New thermodynamic potentials for surface science
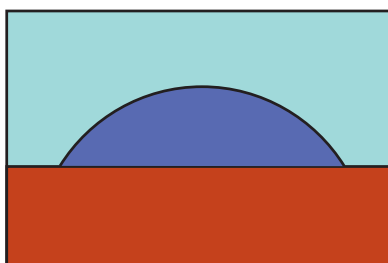
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HIGHLIGHTS

- *J*-potential is defined and characterized as a thermodynamic potential.
- Fundamental equations are derived for *J*-potential of bulk phases, surfaces and lines.
- The hybrid form of *J*-potential with fundamental equations is introduced.
- Novel mathematical formulations of the Gibbs and Neumann equations are given.

GRAPHICAL ABSTRACT

ABSTRACT

J-potential belongs to the group of novel thermodynamic potentials for arbitrarily loaded solids. The article considers two modified forms of *J*-potential especially convenient for surface science. Definitions are given and fundamental equations are derived for bulk phases, interfaces, and interfacial lines. The application of *J*-potential is illustrated by deriving the Neumann and Gibbs equations for a number of interfaces meeting at a line, and the classical Young equation.

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1. Introduction

The necessity of introducing new thermodynamic potentials appears in the thermodynamics of solid or mixed systems subjected to complex external mechanical forces when ordinary free energy and Gibbs energy cannot serve as potentials, i.e. do not produce work. Indeed, using, for example, free energy as a thermodynamic potential requires invariability of the system boundaries, but this condition cannot be fulfilled for a loaded solid because of strain. Classical Gibbs energy is better in that respect and can serve as a thermodynamic potential, but only in the case when the external force is a uniform outer pressure (for a capillary system with phases of different pressures, Gibbs energy should be defined with respect to one chosen pressure to be under the control, which is typically outer pressure). The case of arbitrary loading requires a more general potential corresponding to a given constant loading.

The novel-for-chemical-thermodynamics *J*-potential is defined as [1]

$$J \equiv \Omega - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA \tag{1}$$

where Ω is grand thermodynamic potential, $\mathbf{P}$ is an external force (stress) per unit area of the system surface as a function of location on the surface (A), $\mathbf{u}$ is the local vector of the surface displacement, and A is the surface area; the integration is carried out over the whole surface of the system. Naturally, a complex external force bears a complex internal state of a system characterizing by a certain field of the stress tensor $\hat{E}(x, y, z)$ in each solid phase.

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Mathematically, the integration over the surface in Eq. (1) can be transformed into integration over the system volume to give

$$\oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) \, dA = \iiint_{(V)} (\hat{\mathbf{E}} : \hat{\mathbf{e}}) \, dx dy dz,$$

where $\hat{e}$ is the strain tensor, and the colon symbolizes the biscalar product of tensors. We now see that Eq. (1) rigorously accounts for the tensorial mechanical state of a system. It its turn, tensorial stress induces a tensorial character of the chemical potential of an immobile species of a solid (forming the solid lattice). The detailed formulation of the thermodynamics of solids and solid surfaces in terms of stress and chemical potential tensors can be found in the author's reviews [2,3].

The quantity Ω in Eq. (1) is read as the grand thermodynamic potential generalized for solids with account of chemical potentials of both mobile and immobile (forming the solid lattice) species in the form [4]

$$\Omega \equiv F - \sum_i \mu_i N_i - \mu_j^\beta N_j = F - \sum_i \mu_i N_i - \mu_{j(nn)}^\alpha N_j \qquad (2)$$

where F is free energy, μ is chemical potential, N is the number of molecules, the subscript i and j refer to mobile and immobile species, respectively, the superscript α refers to a solid phase, and the superscript β refers to a real or imaginary fluid phase in contact and equilibrium with phase α. The quantity μ_j^β is the chemical potential of species j in solution, while $\mu_{j(nn)}^\alpha$ is the normal-to-the-surface component of the chemical potential tensor of species j in the solid phase (we assume j to be a single species of a solid). The identity of the two forms of definition given in Eq. (2) is secured by the equilibrium condition

$$\mu_{j(nn)}^\alpha = \mu_j^\beta, \qquad (3)$$

established by Gibbs for a flat solid/fluid interface. The essential feature of the definition expressed in Eq. (2) is referencing to a certain surface through which a solid can dissolute or evaporate. If a solid is in anisotropic state and has several surfaces of various orientation (and, possibly, of various nature), there will be also several definitions of Ω. In this case, grand thermodynamic potential will be defined ambiguously. As we shall show below, J-potential does not possess this disadvantage. We shall also consider a hybrid version of J-potential that is not related to a surface at all.

The equilibrium principle for J-potential is written as [1]

$$(\delta J)_{T,P,\mu_i,\mu_{j(nn)}} = 0 \qquad (4)$$

and can be used for finding equilibrium configurations in complex capillary systems. However, we preliminary have to derive fundamental equations separately for bulk phases, interfaces, and interfacial lines. For the sake of simplicity, we shall regard a uniform (but mechanically anisotropic) solid, which will allow us to modify slightly the definition expressed in Eq. (1).

2. Fundamental equations for *J*-potential

Any system consists of bulk phases, interfaces, and interfacial lines, and fundamental equations in terms of free energy are known for each of these structural objects. Using these equations, we can derive corresponding equations in terms of J-potential. We first turn to a bulk phase. As was already noted, the generalized grand thermodynamic potential is related to the choice of a certain surface through which an immobile species of a solid can pass to the mobile state and through which one can govern the normal component of its chemical potential tensor. The surface of a uniform anisotropic solid phase α is assumed to be flat (this condition is

mandatory for Ω [4]) and adjacent to a fluid phase β with pressure p. Then the external stress $P = -p$ acts on the solid, and the free energy of phase α is given by the expression [2,4]

$$F^\alpha = -pV^\alpha + \sum_i \mu_i N_i + \mu_{j(nn)}^\alpha N_j^\alpha \qquad (5)$$

In this case, it is convenient to modify the definition given in Eq. (1) to the form

$$J \equiv \Omega - PV = \Omega + pV, \qquad (6)$$

which differs from Eq. (1) by replacing ΔV for V (practical tasks with the use of J-potential are typically solved at constant P, so that the product $P\Delta V$ differs from PV by a constant, but thermodynamic potentials are defined within a constant at all). According to Eqs. (2) and (5), $\Omega^\alpha = -pV^\alpha$ and this means that grand thermodynamic potential will be different for surfaces with different pressures. By contrast, Eqs. (2), (5) and (6) yield, irrespective of direction,

$$J^\alpha = 0. \qquad (7)$$

This important result shows that bulk phases do not contribute to J-potential in the case of a flat surface. It follows from here the significance of J-potential for surface science. It is of note that the above result was obtained for a mechanically anisotropic state of a solid bulk phase when the principal stresses and principal values of the chemical potential tensor of immobile species are different. A reader will easily verify Eq. (7) to remain the more valid for an isotropic state of the phase.

As for fundamental equations for interfacial surfaces and lines, we have, first of all, to note the following. The procedure of taking Gibbs excesses is evident to be inapplicable to the last term in Eq. (1). The definition given in Eq. (6) is still more demonstrative since the zero excess of $-PV$ is obvious. For this reason any excesses for J-potential coincide with excesses for Ω. As was shown by Gibbs, mechanical (as excess stress) and thermodynamic (as the work of formation of unit new surface) definitions coincide for fluids but differ for solids. Gibbs himself always worked with thermodynamic surface tension σ, and grand thermodynamic potential was generalized for solids [4] just to show that σ is defined as an excess of Ω per unit surface area at an arbitrary location of a dividing surface. Thus, we can write for the surface excess of J-potential

$$\bar{J} = \bar{\Omega} = \sigma A \qquad (8)$$

where the upper bar denotes excess. On the other side, we have from Eq. (2)

$$\bar{J} = \bar{\Omega} \equiv \bar{F} - \sum_i \mu_i \bar{N}_i - \mu_j^\beta \bar{N}_j = \bar{F} - \sum_i \mu_i \bar{N}_i - \mu_{j(nn)}^\alpha \bar{N}_j \qquad (9)$$

Following the procedure accepted, we find the fundamental equation for $\bar{J}$ from the differential expression (we choose the second form of Eq. (9) as a more general one)

$$d\bar{J} = d\bar{F} - \sum_i \mu_i d\bar{N}_i - \sum_i \bar{N}_i d\mu_i - \mu_{j(nn)}^\alpha d\bar{N}_j - \bar{N}_j d\mu_{j(nn)}^\alpha \qquad (10)$$

The fundamental equation for excess free energy is of the form (Eq. (6.5) in Ref. [2], we have only added the last term)

$$d\bar{F} = -\bar{S} dT + A(\hat{\gamma} : d\hat{e}^\sigma) - A(\hat{\gamma} - \sigma \hat{1}) : d\hat{N}_j / N_j$$

$$+ \sum_i \mu_i d\bar{N}_i + \mu_{j(nn)}^\alpha d\bar{N}_j \qquad (11)$$

where S is entropy, T is temperature, $\hat{\gamma}$ is the two-dimensional tensor of mechanical surface tension (a surface excess from the stress tensor), $\hat{e}^\sigma$ is the two-dimensional tensor of apparent strain (the colon symbolizes the biscalar product of tensors), and $\hat{N}_j$ is the two-dimensional mass displacement tensor [3] ($d\hat{N}_j / N_j$ imitates the part