface) using a simple transformation. The sole purpose of such a transformation is to facilitate interpreting the properties of the graph representation. Graph faces represent individual phases of the system. One may suggest that the conventional representation of a thermodynamic equilibrium state (a point in a space drawn on thermodynamic parameters) is sufficient and ask why the additional, graph-based representation of equilibrium states is necessary. Below is a list of conclusions, i.e., information obtained by applying the graph-based representation of equilibrium states in phenomenological thermodynamics. One can easily notice that this information cannot be obtained using the conventional representation of equilibrium states.

1. The values of the Gibbs function $G(p, T, x_1, x_2, \dots, \tilde{x}_C)$ for a closed isothermal–isobaric system, due to constraints imposed on the function by the Gibbs–Duhem equation, create a two-dimensional topological manifold in a space drawn on thermodynamic parameters regardless of the number of components (C).
2. Phenomenological thermodynamics allows a graph-based interpretation of equilibrium states. The state graph of an equilibrium is a graphical representation of the value of the Gibbs function in equilibrium. It is surprising that the state graph is located on a 2-D surface, i.e., on a Gibbs function topological manifold. The vertices of such a graph are the degrees of freedom in the system, its edges are the weighted chemical potentials of individual components, and its faces are the individual phases, the composition of which is determined by components represented by the edges that form a given face.
3. Applying the graph-based representation of states allows us to count the number of equilibrium state types in a one-phase system. The number is equal to the number of trees with a particular number of edges. In turn, the number of trees is equal to the number of independent components in the system.
4. With the increase in the complexity of one-phase systems beginning with $C = 3$, ‘exotic’ states begin to appear in addition to normal states in equilibrium thermodynamics. These exotic states are represented by branching trees and are the subject of the following part of the publication.
5. As far as the author is concerned, it is only graph theory that allows one to classify the types of invariant states. Only one such state exists for systems with $C = 1$, three exist for $C = 2$, and as many as five exist for $C = 3$.
6. The number of equilibrium types with more than two phases increases with the complexity of the system up to equilibria with $C + 1$ phases. From a topological perspective, there exists only one type of such an equilibrium, represented by C loops suspended on a single vertex.
7. The graph-based representation of states enables the division of two-phase equilibria into classes. The number of these classes increases with the increase in the number of independent components (C). Two classes exist for $C = 2$, four exist for $C = 3$, and as many as nine exist for $C = 4$. One of these classes always represents congruent processes (a cycle with C edges constitutes the state graph in this case), while other classes represent non-congruent processes.

In my opinion, the results presented in this paper will lead to Professor Nenad Trinajstić’s [15] statement on the relationship between Euler’s formula (5) and Gibbs’ phase rule (4) becoming outdated.

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