Phases, phase equilibria and phase rules in low-dimensional systems

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(Dated: July 1, 2015)

Abstract

We present a unified approach to thermodynamic description of one, two and three dimensional phases and phase transformations among them. The approach is based on a rigorous definition of a phase applicable to thermodynamic systems of any dimensionality. Within this approach, the same thermodynamic formalism can be applied for the description of phase transformations in bulk systems, interfaces, and line defects separating interface phases. For both lines and interfaces, we rigorously derive an adsorption equation, the phase coexistence equations, and other thermodynamic relations expressed in terms of generalized line and interface excess quantities. As a generalization of the Gibbs phase rule for bulk phases, we derive phase rules for lines and interfaces and predict the maximum number of phases than may coexist in systems of the respective dimensionality.

PACS numbers:

Keywords: Thermodynamics; phase; phase rule; interface; line defect
I. INTRODUCTION

Surfaces and interfaces can affect many properties of materials ranging from chemical reactivity to wetting, mechanical behavior and thermal and electric resistance. It has long been known that interface properties can suddenly change due to an abrupt change in their atomic structure and/or local chemical composition. Such changes are often interpreted as transformations between different interface phases and are usually described by well-established thermodynamic theories of phase transformations. Despite many years of experimental and theoretical studies, certain thermodynamic aspects of interface phases and interface phase transformations remain unclear. In fact, there is even a controversy about the thermodynamic nature of interface phases, namely, whether they should be treated as a particular case of the general concept of a phase in thermodynamics, or as something fundamentally different from bulk phases. As a consequence, terminological disagreements arose in the materials community, with some authors referring to interface phases as “phases” while others prefer the new term “complexion” introduced to avoid the association with bulk phases.

The goal of this paper is to examine the parallel between phase transformations in bulk and low-dimensional systems from the standpoint of classical thermodynamics. Some of the questions that we seek to answer include: To what extent can one apply the formalism and terminology of classical three-dimensional (3D) thermodynamics to describe two-dimensional (2D) phases at interfaces and one-dimensional (1D) phases within line defects? Is it justifiable to treat transformations between 2D and 1D phases the same way as we treat transformations between bulk (3D) phases?

To answer these questions, we start by reviewing the original definition of a phase, the modern definitions, and their applicability low-dimensional thermodynamic systems. We then formulate a unified definition of a phase that spans all dimensionalities. This definition identifies the concept of a phase with a fundamental equation of state possessing a particular set of mathematical properties. This unified definition leads to a unified treatment of phase equilibria among phases of different dimensionality. Applying this unified thermodynamic formalism, we rigorously derive 2D and 1D versions of the adsorption equation, both expressed in terms of generalized interface (respectively, line) excesses. We also derive generalized Clapeyron-Clausius type equations describing the hypersurfaces of thermodynamic equilibrium between bulk, interface or line phases, as well as generalized phase rules for interfaces and line defects.

The approach applied in this work is largely influenced by the attempts of many authors to formulate the logical structure of thermodynamics in the form of axioms and postulates in a manner similar to mathematical theories. It is not our goal to pursue a complete axiomatic structure of thermodynamics in the present paper. However, the formulation of certain key points in the form of definitions and postulates helps us emphasize important
concepts, logical connections and assumptions that are often implied but not stated explicitly, or simply overlooked. The fundamental equations of state are formulated for simple isotropic systems such as multi-component fluids. While extensions to other systems are possible in the future, in this paper we wish to focus the attention on the most basic concepts and not be distracted by technical difficulties that arise in addressing more complex systems.

As already mentioned, the approach proposed here is restricted to classical thermodynamics. Thus, statistical-mechanical treatments of phases of any dimensionality are beyond the scope of this paper. The interested reader is referred to special literature in the respective fields, such as the Rowlinson and Widom book on molecular-level theories of interfaces. Likewise, we refrain from making any model assumptions regarding the local behavior of properties inside low-dimensional phases. In particular, despite the success of interface theories based on gradient thermodynamics, they are not part of the present discussion. Instead, we adhere to the purely thermodynamic approach in which low-dimensional phases are treated in terms of interface or line excess quantities without attempting to characterize the excess regions in a more detailed (but necessarily approximate) manner.

II. PHASES IN BULK THERMODYNAMICS

A. Definition of a phase

The term “phase” was introduced by Gibbs, who defined phases rather vaguely as “different homogeneous bodies” that “differ in composition or state” (Ref. p.96). Despite the vagueness of this verbal definition, the equations written by Gibbs make it clear that by a phase Gibbs understood a continuum of spatially homogeneous thermodynamic states that follow a given fundamental equation. The concept of a fundamental equation was introduced by Gibbs 10 pages earlier (Ref. p.86) and was defined as “a single equation from which all these relations [thermodynamic properties] may be deduced”. In most of his work, Gibbs used the fundamental equation expressing the entropy $S$ as a function of energy $U$, volume $V$, and the amounts of $k$ chemical components $N_1,...,N_k$ present in the system. Thus, in modern notations, Gibbs’ fundamental equation has the form

$$S = S(U,V,N_1,...,N_k).$$

Occasionally, Gibbs used the function

$$U = U(S,V,N_1,...,N_k),$$

which is nowadays called the fundamental equation in the energy representation. The term “fundamental” expresses the important property of this equation that, knowing it, all
thermodynamic properties of the phase can be derived by computing first and higher partial derivatives.

For solid phases, which were treated by Gibbs in a separate chapter, the fundamental equations are more complex because the extensive properties depend not only on the system volume but also on the elastic strain relative to a chosen reference state. In addition, crystalline solids are subject to a constraint on variations in the numbers of chemical components imposed by the integrity of the crystalline lattice. Here, we will limit the analysis to simple fundamental equations in the form of Eqs. (1) and (2).

The association of phases with fundamental equations is also evident from Gibbs’ treatment of phase equilibria and phase transformations. Fixing one of the extensive variables, say volume, the fundamental equation can be rewritten in the density form, e.g.,

\[ u = u(s, n_1, ..., n_k), \]  

where the small letters represent volume densities. The density form reflects the fact that the identity of a phase does not depend on its amount. Equation (3) can be represented by a hypersurface in the space spanned by the density variables \((s, u, n_1, ..., n_k)\), sometimes referred to as the Gibbs space. Different phases are represented by different hypersurfaces, which Gibbs called the “primitive surfaces”. Equilibria between different phases are then described by imagining common tangent planes to the primitive surfaces, the traces of their intersection with the primitive surfaces, and other geometric constructions. Local curvature of the primitive surface determines intrinsic thermodynamic stability of the respective phase. Details of Gibbs’ geometric thermodynamics will not be discussed here. The important point is that these constructions imply an association of phases with different hypersurfaces and thus different fundamental equations which define them.

After Gibbs, a number of authors re-examined the conceptual foundations of the Gibbs’ thermodynamics in pursuit of a more rigorous, axiomatic structure of the discipline. The effort to create a formal structure of thermodynamics started with the works of Carathéodory and Ehrenfest and continues to this day. Probably, the most complete axiomatic formulation of thermodynamics was developed by Tisza. We will take his approach as a foundation for the present analysis. An important common feature of all axiomatic structures of thermodynamics is the firm association of the concept of phase with a fundamental equation. In essence, phases are identified with fundamental equations.

Symbolically,

\[ \text{Phase} = \text{Fundamental Equation}. \]  

We will, therefore, adopt the following definition of a bulk phase:

**Definition.** Bulk phase is a set of spatially homogeneous states of matter described by a given fundamental equation (1) with the following properties:

- \((U, V, N_1, ..., N_k)\) are extensive (additive) parameters conserved in any isolated system (“additive invariants”)
• \( S(U, V, N_1, ..., N_k) \) is a homogeneous function of first degree with respect to all arguments.

• \( S(U, V, N_1, ..., N_k) \) is a smooth (infinitely differentiable) function.

The additivity of energy is only satisfied for short-range interatomic forces. The requirement that \( S(U, V, N_1, ..., N_k) \) be a homogeneous first degree function is critically important and implies scale invariance of all thermodynamic properties of a phase. It is this property that allows us to reformulate the fundamental equation in the density form. The scale invariance breaks down near critical points.

According to the above definition, if two states of a system satisfy the same fundamental equation, then thermodynamically, they represent the same phase.

**B. Properties of a single phase**

All equilibrium thermodynamic properties of a single phase can be derived from its fundamental equation by straightforward application of calculus without any additional assumptions or approximations. The calculations are simplified by using the following properties of homogeneous functions.

A function \( f(x_1, ..., x_n, y_1, ..., y_m) \) is homogeneous of degree one with respect to the variable set \((x_1, ..., x_n)\) if for any \( \lambda > 0 \)

\[
f(\lambda x_1, ..., \lambda x_n, y_1, ..., y_m) = \lambda f(x_1, ..., x_n, y_1, ..., y_m).
\]

(5)

For such functions, the Euler theorem states that

\[
f(x_1, ..., x_n, y_1, ..., y_m) = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} x_i.
\]

(6)

Taking the full differential of this equation, we obtain

\[
\sum_{j=1}^{m} \frac{\partial f}{\partial y_j} dy_j - \sum_{i=1}^{n} x_i d\left( \frac{\partial f}{\partial x_i} \right) = 0.
\]

(7)

The presence of the non-scalable variables \( y_j \) is optional. They are needed in some applications.

We now apply Euler’s theorem to the fundamental equation (2) with \( x_i \) identified with \( S, V \) and \( N_i \) and without the \( y_j \)-variables. We have

\[
U = TS - pV + \sum_{i=1}^{k} \mu_i N_i,
\]

(8)
where the temperature $T$, pressure $p$ and chemical potentials $\mu_i$ are defined by $T \equiv \partial U/\partial S$, $p \equiv -\partial U/\partial V$ and $\mu_i \equiv \partial U/\partial N_i$, respectively. Next, we apply Eq. (7) to obtain

$$-SDT + Vdp - \sum_{i=1}^{k} N_id\mu_i = 0, \quad (9)$$

which is the well-known the Gibbs-Duhem equation. The calculations can be continued by computing higher derivatives of $U(S,V,N_1,...,N_k)$ to obtain the heat capacity, compressibility, thermal expansion factor and all other commonly used thermodynamic properties.

Equation (9) imposes a constraint on possible variations of the $(k+2)$ intensive variables $(T,p,\mu_1,...,\mu_k)$ characterizing the phase. Due to this constraint, any fixed amount of a single phase is capable of

$$f = k + 1 \quad (10)$$

independent variations called the thermodynamic degrees of freedom.

C. Equilibrium in heterogeneous systems. The phase rule

To address heterogeneous systems, i.e., systems composed of multiple phases, we introduce two postulates:

Postulate 1. Any homogeneous substance can potentially exist in multiple phases, each with its own fundamental equation.

Postulate 2. Any inhomogeneous substance is composed of homogeneous subsystems representing phases.

Note that in the second Postulate, the subsystems can be either different phases or different states of the same phase.*

Consider an isolated heterogeneous systems composed of $\varphi$ phases described by the fundamental equations

$$S_n(U_nV_n, N_{n1}, ..., N_{nk}), \quad n = 1, ..., \varphi. \quad (11)$$

Neglecting, for right now, the role of interfaces between the phases, the additivity of entropy dictates that the total entropy of the system is

$$S_{tot} = \sum_n S_n(U_nV_n, N_{n1}, ..., N_{nk}). \quad (12)$$

According to the entropy maximum principle,[19][21] the necessary and sufficient condition of equilibrium of the system is the maximum of $S_{tot}$ under the isolation constraints[10]

$$\sum_n U_n = \text{const.} \quad (13)$$

* A homogeneous state is defined by a set of variables $(U,V,N_1,...,N_k)$. Two homogeneous states represent the same phase if both satisfy the same fundamental equation.
\[ \sum_n V_n = \text{const}, \]  
\[ \sum_n N_{ni} = \text{const}, \quad i = 1, \ldots, k, \]  
expressing the conservation of energy, volume and the amount of each chemical component, respectively. This variational problem is solved by using a set of Lagrange multipliers \( \lambda_u, \lambda_v \) and \( \lambda_i, \)

\[
\sum_n S_n - \lambda_u \left( \sum_n U_n \right) - \lambda_v \left( \sum_n V_n \right) - \sum_i \lambda_i \left( \sum_n N_{ni} \right) \to \text{max}.
\]

The well-known solution is the equality of temperatures, pressures and chemical potentials in all phases:

\[
T_1 = \ldots = T_\varphi \equiv T, \quad (17)
\]
\[
p_1 = \ldots = p_\varphi \equiv p, \quad (18)
\]
\[
\mu_{1i} = \ldots = \mu_{\varphi i} \equiv \mu_i, \quad i = 1, \ldots, k. \quad (19)
\]

Thus the entire heterogeneous system is described by \( (k + 2) \) intensive variables \( (T, p, \mu_1, \ldots, \mu_k) \). However, these variables are not independent. Each phase must satisfy its own Gibbs-Duhem equation, which imposed \( \varphi \) constraints

\[ - S_n dT + V_n dp - \sum_{i=1}^k N_{ni} d\mu_i = 0, \quad n = 1, \ldots, \varphi. \]

As a result, the number of independent variations of the heterogeneous system becomes

\[ f = k + 2 - \varphi, \]

a relation known as the Gibbs phase rule.\(^{19}\)

The global properties \( (T, p, \mu_1, \ldots, \mu_k) \) are referred to as intensities or fields. They are distinguished from densities (ratios of extensive properties), such as energy, entropy, or the amounts of chemical components per unit volume or per particle. Both intensities and densities are local variables that characterize physical points. However, while the intensities are uniform across the heterogeneous system, the densities are generally different in different phases and experience discontinuities across phase boundaries. The geometric common-tangent constructions describing phase equilibria apply to densities but not intensities.

III. INTERFACE PHASES

A. Definition of interface phase

The concept of an interface phase can be traced back to Gibbs.\(^{19}\) When analyzing the stability of interfaces with respect to changes in state (Ref. p. 237-240), Gibbs recognized
the possibility of different interface states that can reach equilibrium with the same bulk phases. Gibbs did not call these equilibrium states phases, but he treated them exactly the same way as he treated bulk phases in other parts of his work. He showed that if the interface “states” coexist in equilibrium with each other, they must have the same surface tension $\gamma$. He also showed that interface states with lower $\gamma$ are more stable than interface states with larger $\gamma$. In other words, the most stable state of the interface is that which minimizes the interface tension. Gibbs even discussed metastable states of interfaces and pointed out that they can transform to more stable states by a nucleation and growth mechanism.

Later on, the interface “states” discussed by Gibbs came to be called surface or interface phases, especially in the surface physics and chemistry communities where a large variety of surface phases were found in adsorbed surface layers and represented as surface phase diagrams. In the 1970s, Hart published influential papers analyzing structural transformations in grain boundaries. Hart applied the thermodynamic formalism developed by Gibbs except that he referred to Gibbs’ interface “states” as 2D grain boundary phases. Furthermore, Hart explicitly associated the grain boundary phases with different fundamental equations. Using the analogy with Gibbs’ bulk thermodynamics, he derived a generalized version of the Clapeyron-Clausius equation that contained jumps of interface excess properties between the grain boundary phases, including a jump of the excess volume. Cahn published a thorough thermodynamic analysis and the most complete classification of interface phase transformations. Over the recent years, experiments have revealed a number of phases and phase transformations in both metallic and ceramic grain boundaries, see Refs. for recent reviews. Atomistic computer simulations have reached the stages where reversible structural phase transformation can be identified and studied in both low- and high-angle grain boundaries.

To formulate a rigorous definition of an interface phase, consider two bulk phases, $\alpha$ and $\beta$, separated by a plane interface (Fig. 1(a)). Following Gibbs, we choose a geometric dividing surface by some rule. For example, it can be the equimolar surface of component 1 (zero excess of this component). This choice is unimportant and is only needed as a starting point. We will soon replace it by a general formulation that does not require a dividing surface. For any extensive property $X$, we define its excess $\tilde{X}$ by

$$\tilde{X} = X - X_\alpha - X_\beta.$$  

Here $X$ is the value of the property for an imaginary box containing the interface and $X_\alpha$ and $X_\beta$ are the values assigned to the phases assuming that they remain homogeneous all the way to the dividing surface.

**Definition.** Interface phase is a set of spatially homogeneous (over the dividing surface) states of the interface described by a given fundamental equation

$$\tilde{S} = \tilde{S}(\tilde{U}, A, \tilde{N}_2, \ldots, \tilde{N}_k)$$  

8
with the following properties:

- \((\tilde{S}, \tilde{U}, \tilde{A}, \tilde{N}_2, ..., \tilde{N}_k)\) are extensive (additive) parameters on the dividing surface

- \(\tilde{S}(\tilde{U}, \tilde{A}, \tilde{N}_2, ..., \tilde{N}_k)\) is a homogeneous function of first degree with respect to the variable set \((\tilde{U}, \tilde{A}, \tilde{N}_2, ..., \tilde{N}_k)\)

- \(\tilde{S}(\tilde{U}, \tilde{A}, \tilde{N}_2, ..., \tilde{N}_k)\) is a smooth (infinitely differentiable) function

Here, \(A\) is the area of the dividing surface. The excesses of the components, \(\tilde{N}_i\), represent interface segregations or depletions. Note that \(\tilde{N}_1\) is not listed as a variable due to our choice of the dividing surface \((\tilde{N}_1 = 0)\). This definition is similar to the bulk phase definition (Sec. II A), except that the volume is replaced by the area and the spatial homogeneity is understood in the 2D sense (over the surface). While there can be situations in which the excess properties display strong variations along the interface, the present theory is limited to systems in which gradients along the interface can be neglected. Small variations can be easily handled by mentally partitioning the interface into regions that can be treated as homogeneous with sufficient accuracy. Of course, most properties exhibit extremely rapid spatial variations across the interface. As already mentioned, the present theory does not set the goal of describing such local variations but instead focuses on the total, integrated amounts of the respective properties and their excesses over bulk properties.

Note that, similar to bulk phases, we postulate a one-to-one mapping between interface phases and fundamental equations: different interface phases - different fundamental equations.

It is important to note that the very existence of the interface fundamental equation implies that interfaces can exist in states of internal equilibrium that follow a fundamental equation without being in equilibrium with the bulk phases or other interface phases. Recall that the same is implied in bulk thermodynamics: bulk phases satisfy their fundamental equations whether or not they are in equilibrium with each other.

### B. Equilibrium among interface phases.

To describe multiple interface phases, we introduce the following postulates:

**Postulate 1.** Any homogeneous interface can potentially exist in multiple interface phases, each with its own fundamental equation.

**Postulate 2.** Any inhomogeneous interface is composed of homogeneous regions representing interface phases.

As with bulk phases, the homogeneous regions mentioned in Postulate 2 can be either different interface phases or different states of the same interface phase.

We next derive the conditions of thermodynamic equilibrium between different interface phases and between the interface and the adjoining bulk phases. Let the interface be com-
posed of $\nu$ phases occupying different areas $A_m$ (Fig. 1(b)). Their fundamental equations are
\[
\tilde{S}_m = \tilde{S}_m(\tilde{U}_m, A_m, \tilde{N}_m, \ldots, \tilde{N}_{mk}), \quad m = 1, \ldots, \nu. \tag{24}
\]
Note that the dividing surfaces of the interface phases are generally different. To find the conditions of equilibrium, we apply the entropy maximum principle with respect to the total entropy of the system considered to be isolated. The calculation is similar to the bulk case (Sec. II C), except that we now include the contributions of interface phases that were previously ignored. The total entropy combines the fundamental equations of the bulk and interface phases:
\[
S_{\text{tot}} = S_\alpha(U_\alpha V_\alpha, N_{\alpha 1}, \ldots, N_{\alpha k}) + S_\beta(U_\beta V_\beta, N_{\beta 1}, \ldots, N_{\beta k}) + \sum_{m=1}^{\nu} \tilde{S}_m(U_m, A_m, \tilde{N}_{m 2}, \ldots, \tilde{N}_{mk}). \tag{25}
\]
This entropy is maximized at fixed values of the total energy, volume, interface area and the amounts of all chemical components:
\[
U_\alpha + U_\beta + \sum_{m=1}^{\nu} \tilde{U}_m = \text{const}, \tag{26}
\]
\[
V_\alpha + V_\beta = \text{const}, \tag{27}
\]
\[
\sum_{m=1}^{\nu} A_m = \text{const}, \tag{28}
\]
\[
N_{\alpha i} + N_{\beta i} + \sum_{m=1}^{\nu} \tilde{N}_{mi} = \text{const}, \quad i = 1, \ldots, k. \tag{29}
\]
These constraints are imposed by Lagrange multipliers $\lambda_u$, $\lambda_v$, $\lambda_a$ and $\lambda_i$, reducing the variational problem to
\[
S_\alpha + S_\beta + \sum_{m=1}^{\nu} \tilde{S}_m - \lambda_u \left( U_\alpha + U_\beta + \sum_{m=1}^{\nu} \tilde{U}_m \right) - \lambda_v (V_\alpha + V_\beta)
\]
\[
- \lambda_a \left( \sum_{m=1}^{\nu} A_m \right) - \sum_{i} \lambda_i \left( N_{\alpha i} + N_{\beta i} + \sum_{m=1}^{\nu} \tilde{N}_{mi} \right) \to \text{max}. \tag{30}
\]
The following equilibrium conditions are obtained:

- **Thermal equilibrium**
\[
T_\alpha = T_\beta = \left( \frac{\partial \tilde{S}_1}{\partial \tilde{U}_1} \right)^{-1} = \ldots = \left( \frac{\partial \tilde{S}_\nu}{\partial \tilde{U}_\nu} \right)^{-1} \equiv T. \tag{31}
\]

- **Mechanical equilibrium**
\[
p_\alpha = p_\beta. \tag{32}
\]
• Chemical equilibrium

\[ \mu_{ai} = \mu_{\beta i} = -T \left( \frac{\partial \tilde{S}_1}{\partial \tilde{N}_{i1}} \right) = ... = -T \left( \frac{\partial \tilde{S}_\nu}{\partial \tilde{N}_{\nu i}} \right) \equiv \mu_i \quad i = 2, ..., k, \]

(33)

\[ \mu_{a1} = \mu_{\beta 1}. \]

(34)

• Interface tension equilibrium

\[ \frac{\partial \tilde{S}_1}{\partial \tilde{A}_1} = ... = \frac{\partial \tilde{S}_\nu}{\partial \tilde{A}_\nu}. \]

(35)

The derivatives \((\partial \tilde{S}_m / \partial \tilde{U}_m)^{-1}\) can be called the “temperatures” of the interface phases, in which case Eq. (31) expresses the uniformity of temperature across the entire equilibrium system, including the interface and bulk phases. Likewise, \(-T(\partial \tilde{S}_m / \partial \tilde{N}_{mi})\) can be called the “chemical potential” of component \(i\) in the interface phase \(m\).† The chemical equilibrium can be then formulated as equality of chemical potentials \(\mu_i\) in all interface and bulk phases of the system. Finally,

\[ \gamma_m \equiv -T \frac{\partial \tilde{S}_m}{\partial \tilde{A}_m} \]

(36)

is defined as the interface free energy or interface tension of phase \(m\). Since we have postulated that the excess entropy is a homogeneous function of first degree with respect to the area, it follows that \(\gamma_m\) is a local property that does not depend on the area. For small interface regions bounded by other defects this may not be the case. Such situations are not considered in the present theory.

Thus, the interface tension equilibrium can be expressed as the equality of tensions in all coexisting interface phases:

\[ \gamma_1 = ... = \gamma_\nu. \]

(37)

This equation recovers the interface equilibrium condition derived by Gibbs.† Just like the interface area is a 2D analog of volume, the interface tension \(\gamma\) is a 2D analog of the bulk pressure \(-p\). In this sense, Eq. (35) is a 2D analog of the equality of pressures in coexisting bulk phases.

C. Equilibrium properties of a single interface phase

Similar to bulk phases, the fundamental equation \((23)\) encapsulates all properties of the interface phase. Consider reversible processes in which a single-phase interface always remains in equilibrium with the bulk phases. Since the fundamental equation is homogeneous

† The interface chemical potential of component 1 is not defined by Eqs. (33) and (34) since its interface excess is zero. However, we can repeat the calculation by choosing the dividing surface as equimolar with respect to another component. This will lead to the expected result that \(\mu_1 = \mu_{\alpha i} = \mu_{\beta i}\).
first degree, we apply Euler’s theorem to obtain

\[
\tilde{S} = \frac{\partial \tilde{S}}{\partial \tilde{U}} \tilde{U} + \frac{\partial \tilde{S}}{\partial A} A + \sum_{i=2}^{k} \frac{\partial \tilde{S}}{\partial \tilde{N}_i} \tilde{N}_i
\]

\[
= \frac{1}{T} \tilde{U} - \frac{\gamma}{T} A - \frac{1}{T} \sum_{i=2}^{k} \mu_i \tilde{N}_i,
\]

(38)

which can be rewritten as

\[
\gamma A = \tilde{U} - T \tilde{S} - \sum_{i=2}^{k} \mu_i \tilde{N}_i.
\]

(39)

This equation appears in Gibbs (Ref. 19, Eq. (502)) and expresses \(\gamma\) as the excess of the grand potential \(\tilde{U} - T \tilde{S} - \Sigma \mu_i \tilde{N}_i\) per unit interface area. On the other hand, differentiation of the fundamental equation (23) gives

\[
d\tilde{S} = \frac{1}{T} d\tilde{U} - \frac{\gamma}{T} dA - \frac{1}{T} \sum_{i=2}^{k} \mu_i d\tilde{N}_i,
\]

(40)

from which

\[
d\tilde{U} = T d\tilde{S} + \sum_{i=2}^{k} \mu_i d\tilde{N}_i + \gamma dA.
\]

(41)

This well-known equation also appears in Gibbs (Ref. 19, Eq. (501)) and shows that the interface adds an extra work term which is a 2D analog of the mechanical work \(-p dV\) in bulk systems. In fact, this equation was the starting point of Gibbs’ interface thermodynamics from which all other equations were derived. Finally, by adding Eq. (41) to the differential of Eq. (39) we obtain the Gibbs adsorption equation (Ref. 19, Eq. (508))

\[
Ad \gamma = -\tilde{S} dT - \sum_{i=2}^{k} \tilde{N}_i d\mu_i.
\]

(42)

Note the ease with which these equations have been derived starting from the fundamental equation and using known properties of homogeneous functions.

Equation (42) shows that the state of a single-phase interface that maintains equilibrium with the bulk phases is defined by \(k\) independent intensive variables. This is consistent with the Gibbs phase rule (21) predicting \(f = k\) degrees of freedom for a two-phase (\(\varphi = 2\)) system with \(k\) chemical components.

### D. Reformulation in generalized interface excesses

Until this point, the interface excess quantities were defined relative to a certain choice of the dividing surface. We can now remove this restriction and reformulate all equations
in terms of generalized excess introduced by Cahn. We start with the adsorption equation (42) and replace all excesses appearing in this equation by their definitions according to Eq. (22). As a result, the adsorption equation takes the “global” form

\[ Ad\gamma = -SdT + Vdp - \sum_{i=1}^{k} N_i d\mu_i, \] (43)

where \( S, V \) and \( N_i \) refer to the entire system containing two bulk phases and the interface. The terms with \( X_\alpha \) and \( X_\beta \) canceled out due to the Gibbs-Duhem equations for the bulk phases:

\[ 0 = -S_\alpha dT + V_\alpha dp - \sum_{i=1}^{k} N_{\alpha i} d\mu_i, \] (44)

\[ 0 = -S_\beta dT + V_\beta dp - \sum_{i=1}^{k} N_{\beta i} d\mu_i. \] (45)

Since these equations remain valid after re-scaling by an arbitrary factor, they can be thought of as representing arbitrarily chosen homogeneous regions inside the bulk phases. Note that the global adsorption equation (43) does not contain excess quantities, which demonstrates that \( \gamma \) is independent of definitions of excesses.

As a result of this “unwrapping” procedure, the adsorption equation (42) has been recast in the global form (43) where it does not depend on any definitions of interface excesses. However, this equation must be considered simultaneously with the Gibbs-Duhem equations (46) and (45). The advantage of this global form is that we can now eliminate any two differentials from Eq. (43), not necessarily \( dp \) and \( d\mu_1 \) as it was done before by choosing the equimolar dividing surface of component 1. The elimination is accomplished most elegantly by using the Kramer rule of linear algebra, resulting in the generalized adsorption equation:

\[ Ad\gamma = -[S]_{XY} dT + [V]_{XY} dp - \sum_{i=1}^{k} [N_i]_{XY} d\mu_i. \] (46)

Here, \( X \) and \( Y \) are any two extensive variables from the list \( (S, V, N_1, ..., N_k) \) and the square brackets denote ratios of two determinants. Namely, for any extensive property \( Z \),

\[ [Z]_{XY} \equiv \begin{vmatrix} Z & X & Y \\ Z_\alpha & X_\alpha & Y_\alpha \\ Z_\beta & X_\beta & Y_\beta \end{vmatrix}, \] (47)

where \( Z, X \) and \( Y \) are computed for the two-phase system and the remaining quantities represent arbitrarily chosen homogeneous regions inside the bulk phases. The generalized
excess \([Z]_{XY}\) has the meaning of the interface excess of the extensive property \(Z\) in a two-phase system that contains the same amounts of \(X\) and \(Y\) as the two single-phase regions combined. By properties of determinants, \([X]_{XY} = [Y]_{XY} = 0\). Thus, the excesses of \(X\) and \(Y\) are zero and two terms in Eq. (46) automatically vanish. By choosing the properties \(X\) and \(Y\) we can control which two differentials in Eq. (46) disappear and which \(k\) remain as independent variables.

If \(X\) is volume, then \([Z]_{XY}\) defines an excess of \(Z\) relative to a geometric dividing surface as in Gibbs’ interface thermodynamics\(^{19}\). The position of the dividing surface is then dictated by the choice of the second variable \(Y\). For example, by choosing \(Y = N_1\) we return to the previously defined excesses relative to the equimolar surface of component 1. When neither \(X\) nor \(Y\) is volume, the generalized interface excess is defined without using any dividing surface. This generalization enables us to define the interface excess volume \([V]_{XY}\). As all other excesses, the excess volume is not unique. For example, if we choose \(X = S\) and \(Y = N_1\), the excess volume becomes

\[
[V]_{SN_1} = \begin{vmatrix}
V & S & N_1 \\
V_\alpha & S_\alpha & N_{\alpha 1} \\
V_\beta & S_\beta & N_{\beta 1} \\
S_\alpha & N_{\alpha 1} \\
S_\beta & N_{\beta 1}
\end{vmatrix}.
\] (48)

Other interface properties can also be reformulated in terms for generalized excesses. For example, the interface tension equation (39) can be generalized to\(^{11}\)

\[
\gamma A = [U]_{XY} - T [S]_{XY} + p [V]_{XY} - \sum_{i=1}^{k} \mu_i [N_i]_{XY}.
\] (49)

This leads to several equivalent excess formulations of \(\gamma\), such as

\[
\gamma A = \left[ U + pV - \sum_{i=2}^{k} N_i \mu_i \right]_{SN_1} = \left[ U - TS + pV - \sum_{i=3}^{k} N_i \mu_i \right]_{N_1N_2}.
\] (50)

We can also derive an interface analog of the Clapeyron-Clausius equation describing phase coexistence. Indeed, for two coexisting interface phase, labeled by a single and double prime, Eq. (46) takes the form

\[
d\gamma' = -\frac{[S']_{XY}}{A'}dT + \frac{[V']_{XY}}{A'}dp - \sum_{i=1}^{k} \frac{[N_i']_{XY}}{A'}d\mu_i,
\] (51)

\[
d\gamma'' = -\frac{[S'']_{XY}}{A''}dT + \frac{[V'']_{XY}}{A''}dp - \sum_{i=1}^{k} \frac{[N_i'']_{XY}}{A''}d\mu_i.
\] (52)
In reversible processes when the phases remain in equilibrium with each other, their tensions must remain equal, \( d\gamma' = d\gamma'' \). This immediately gives

\[
- \Delta \left( \frac{[S]_{XY}}{A} \right) dT + \Delta \left( \frac{[V]_{XY}}{A} \right) dp - \sum_{i=1}^{k} \Delta \left( \frac{[N_i]_{XY}}{A} \right) d\mu_i = 0,
\]

(53)

where \( \Delta \) denotes the difference between the two interface phases. For example, by choosing \( X = S \) and \( Y = V \), we obtain the Clapeyron-Clausius type equation

\[
- \sum_{i=1}^{k} \Delta \left( \frac{[N_i]_{XY}}{A} \right) d\mu_i = 0
\]

(54)

defining a \((k - 1)\)-dimensional hypersurface of interface phase coexistence in the \( k \)-dimensional space of variables \((\mu_1, ..., \mu_k)\). The coefficients in Eq.(54) are the jumps of interface segregations (per unit area) across this hypersurface.

E. The interface phase rule

We can now formulate the interface phase rule. Consider an equilibrium heterogeneous system composed of \( \varphi \) coexisting bulk phases. We will focus the attention on one particular interface separating two phases. Suppose this interface contains \( \nu \) coexisting interface phases. We wish to find the number of independent variables that can be varied while keeping the same number of bulk and interface phases. Let us call this number \( f_i \) degrees of freedom.

The system is described by \((k + 2)\) intensive parameters: \( T, p, \) and \( k \) chemical potentials \( \mu_i \). But they are not independent. First, we have \( \varphi \) Gibbs-Duhem equations (20) for the bulk phases that impose \( \varphi \) constraints on variations of intensities. Second, we have \( \nu \) adsorption equations for the coexisting interface phases. They contain an additional variable \( \gamma \), which we can eliminate and obtain \((\nu - 1)\) equations of constraint. As a result, the number of degrees of freedom is \((k + 2) - \varphi - (\nu - 1)\). The interface phase rule becomes

\[
f_i = k + 3 - \varphi - \nu.
\]

(55)

From this rule, we can find the maximum possible number of coexisting interface phases (when \( f_i = 0 \)):

\[
\nu_{\text{max}} = k + 3 - \varphi.
\]

(56)

For example, in a single-component two-phase system, only two interface phases can coexist at the interface. At a triple point (\( \varphi = 3 \)), only one phase can exist at each interface. On the other hand, if we have a binary single-phase system, an interface such as a surface, can support up to four coexisting interface phases.
IV. LINE PHASES

A. Definition of a line phase

In the analysis of coexisting interface phases, we have so far neglected the contributions of the line defects lying in the interface plane and separating interface phases. Such line defects, or simply lines, are 1D analogs of phase boundaries in bulk thermodynamics. We are not aware of experimental studies of lines, but they have recently been observed in atomistic computer simulations of metallic grain boundaries. Fig. 2(a) shows an example of a straight line separating two grain boundary phases, called kites and split kites, in a symmetrical tilt boundary in Cu. The structure of this grain boundary undergoes a reversible transformation from one phase to another with temperature. At some temperature, the two phases coexist in equilibrium and are separated by a line. It is also possible to equilibrate and isolated inclusion of the split-kite phase bounded by a curved line (Fig. 2(b)). The oval shape of the line indicates that its properties are anisotropic. These observations motivate the development of a thermodynamic theory of lines. Similar to bulk and interface phases, one can expect that lines may exist in multiple phases. The goal of this section is to examine thermodynamic properties of line phases. It should be noted that line phases were not discussed by Gibbs or analyzed by other researchers after Gibbs. However, they are important as they influence the nucleation of new interface phases.

As a first step, we define excess properties of a line. Consider two bulk phases \( \alpha \) and \( \beta \) and two interface phases 1 and 2 joining along a line as in Fig. 3. We first choose a geometric dividing surface for each interface phase as we did before; for example, it can be the equimolar surface of component 1. This choice is unimportant because it will later be generalized to arbitrary excesses. Next, we choose a geometric dividing plane between the interface phases. This plane is normal to the interface and parallel to the line, but otherwise is arbitrary. For any extensive property \( X \), we define its line excess \( \hat{X} \) as the total amount of \( X \) in the system, minus the bulk values of \( X \) as if the bulk phases were homogeneous all the way to the dividing surfaces, and minus the excesses for the interface phases computed as if these phases remained homogeneous (over the interface plane) all the way to the dividing plane:

\[
\hat{X} \equiv X - X_\alpha - X_\beta - \tilde{X}_1 - \tilde{X}_2.
\] (57)

For definitiveness, let us choose the dividing plane so that the line excess of component 1 is zero, \( \hat{N}_1 = 0 \).

We now define a line phase by direct analogy with the previous definitions of bulk and interface phases.

**Definition.** Line phase is a set of spatially homogeneous (along the line) states of a line described by a given fundamental equation

\[
\hat{S} = \hat{S}(\hat{U}, \hat{L}, \hat{N}_2, ..., \hat{N}_k)
\] (58)
with the following properties:

- \((\hat{S}, \hat{U}, \hat{N}_2, ..., \hat{N}_k)\) are extensive (additive) parameters along the line
- \(\hat{S}(\hat{U}, L, \hat{N}_2, ..., \hat{N}_k)\) is a homogeneous function of first degree with respect to the variable set \((\hat{U}, L, \hat{N}_1, ..., \hat{N}_k)\)
- \(\hat{S}(\hat{U}, L, \hat{N}_2, ..., \hat{N}_k)\) is a smooth (infinitely differentiable) function

Here, \(L\) is the length of the line. The only difference between this definition and the previous definition of an interface phase is that the spatial homogeneity is understood in the 1D sense (along the line). As with bulk and interface phases, it is assumed that the line phase follows its fundamental equation \([58]\) even when it is not in equilibrium with the surrounding phases.

**B. Coexistence of line phases**

To describe heterogeneous lines, we introduce the following postulates:

1. **Postulate 1.** Any homogeneous line can potentially exist in multiple line phases, each with its own fundamental equation.
2. **Postulate 2.** Any inhomogeneous line is composed of homogeneous segments representing line phases.

As before, the homogeneous segments mentioned in Postulate 2 can be either different line phases or different states of the same line phase.

We can now formulate the conditions of thermodynamic equilibrium in a system composed of two bulk phases \(\alpha\) and \(\beta\), two interface phases 1 and 2, and several line phases. Let the total number of line phases be \(\omega\). The total entropy of the system is obtained by summing up the relevant fundamental equations:

\[
S_{tot} = S_\alpha(U_\alpha, V_\alpha, N_{\alpha1}, ..., N_{\alpha k}) + S_\beta(U_\beta, V_\beta, N_{\beta1}, ..., N_{\beta k})
+ \hat{S}_1(\hat{U}_1, A_1, \hat{N}_{12}, ..., \hat{N}_{1k}) + \hat{S}_2(\hat{U}_2, A_2, \hat{N}_{22}, ..., \hat{N}_{2k})
+ \sum_{n=1}^{\omega} \hat{S}_n(\hat{U}_n, L_n, \hat{N}_{n2}, ..., \hat{N}_{nk}).
\]  

(59)

In an isolated system, variations of \(S_{tot}\) are subject to the constraints of fixed total energy, total volume, total area of the interface phases, total length of the line phases, and the total amount of each chemical component:

\[
U_\alpha + U_\beta + \hat{U}_1 + \hat{U}_2 + \sum_{n=1}^{\omega} \hat{U}_n = \text{const},
\]

(60)

\[
V_\alpha + V_\beta = \text{const},
\]

(61)
A_1 + A_2 = \text{const}, \quad (62)

\sum_{n=1}^{\omega} L_n = \text{const}, \quad (63)

N_{\alpha i} + N_{\beta i} + \tilde{N}_{1i} + \tilde{N}_{2i} + \sum_{n=1}^{\omega} \hat{N}_{ni} = \text{const}, \ i = 1, \ldots, k. \quad (64)

Imposing these constraints by appropriate Lagrange multipliers, the necessary conditions of $S_{tot} \rightarrow \max$ are summarized as follows:

- **Thermal equilibrium**

\[
T_\alpha = T_\beta = \left( \frac{\partial \tilde{S}_1}{\partial U_1} \right)^{-1} = \left( \frac{\partial \tilde{S}_2}{\partial U_2} \right)^{-1} = \left( \frac{\partial \tilde{S}_1}{\partial U_1} \right)^{-1} = \ldots = \left( \frac{\partial \tilde{S}_\omega}{\partial U_\omega} \right)^{-1} \equiv T. \quad (65)
\]

- **Mechanical equilibrium**

\[p_\alpha = p_\beta. \quad (66)\]

- **Chemical equilibrium**

\[
\mu_{\alpha i} = \mu_{\beta i} = -T \left( \frac{\partial \tilde{S}_1}{\partial N_{1i}} \right) = -T \left( \frac{\partial \tilde{S}_2}{\partial N_{2i}} \right) = \ldots = \left( \frac{\partial \tilde{S}_\omega}{\partial N_{\omega i}} \right) \equiv \mu_i, \ i = 2, \ldots, k, \quad (67)
\]

\[
\mu_{\alpha 1} = \mu_{\beta 1}. \quad (68)
\]

- **Interface tension equilibrium**

\[
\frac{\partial \tilde{S}_1}{\partial A_1} = \frac{\partial \tilde{S}_2}{\partial A_2}. \quad (69)
\]

- **Line tension equilibrium**

\[
\frac{\partial \tilde{S}_1}{\partial L_1} = \ldots = \frac{\partial \tilde{S}_\omega}{\partial L_\omega}. \quad (70)
\]

Equation (65) expresses the uniformity of temperature across the equilibrium system, including the bulk, interface and line phases. It is convenient to call the derivative $-T(\partial \tilde{S}_n/\partial \tilde{N}_{ni})$ the “chemical potential” of component $i$ in the line phase $n$. Then the chemical equilibrium condition can be formulated as equality of chemical potentials $\mu_i$ in the bulk, interface and line phases. The interface tension equilibrium condition (69) reduces to $\gamma_1 = \gamma_2$. Finally, defining the line tension of a line phase $n$ by

\[
\tau_n = -T \frac{\partial \tilde{S}_n}{\partial L_n}, \quad (71)
\]
Eq. (70) states that the line tensions of coexisting line phases must be equal:
\[ \tau_1 = \ldots = \tau_\omega. \]  
(72)

The line tension is obviously a 1D analog of the bulk pressure (up to the sign) and the interface tension \( \gamma \).

C. The line adsorption equation

Returning to a single line phase, consider reversible thermodynamic processes in which the line remains in equilibrium with the interface and bulk phases. Applying, as usual, the Euler theorem to the fundamental equation (58) we have
\[
\dot{S} = \frac{\partial \dot{S}}{\partial U} \dot{U} + \frac{\partial \dot{S}}{\partial L} \dot{L} + \sum_{i=2}^{k} \frac{\partial \dot{S}}{\partial N_i} \dot{N}_i \\
= \frac{1}{T} \dot{U} - \frac{\tau}{T} \dot{L} - \frac{1}{T} \sum_{i=2}^{k} \mu_i \dot{N}_i, 
\]  
(73)

from which
\[
\tau L = \dot{U} - T \dot{S} - \sum_{i=1}^{k} \mu_i \dot{N}_i. 
\]  
(74)

On the other hand, differentiation of the fundamental equation (58) gives
\[
d\dot{S} = \frac{1}{T} d\dot{U} - \frac{\tau}{T} d\dot{L} - \frac{1}{T} \sum_{i=2}^{k} \mu_i d\dot{N}_i, 
\]  
(75)

and thus
\[
d\dot{U} = T d\dot{S} + \sum_{i=2}^{k} \mu_i d\dot{N}_i + \tau d\dot{L}. 
\]  
(76)

Finally, adding Eq. (76) to the differential of Eq. (74) we obtain the Gibbs adsorption equation for a line phase:
\[
L d\tau = -\dot{S} dT - \sum_{i=2}^{k} \dot{N}_i d\mu_i. 
\]  
(77)

Equations (73) to (77) bear a close similarity with the respective equations (38) to (42) of interface thermodynamics. This is not surprising given the similar structures of the fundamental equations (23) and (58) defining the interface and line phases, respectively.

D. Reformulation in generalized line excesses

The \( k \) differentials appearing in the line adsorption equation (77) are not all independent because we have not yet imposed the condition of equality of the surface tensions of the
interface phases separated by the line. The latter condition reduces the number of independent differentials to \((k - 1)\). To express the adsorption equation in terms of independent differentials, we will reformulate it in terms of generalized excesses.

The first step is to “unwrap” Eq. (77) by replacing all excess quantities by their definitions (57). After rearrangements with the aid of Eqs. (9) and (42), we obtain the global form of the line adsorption equation:

\[
Ld\tau = -SdT + Vdp - \sum_{i=1}^{k} N_i d\mu_i - Ad\gamma.
\] (78)

Here, the quantities \(S, V, N_i\) and \(A\) refer to an arbitrarily chosen rectangular box containing the two interface phases and the line (Fig. 4(a)). The dimensions of the box must be much larger than the characteristic thickness of the interface and the cross-section of the line. Equation (78) shows that \(\tau\) is independent of definitions of excesses. It must be supplemented by four other equations containing the same differentials, namely, the global forms of the adsorption equations for the interface phases,

\[
0 = -S'dT + V'dp - \sum_{i=1}^{k} N'_i d\mu_i - A'd\gamma,
\] (79)

and the Gibbs-Duhem equations for the bulk phases,

\[
0 = -S_\alpha dT + V_\alpha dp - \sum_{i=1}^{k} N_{\alpha i} d\mu_i,
\] (81)

\[
0 = -S_\beta dT + V_\beta dp - \sum_{i=1}^{k} N_{\beta i} d\mu_i.
\] (82)

Equations (79) and (80) are written for imaginary boxes containing a single interface phase, either 1 or 2, and uninfluenced by the line (Fig. 4(b,c)). The cross-sectional areas and the total amounts of extensive properties in these boxes are distinguished by the prime and double prime, respectively. Likewise, Eqs. (81) and (82) represent homogeneous bulk regions of phases \(\alpha\) and \(\beta\), respectively (Fig. 4(d)). Because the differential coefficients in each of the Eqs. (78) to (82) can be scaled by an arbitrary common multiplier, the choice of dimensions of all boxes is arbitrary as long as the conditions stated above (e.g., the homogeneity of the bulk regions) are satisfied.

The right-hand side of Eq. (78) contains \((k + 3)\) terms. Equations (79) to (82) impose four constraints, leaving \((k - 1)\) independent differentials as the variables of \(\tau\). Which variables to eliminate is a matter choice and can be conveniently controlled by re-writing Eq. (78) in...
terms of generalized excess as it was done for interfaces (sec. III D). Applying the Kramer
rule of linear algebra, we obtain

\[ Ld\tau = -[S]_{WXYZ}dT + [V]_{WXYZ}dp - \sum_{i=1}^{k} [N_i]_{WXYZ}d\mu_i - [A]_{WXYZ}d\gamma, \quad (83) \]

where \( W, X, Y \) and \( Z \) are any four of the extensive variables \( (S,V,N_1,...,N_k,A) \). The
square brackets are generalized excesses defined by ratios of two determinants of ranks 5
and 4. Namely, for any extensive property \( R \),

\[ [R]_{WXYZ} \equiv \frac{\left| \begin{array}{cccccc}
R & W & X & Y & Z \\
R'' & W'' & X'' & Y'' & Z'' \\
R' & W' & X' & Y' & Z' \\
R_{\alpha} & W_{\alpha} & X_{\alpha} & Y_{\alpha} & Z_{\alpha} \\
R_{\beta} & W_{\beta} & X_{\beta} & Y_{\beta} & Z_{\beta} \\
W'' & X'' & Y'' & Z'' \\
W' & X' & Y' & Z' \\
W_{\alpha} & X_{\alpha} & Y_{\alpha} & Z_{\alpha} \\
W_{\beta} & X_{\beta} & Y_{\beta} & Z_{\beta} 
\end{array} \right|}{\left| \begin{array}{cccccc}
W'' & X'' & Y'' & Z'' \\
W' & X' & Y' & Z' \\
W_{\alpha} & X_{\alpha} & Y_{\alpha} & Z_{\alpha} \\
W_{\beta} & X_{\beta} & Y_{\beta} & Z_{\beta} 
\end{array} \right|}. \quad (84) \]

The meaning of \([R]_{WXYZ}\) is the line excess of property \( R \) computed with a set of reference
boxes such that the excesses of \( W, X, Y \) and \( Z \) are zero. Equation (83) reveals two
new excess quantities that did not appear in Eq.(77): the line excess volume \([V]_{WXYZ}\)
characterizing the contribution of the line to the total interface excess volume, and the
line excess area \([A]_{WXYZ}\) characterizing the interface area attributed to the line. Equation
(76) shows that a line tension depends on both the 3D pressure \( p \) and the 2D “pressure” \( \gamma \).
The line excess volume and area, as well as the line excess entropy \([S]_{WXYZ}\) and the line
segregations \([N_i]_{WXYZ}\), are not unique. Their values depend on the choice of the properties
\( W, X, Y \) and \( Z \). Whatever their choice is, the terms with the excesses of \( W, X, Y \) and \( Z \)
disappear and we are left with \((k - 1)\) independent differentials. For example, by choosing
\( WXYZ = ASVN_1 \), the line adsorption equation reduces to

\[ Ld\tau = -\sum_{i=2}^{k} [N_i]_{ASVN_1}d\mu_i, \quad (85) \]

involving only line segregations.

The excess form of the line tension, which was previously given by Eq.(74), can also be
generalized to

\[ \tau L = [U]_{WXYZ} - T[S]_{WXYZ} + p[V]_{WXYZ} - \sum_{i=1}^{k} \mu_i [N_i]_{WXYZ} - [A]_{WXYZ} \gamma. \quad (86) \]
For example, the choice of $WXYZ = ASVN_1$ reduces this equation to

$$\tau L = \left[U - \sum_{i=2}^{k} \mu_i N_i\right].$$  \hspace{1cm} (87)$$

As an application of Eq. \hspace{1cm} (83), consider two coexisting line phases that remain in equilibrium with each other during a reversible process. Writing Eq. \hspace{1cm} (83) for each phase, subtracting these equations and taking into account that the differentials $d\tau$ remain equal for both phases, we obtain

$$- \Delta \left(\frac{[S]_{WXYZ}}{L}\right) dT + \Delta \left(\frac{[V]_{WXYZ}}{L}\right) dp - \sum_{i=1}^{k} \Delta \left(\frac{[N_i]_{WXYZ}}{L}\right) d\mu_i$$

$$- \Delta \left(\frac{[A]_{WXYZ}}{L}\right) d\gamma = 0.$$  \hspace{1cm} (88)$$

Here, the symbol $\Delta$ designates the difference between the excess properties (per unit length) of the two line phase. This equation describes a $(k-2)$-dimensional phase coexistence hypersurface in the $(k-1)$-dimensional space of variables and is analogous to the Clapeyron-Clausius equation for coexisting bulk systems. For example, for $WXYZ = ASVN_1$ the coexistence hypersurface exists in the space of chemical potentials $(\mu_2, ..., \mu_k)$ and is described by the equation

$$\sum_{i=2}^{k} \Delta \left(\frac{[N_i]_{WXYZ}}{L}\right) d\mu_i = 0,$$  \hspace{1cm} (89)$$

where the differential coefficients are the jumps in line segregations (per unit length) across the hypersurface.

E. The line phase rule

Consider an equilibrium system containing $\varphi$ bulk phases that we want to keep during all reversible variations of parameters. We single out one particular interface containing $\nu$ interface phases and consider a particular line between two interface phases 1 and 2. Suppose this line contains $\omega$ line phases. How many variables can we vary while keeping all these phases in coexistence?

Out of the $(k + 2)$ intensities of our system, $\varphi$ can be eliminated by the Gibbs-Duhem equations for the bulk phases. The adsorption equations for the interface phases impose $\nu$ more constraints. The adsorption equations for the line phases add another $\omega$ constraints. However, the interface and line adsorption equations contain the additional differentials $d\gamma$ and $d\tau$. Eliminating them, the total number of constraints becomes $(\varphi + \nu + \omega - 2)$. Thus, the number of remaining degrees of freedom is

$$f_L = k + 4 - \varphi - \nu - \omega.$$  \hspace{1cm} (90)"
This equation is the phase rule for line phases. The maximum possible number of coexisting line phases (when $f_L = 0$) is

$$\omega_{\text{max}} = k + 4 - \varphi - \nu. \quad (91)$$

If we only concerned with two bulk phases separated by an interface containing one line, then $\varphi = 2$, $\nu = 2$, and the phase rule reduces to $f_L = k - \omega$. Accordingly, the maximum number of coexisting line phases is $\omega_{\text{max}} = k$.

V. DISCUSSION

Table I summarizes the phase rules derived here for the bulk, interface and line phases. The last column contains the maximum number of phases that can coexist in equilibrium. All these phase rules can be summarized in the equations

$$f = k + 5 - d - \theta, \quad (92)$$

$$\theta_{\text{max}} = k + 5 - d, \quad (93)$$

where $d$ is the smallest dimensionality of phases included into consideration and $\theta = \varphi + \nu + \omega$ is the number of coexisting phases in the system. For a given $d$, the number of phases of a lower dimensionality must be excluded from $\theta$. For example, $\omega = 0$ for interface phases (Table I).

These equations can be used to predict the number of independent variables and the maximum possible number of coexisting phases, depending on the dimensionality of the phases. For example, in a binary system, a phase boundary can support a maximum of $\nu_{\text{max}} = 3$ coexisting interface phases ($d = 2$, $k = 2$, $\varphi = 2$, $\omega = 0$). If pressure is fixed, then only two. In a single-component system, an interface can support only two interface phases and the line separating them can have only one line phase ($d = 1$, $k = 1$, $\varphi = 2$, $\nu = 2$).

In the foregoing discussion, we assumed that interfaces and lines separated distinct phases. This analysis is readily extended to single-phase interfaces such as grain boundaries and lines separating regions of the same interface phase with different crystallographic orientations. In such cases, the choice of the dividing surface is arbitrary and all excesses $\tilde{N}_1, ..., \tilde{N}_k$ (accordingly, $\tilde{N}_1, ..., \tilde{N}_k$) must appear as arguments in the fundamental equations. All calculations remain similar and lead to the same phase rules with an appropriate count of phases (e.g., $\varphi = 1$ for a grain boundary).

Using the same thermodynamic approach, it is straightforward to derive a phase rule for 0-dimensional defects formed between neighboring line phases (Fig. I(b)), which could be called “points”.

The analysis presented here was based on a simplified treatment and its immediate applications are restricted to multicomponent fluids. This treatment is not applicable to
solid phases without appropriate modifications. Interfaces in solid systems are often anisotropic and their properties may depend on the crystallographic orientation of the interface plane. In terms of Cahn’s classification all interface phase transformations considered here are congruent. Furthermore, we identified the interface free energy with the interface stress and referred to this common property as “tension”. While this is correct for fluid systems, for solid-solid interfaces the interface free energy and interface stress are different quantities both conceptually and numerically. A line phase can also be characterized by a line free energy and a line stress, which are different properties. We neglected chemical reactions in the bulk or at interfaces and lines. Finally, for the sake of simplicity we neglected the curvature effects on the interface and line properties. The goal of the present work was to demonstrate the general approach and outline the direction of future work. Extensions of the present analysis to include the effects mentioned above are possible and would result in thermodynamic theories and phases rules for low-dimensional phases in a wider range of real materials. The nucleation of new interface phases is not well understood or theoretically described. Developing a more detailed thermodynamic theory of lines is the first necessary step in this direction. Much can be done in this field.

It should be clarified that the proposed approach does not ignore the fundamental differences in physical properties of low-dimensional versus bulk phases. In fact, the phase rules derived here contain the dimensionality of the system as a parameter. Bulk phases, interfaces and lines belong to different universality classes and exhibit different critical behaviors (e.g., critical exponents), as well as many other physical properties. However, the basic thermodynamic formalism and the rules for the identification of independent thermodynamic variables and description of phase equilibria remain exactly the same for any dimensionality of space. In its postulational basis, thermodynamics is blind to the dimensionality of space. The postulates of thermodynamics are formulated in abstract concepts such as a system, a state, a variable, extensive and intensive parameters, conservation, etc. that do not involve the real space or its dimensionality. As a consequence, the fundamental equation of any phase has the same mathematical structure regardless of whether the phase exists in 3D space, at an interface or in a line defect. This explains the remarkable similarity, in fact identity, in the phase equilibrium descriptions for the bulk and low-dimensional systems.

While the concepts of 2D phases and 2D phase diagrams have long been accepted and successfully used in the surface/interface physics and chemistry communities and were later adopted in materials science, a recent trend in the materials community is to reject the terms “interface phase” and “2D phase” on the ground that such phases “do not satisfy the Gibbs definition of a phase”. It is pointed out that they do not meet Gibbs’ requirement of homogeneity and in addition cannot exist without being in contact with bulk phases. Gibbs’ definition of a phase was discussed in Sec. II A. Mathematically, his requirement of homogeneity is expressed by the homogeneity of first degree of the fundamental equation
of the phase. For interfaces, the fundamental equation is homogeneous with respect to the area, and for lines with respect to the length. In other words, the homogeneity of a phase is embedded in its definition \(\text{(4)}\) for any dimensionality. The requirement that we should be able to physically extract any given phase from the rest of the system is not part of Gibbs’ thermodynamics. Is it not part of the modern logical structure of thermodynamics either, nor is it needed for any thermodynamic derivations involving phases. As long as a particular part of a system follows its own fundamental equation satisfying the mathematical properties stated above and can exchange extensive properties with the rest of the system, it satisfies the thermodynamic definition of a phase.

VI. CONCLUSIONS

To summarize, we have presented a unified thermodynamic description of phases and phase equilibria in 3D, 2D and 1D systems. In all cases, the phase is identified with a fundamental equation of state, see Eq.\(\text{(4)}\). The fundamental equation defines a phase and encapsulates all of its properties. In all dimensions, the phases are treated the same way and are described by similar thermodynamic equations. The same thermodynamic formalism can be applied for the description of phase equilibria and phase transformations in bulk systems, interfaces and line defects separating 2D interface phases. For both lines and interfaces, we have rigorously derived adsorption equations in terms of generalized excess quantities. We have also derived phase coexistence equations that can be utilized for the construction of phase diagrams for low-dimensional systems. The Gibbs phase rule describing the coexistence of bulk phases has been generalized to phase rules for interfaces and lines. Such rules predict the number of thermodynamic degrees of freedom and the maximum number of phases than can coexist in the systems of the respective dimensionality.

Recent years have seen a significant increase in the research activity dedicated to interface phase transformations. Experiments have uncovered a number GB phases with discrete thicknesses and various segregation patterns in binary and multi-component metallic alloys and ceramic materials. It has been demonstrated that transformations among such phases can strongly impact many engineering properties of materials such as grain growth, mechanical behavior and interface transport. On the modeling side, atomistic simulations have revealed reversible temperature-induced transformations between different structural phases in metallic systems and their effect on GB diffusion, response to applied mechanical stresses and other properties. Phases inside line defects have never been reported by either experimentalists or modelers. However, we envision that such phases may be discovered in the future. The present work predicts their possible existence and describes the conditions of their thermodynamic coexistence. It should be emphasized that lines play a critical role in 2D phase transitions. For example, their excess free energy and other properties determine the nucleation barriers of 2D phases as illustrated by Fig. \(\text{2}\)
At this juncture, it is important to develop theories capable of explaining the experimental observations and simulation results and guiding new research in this field. It is hoped that the present work contributes to this course by providing a rigorous thermodynamic framework for the description and prediction of phase equilibria in interfaces and lines. As one example, the phase rules derived in this work provide a guidance for phase diagram construction and design of new experiments and simulations, as usually does the existing phase rule for bulk systems.

Acknowledgements. – T.F. was supported by a post-doctoral fellowship from the Miller Institute for Basic Research in Science at the University of California, Berkeley. Y.M. was supported by the National Science Foundation, Division of Materials Research, the Metals and Metallic Nanostructures Program.

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|       | Bulk phases | Interface phases | Line phases | $f$        | Maximum # of phases |
|-------|-------------|------------------|-------------|-----------|---------------------|
| Bulk  | $\varphi$   | 0                | 0           | $k + 2 - \varphi$ | $k + 2$           |
| Interface | $\varphi$ | $\nu$          | 0           | $k + 3 - \varphi - \nu$ | $k + 3 - \varphi$ |
| Line  | $\varphi$   | $\nu$          | $\omega$   | $k + 4 - \varphi - \nu - \omega$ | $k + 4 - \varphi - \nu$ |

Table I: Summary of phase rules for bulk, interface and line phases. $k$ is the number of chemical components, $\varphi$ is the number of bulk phases, $\nu$ is the number of interface phases, $\omega$ is the number of line phases, and $f$ is the number of degrees of freedom.
Figure 1: (a) Single-phase interface between bulk phases $\alpha$ and $\beta$. (b) Interface between the same bulk phases composed of $\nu = 4$ interface phases numbered by index $m$. The dividing surfaces are indicated by dashed lines.
Figure 2: Examples of lines: 1D defects separating interface phases. (a) Phase transformation in the Cu Σ5 (310) grain boundary at the temperature of 1000 K. The boundary was initially composed of kite-shape structural units (light blue). A new phase composed of split-kite structural units (red) grows from the surface and eventually penetrates all through the sample. (b) Top view of a two-phase state of the Cu Σ5 (210) grain boundary at the temperature of 700 K. An inclusion of a split-kite phase is surrounded by a matrix of the filled-kite phase. The interface phases are separated by an oval-shape line defect.
Figure 3: Two interface phases separated by a line normal to the page.
Figure 4: Reference boxes used for the calculation of line excess properties. (a) Two interface phases separated by a line. (b) Interface phase 1. (c) Interface phase 2. (d) Bulk phases α and β. The values of an extensive property $X$ are indicated next to the boxes.