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Interfaces at equilibrium: A guide to fundamentals

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ABSTRACT

The fundamentals of the thermodynamics of interfaces are reviewed and concisely presented. The discussion starts with a short review of the elements of bulk thermodynamics that are also relevant to interfaces. It continues with the interfacial thermodynamics of two-phase systems, including the definition of interfacial tension and adsorption. Finally, the interfacial thermodynamics of three-phase (wetting) systems is discussed, including the topic of non-wettable surfaces. A clear distinction is made between equilibrium conditions, in terms of minimizing energies (internal, Gibbs or Helmholtz), and equilibrium indicators, in terms of measurable, intrinsic properties (temperature, chemical potential, pressure). It is emphasized that the equilibrium indicators are the same whatever energy is minimized, if the boundary conditions are properly chosen. Also, to avoid a common confusion, a distinction is made between systems of constant volume and systems with drops of constant volume.

Contents

1. Introduction

> "In the beginning, God created the heavens and the earth."
> [(Genesis 1:1)]

Whenever two materials meet there is an interface, unless they completely dissolve in each other. The qualitative importance of interfaces goes much beyond their technological significance: Interfaces provide the ability to distinguish between different bodies, thus, in a way, they define the identity of the bulk they surround. It is not surprising then that the first verse of the Bible describes the creation of an interface as the first step towards the creation of the world.

The quantitative effect of interfaces on technological systems and processes depends on the surface to volume ratio of the system under discussion. The smaller the particle size, the larger the contribution of

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the surface. Since nanotechnology is a central topic at this time, the importance of the effects of surfaces cannot be underestimated.

Thermodynamic analysis is in many cases based on subtleties that may be perplexing. For example, the system to be studied may be defined in various ways in terms of boundary types and conditions imposed by the environment. Moreover, thermodynamics was originally developed for isotropic bulk phases, while interfaces are very thin and anisotropic. Thus, the goal of this review is, in general, to systematically present the fundamental principles of surface thermodynamics, in order to assist in understanding interfaces at equilibrium. Specific, subtle issues are emphasized, especially those that are less frequently clarified, such as the application of a bulk-related theory to interfaces, the independence of the equilibrium indicators on the boundary conditions, and wetting-related stability issues.

The review starts with a brief summary of the principles of thermodynamics of bulk phases that are relevant also to interfaces. Then, we discuss the main aspects of interfaces at equilibrium: the definition of surface tension and its dependence on adsorption at the interface; equilibrium of interfaces in two-phase (liquid–gas or liquid–liquid) systems, namely bubbles and drops; and, finally, equilibrium in three-phase systems, mainly those related to wetting of solids. The review goes into detail with regard to topics which are less available in the literature, especially the recent literature, and only briefly summarizes the principles where sufficient information is easily accessible.

1.1. Equilibrium conditions and indicators for bulk systems [1–4]

The term “thermodynamic system” describes that part of space, which is of interest for our study and discussion. Everything outside the system is called “environment.” A most useful theoretical concept is that of an isolated system, for which the boundaries prevent any interaction of the system with its environment. It is very useful, because the second law of thermodynamics states that every isolated system eventually gets to a single state of equilibrium that, by definition, does not further change with time. Since we may always define the system and its environment as being an isolated global system, this concept opens the way to elucidating the equilibrium state of the (original) system by itself. An isolated system can be defined by stating its volume, $\hat{V}$, the chemical composition of its content (number of moles of each species: $n_1, n_2, n_3 \ldots$), and the internal energy of the molecules, $\hat{U}$, namely the sum of their kinetic and potential energies. The second law states that the condition of equilibrium of an isolated system (i.e. with fixed values of $\hat{U}, \hat{V}, n_1, n_2, n_3 \ldots$) is a maximum in the entropy of the system, $\hat{S}$. In other words, equilibrium is the state that has the highest probability to occur

$$\hat{S} = \hat{S}\left(\hat{U}, \hat{V}, n_1, n_2, n_3 \ldots\right) \ \textit{is maximal at equilibrium} \tag{1}$$

It can be shown that an equivalent condition, for fixed values of $\hat{S}$, $\hat{V}$, $n_1, n_2, n_3 \ldots$ is

$$\hat{U} = \hat{U}\left(\hat{S}, \hat{V}, n_1, n_2, n_3 \ldots\right) \ \textit{is minimal at equilibrium} \tag{2}$$

In anticipation of the discussion of interfaces between bulk phases, the system that we analyze first comprises two bulk phases only, disregarding the interface, and is isolated (Fig. 1a, b). A phase is marked as “*c*” (continuous) if it interacts directly with the environment, or if it surrounds another phase, which is marked “*d*” (dispersed). Obviously, if the two phases play the same role, it does not matter which is “*c*” or “*d*.” Now, in general, the laws of thermodynamics state that the internal energy of a system may change (in the absence of external fields) by three processes: heat transfer through the boundary (energy exchange by random collisions of molecules), work (energy exchange by directional motion that is caused by an external force), and mass transfer (energy exchange due to molecules leaving or entering the system). This is expressed by the following well-known equation, where the three terms on the right-hand side correspond to the above three processes.

$$d\hat{U} = Td\hat{S} - Pd\hat{V} + \sum_i \mu_i dn_i \tag{3}$$

In this equation T is absolute temperature, P is pressure, and μ_i is the chemical potential of component i. For a two-phase, isolated system, the total internal energy that is the sum of the internal energies of the two phases must be minimal at equilibrium. Thus,

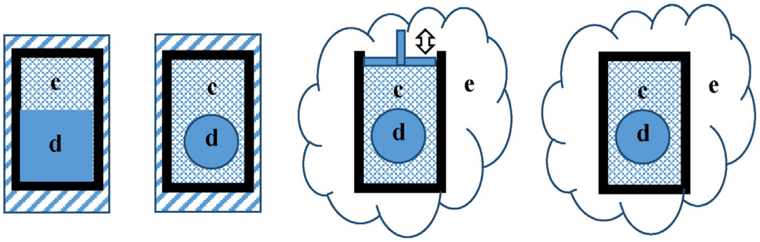
$$d\hat{U}^{total} = -P^c d\hat{V}^c - P^d d\hat{V}^d + T^c d\hat{S}^c + T^d d\hat{S}^d + \sum_i \mu_i^c dn_i^c + \sum_i \mu_i^d dn_i^d = 0 \tag{4}$$

where the superscripts indicate the phases *c* and *d*. In order to make this equilibrium condition useful, it must be expressed in terms of intrinsic, measurable properties. To achieve this purpose, the proper constraints should be considered. An isolated system cannot exchange heat with its environment therefore its entropy must be constant

$$d\hat{S}^c + d\hat{S}^d = 0 \tag{5}$$

In addition, an isolated system does not exchange work with its environment, therefore its volume must be constant

$$d\hat{V}^c + d\hat{V}^d = 0 \tag{6}$$



(a) (b) (c) (d)

Fig. 1. Various two-phase systems; ▬ rigid wall (constant volume); ▨ adiabatic wall: (a) A two-phase, isolated system. (b) A two-phase, isolated system where one phase surrounds the other. (c) A system interacting with an environment at constant pressure and temperature. (d) A system with a constant volume interacting with an environment at constant temperature.

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