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On the equilibrium conditions of curved interfaces

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Abstract

The equilibrium of a curved interface formed between two fluid phases, which are exposed to an external action is examined. The external action is shown to result in an energy jump across the interface thereby affecting the phase equilibrium. If stated in terms of an energy density of the phases, this action appears in both the Laplace and the Thomson equation as additional term.

Keywords: Interfaces; Equilibrium; Thin films; Wall effect

1. Introduction

The knowledge of the equilibrium state of interfaces is required e.g. for modelling of transport processes occurring between fluid phases. In many instances, one of the phases forms a thin film on a solid wall, which affects the film properties, see e.g. [1–3], the latter citing a number of more recent publications. As a rule, the wall effect upon the film is measured in terms of *disjoining* pressure, which is embodied into the respective equations as a positive quantity in some papers, but a negative one in others; it consists of several components arising from different origins. Recently, Stephan [4] discussed the effect of the dispersion component of the disjoining pressure on the equilibrium of a concave motionless liquid film that is adhering to a planar wall. Starting from mass and heat balances, Mitrovic [5] specified the interfacial conditions of an evaporating liquid film, showing the curvature of its surface to depend on the fluxes between the phases and the movement of the interface.

Although our interest in the equilibrium of liquid films bounded to a wall has a long history, the equilibrium conditions of such systems reported in the literature do not always agree with one another. From this point of view further discussion of the issue would seem appropriate. The aim of the present paper is to derive an expression for the vapour pressure of a curved interface taking into account some external effects. The model adopted rests on simplified Gibbs' [6] analysis of the equilibrium of heterogeneous fluid systems. The Clausius–Clapeyron equation has been used to illustrate these effects in terms of temperature. The considerations are restricted to single component static systems.

2. Conditions of mechanical equilibrium

Gibbs [6] extended the equilibrium conditions, stated by Dirichlet [7] in terms of energy for a system of rigid bodies, to fluid systems consisting of several phases. In the case of a fluid system, the energy of the phases as well as of the interfaces, formed between and shaped by the neighbouring phases, must be taken into account. Involving a variational principle, Gibbs obtained a set of relationships thus deducing the conditions of thermal, mechanical, and chemical equilibrium. This method is simplified and applied in the following to a two-phase system.

Indicating by the indices L and V the phases in Fig. 1, denoting by p the pressure and by σ the free energy of the interface, the mechanical energy of the system can be written as

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Nomenclature

A	constant, interface area
B	constant
a, b	van der Waals constants
E	field strength
F	free energy
$\vec{f}$	force per mass unit
Δh	enthalpy of phase change
g	gravity
M	molar mass
n	exponent
p	pressure
Δp	pressure difference
$\vec{r}$	radius vector
$\Re$	universal gas constant
T	temperature
V	volume
v	specific volume
z	height above reference level
δ	film thickness
κ	curvature
ρ	density
σ	surface tension (energy)
μ	chemical potential
$\vec{\varphi}$	force per mass unit
ϕ	potential, energy density
$\Delta\phi$	potential difference
ε	permittivity

Subscripts

F	film
L	liquid
I	interface
T	at constant T
V	vapour
ϕ	due to potential ϕ
0	reference value
∞	semi-infine phase, reference state

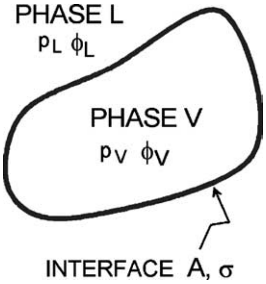

Fig. 1. Two-phase system exposed to an external potential ϕ.

$$F = \int_{V_L} p_L \, dV_L + \int_{V_V} p_V \, dV_V + \int_A \sigma \, dA. \tag{1}$$

In the case that the phases are exposed to the action of an external potential, their free energies will be changed. Denoting by ϕ the energy per unit volume arising from this potential, $\phi = -(\partial F_\phi / \partial V)_T$, instead of (1), we have

$$F = \int_{V_L} (p_L + \phi_L) \, dV_L + \int_{V_V} (p_V + \phi_V) \, dV_V + \int_A \sigma \, dA. \tag{2}$$

Equations of this type have already been used by Gibbs [6] and Neumann [8], the latter giving a comprehensive review of earlier works in this field.

A system in equilibrium requires $\delta F = 0$. A variation of F in Eq. (2) would result in a stable configuration of the phases for $\delta^2 F > 0$. However, for simplicity, the second condition is considered to be fulfilled and the sum $(p + \phi)$ is taken as invariant within the phases. Then, with $\delta V_L + \delta V_V = 0$ and $\delta A = \kappa \delta V$, one gets

$$(p_L + \phi_L) - (p_V + \phi_V) + \sigma\kappa = 0, \tag{3}$$

or

$$p_V = p_L + \sigma\kappa + \Delta\phi, \quad \Delta\phi = \phi_L - \phi_V, \tag{4}$$

where the curvature is positive ($\kappa > 0$) when its centre lies on the side of the V-phase. [1] Another derivation

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[1] A referee insisted on an explanation of the relationship $\delta A = \kappa \delta V$, particularly on the definition of the curvature $\kappa = \delta A / \delta V$. The latter relationship is regularly involved in numerical treatments of capillary phenomena, e.g. Bullard et al. (Computational Materials Science 4 (1995) 103–116): "The mean curvature of an infinitesimal element along a condensed phase interface represents the quantity $\delta A / \delta V$, where δA is the incremental change in the elemental area when it is normally displaced by local addition of material of volume δV."

In the celebrated studies of Gibbs [6], one takes from p. 391: "If all parts of the dividing surface move a uniform normal distance δN, we shall have $\delta S = (c_1 + c_2) S \delta N$, $\delta V' = S \delta N$, $\delta V'' = -S \delta N$." Here, S denotes the surface area, $\delta V'$ and $\delta V''$ the variations of the volumes of the phases forming the interface; c_1 and c_2 are the curvatures.

To transform the definitions in each other, one has to set $\kappa = c_1 + c_2$, from which, for example, for a spherical surface one obtains $\kappa = 2/R$, which also immediately follows from $\kappa = \delta A / \delta V$. For detailed considerations the reader is particularly referred to a paper by Taylor et al. (Acta Metallurgica et Materialia 40 (1992) 1475–1485).

path of this equation is given in Appendix A, where the symbol ϕ represents the potential energy per unit mass.

Eq. (4) is a generalised Laplace expression for the mechanical equilibrium of a capillary system. As it shows, the jump of the pressure across the interface, which is the *surface of tension* according to Gibbs [6], is rooted in the curvature of the interface and in the potential jump $\Delta\phi = \phi_L - \phi_V$. Viewed in terms of an energy density, Eq. (3) expresses the difference of the energies of the phases in dependence of the interface curvature.

If different actions are imposed on the phases, and if these actions arise from potentials, summation applies,

$$\Delta\phi = \phi_L - \phi_V = \sum_k \Delta\phi_k, \tag{5}$$

where $\Delta\phi_k$ denotes the potential difference of kth action.

In what follows, the phases V and L in Fig. 1 are vapour and liquid of the same substance obeying Eq. (4).

Given the quantities $\sigma\kappa$ and $\Delta\phi$, the system has only one degree of freedom, and to describe its equilibrium the pressure p_L (or p_V) must be specified. Setting in Eq. (4), for instance, $p_L = p_{L\infty}$, where $p_{L\infty}$ is the equilibrium pressure of a plane interface at no external action (Fig. 2a), we get

$$p_V = p_{L\infty} + \sigma\kappa + \Delta\phi. \tag{6}$$

For $\sigma\kappa + \Delta\phi > 0$, it is $p_V > p_{L\infty} = p_{V\infty}$. The equilibrium temperature T_V of a system satisfying Eq. (6) is thus larger than the temperature $T_{V\infty}$ corresponding to $p_{L\infty}$. Fig. 2 illustrates such cases with a curved (b) and a plane (c) interface. The pressure in the vapour p_V of these systems in equilibrium at $T_V = T_L = T_{V\infty}$ is less than $p_{L\infty}$ and, to quantify the pressure difference $p_{L\infty} - p_V$, Eq. (6) is necessary, but insufficient.

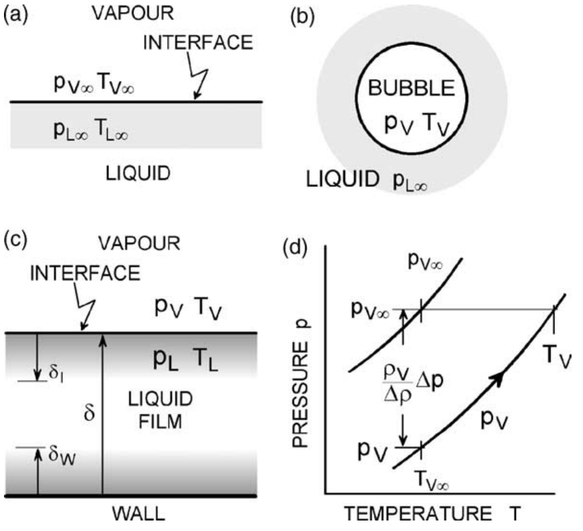

Fig. 2. Equilibrium conditions on a plane interface formed by semi-infinite phases (a), on the surface of a bubble in equilibrium with its liquid (b), and on a planar liquid film (c); (d) illustrates the vapour pressure lowering according to Eq. (17); $\Delta p = \sigma\kappa + \Delta\phi$, $\Delta\rho = \rho_L - \rho_V$.

3. Vapour pressure

3.1. General expression

To obtain the vapour pressure of the systems b and c in Fig. 2 with the mechanical equilibrium (4) at the temperature $T_{V\infty}$, the equilibrium is slightly distorted keeping the temperature unchanged, thus

$$\mathrm{d}p_V = \mathrm{d}p_L + \mathrm{d}(\sigma\kappa + \Delta\phi). \tag{7}$$

Depending on the displacement direction, a phase transition (evaporation for $\mathrm{d}p_V < 0$, condensation for $\mathrm{d}p_V > 0$) will occur. In order to prevent this phase transition, the state of the phases must be changed such that the system remains in equilibrium at any instant. Hence, the well-known relationship,

$$\mathrm{d}\mu = v\,\mathrm{d}p, \tag{8}$$

where v and μ represent the specific volume and the chemical potential, respectively, applied to both phases,

$$v_V \mathrm{d}p_V = v_L\,\mathrm{d}p_L, \tag{9}$$

and combined with Eq. (7), gives

$$(v_V - v_L)\,\mathrm{d}p_V = -v_L\,\mathrm{d}(\sigma\kappa + \Delta\phi), \tag{10}$$

$$(v_V - v_L)\,\mathrm{d}p_L = -v_V\,\mathrm{d}(\sigma\kappa + \Delta\phi). \tag{11}$$

To illustrate the effects of $\sigma\kappa$ and/or $\Delta\phi$ on the pressures p_V and p_L in the phases under equilibrium conditions, the integration of Eqs. (10) and (11) will be performed from the initial pressures $p_{V\infty}$ and $p_{L\infty} = p_{V\infty}$ at $\sigma\kappa + \Delta\phi = 0$ to the pressures p_V and p_L at $\sigma\kappa + \Delta\phi \neq 0$. However, since these equations are not independent from each other, it suffices to treat only one of them, say, Eq. (10), hence

$$\int_{p_{V\infty}}^{p_V} \frac{v_V - v_L}{v_L}\,\mathrm{d}p_V = -\int_0^{\sigma\kappa+\Delta\phi} \mathrm{d}(\sigma\kappa + \Delta\phi). \tag{12}$$

This integration path describes a transient of the system due to external action changing, at the same time, the curvature of the interface. The transient starts from a plane interface at the pressure $p_{V\infty}$ without external effects (Fig. 2a). Strictly, $\sigma\kappa + \Delta\phi = 0$ may not necessarily mean a planar interface, the latter requiring $\kappa = 0$.

During the transient, different assumptions can be made concerning the dependence of the specific volumes on the pressure. Defay et al. [9] have discussed some possibilities for a system without external action. Clearly, the most direct way is to take the volumes constant, but assuming the vapour to be a van der Waals fluid, $p_V = \Re T_{V\infty}/(v_V - b) - a/v_V^2$, and the liquid as incompressible ($v_L = \text{const}$, $a, b = \text{const}$), gives

$$-v_L(\sigma\kappa + \Delta\phi) = -2a\left(\frac{1}{v_V} - \frac{1}{v_{V\infty}}\right) + ab\left(\frac{1}{v_V^2} - \frac{1}{v_{L\infty}^2}\right) + (b - v_L)(p_V - p_{V\infty}) - \Re T_{V\infty} \ln\frac{p_{V\infty} + (a/v_{V\infty}^2)}{p_V + (a/v_V^2)}, \tag{13}$$

where the index ∞ indicates the initial state.

A combination of Eq. (13) with the van der Waals equation would lead to the unknown quantities (v_V, p_V) and, therefore, to a vapour pressure lowering. However, being unhandy for further discussion, Eq. (13) is simplified first by setting $a, b = 0$,

$$(\sigma\kappa + \Delta\phi) = (p_V - p_{V\infty}) + \frac{\Re T_{V\infty}}{v_L} \ln\frac{p_{V\infty}}{p_V}, \tag{14}$$

valid for ideal vapour. Omitting the pressure difference $(p_V - p_{V\infty})$, gives

$$p_V = p_{V\infty} \exp\left(-\frac{v_L(\sigma\kappa + \Delta\phi)}{\Re T_{V\infty}}\right) = p_{V\infty} \exp\left(-\frac{\rho_V}{\rho_L}\frac{\sigma\kappa + \Delta\phi}{p_{V\infty}}\right), \tag{15}$$

where $\rho_V = p_{V\infty}M/(\Re T_{V\infty})$ and ρ_L are the mass densities of the phases.

Finally, supposing

$$\frac{\rho_V}{\rho_L}\frac{\sigma\kappa + \Delta\phi}{p_{V\infty}} \ll 1,$$

Eq. (15) can be written as

$$p_V = p_{V\infty} - \frac{\rho_V}{\rho_L}(\sigma\kappa + \Delta\phi). \tag{16}$$

On the other hand, expanding in Eq. (14) the logarithm in a series, and taking only the first term, gives

$$p_V = p_{V\infty} - \frac{\rho_V}{\rho_L - \rho_V}(\sigma\kappa + \Delta\phi) \quad (\text{at } T_V = T_{V\infty}), \tag{17}$$

which also immediately follows by integrating Eq. (12) at constant volumes. For simplicity, we shall be using Eq. (17) in the following discussion.

Combining (4) and (17) or integrating (11) gives the pressure in the liquid phase

$$p_L = p_{V\infty} - \frac{\rho_L}{\rho_L - \rho_V}(\sigma\kappa + \Delta\phi) \quad (\text{at } T_V = T_{V\infty}). \tag{18}$$

Taking $\Delta\phi$ to arise from a wall action upon a liquid film, Eqs. (15) and (17) become identical to the well-known ones from the literature, see e.g. [3]. For this particular action, they have been reported, apparently for the first time, by Derjaguin [10] in 1940. Eq. (17) is illustrated in Fig. 2d, where Δp stands for $\sigma\kappa + \Delta\phi$ and $\Delta\rho = \rho_L - \rho_V$.

As follows from Eqs. (17) and (18), the pressure lowering is by ρ_V/ρ_L less in vapour than in liquid.

3.2. Particular cases

Choosing κ and $\Delta\phi$, for instance, setting $\kappa = 0$, $\Delta\phi = 0$ or the sum $\sigma\kappa + \Delta\phi = 0$, particular systems follow from Eq. (17). In the case $\sigma\kappa + \Delta\phi = 0$, which is basically possible for $\kappa < 0$, not only the temperature of the system, but also the vapour pressure remains unchanged during the transient described above. Vanishing of the difference $\Delta\phi$ due to equality of the potentials ($\phi_L = \phi_V$) seems less probable as long as the densities of the phases considerably differ from each other. Anyway, for $\Delta\phi = 0$, the Thomson (Kelvin) [11] equation, valid for a bubble in a homogeneous liquid (Fig. 2b), is obtained,

$$p_V = p_{V\infty} - \frac{\rho_V}{\rho_L - \rho_V}\sigma\kappa \quad (\text{at } T_V = T_{V\infty}). \tag{19}$$

For a planar interface ($\kappa = 0$, Fig. 2c), one gets

$$p_V = p_{V\infty} - \frac{\rho_V}{\rho_L - \rho_V}\Delta\phi \quad (\text{at } T_V = T_{V\infty}), \tag{20}$$

$$p_L = p_{V\infty} - \frac{\rho_L}{\rho_L - \rho_V}\Delta\phi. \tag{21}$$

Notice the same shape of Eqs. (19) and (20), which become identical for $\sigma\kappa = \Delta\phi$, irrespective of the nature of the actions affecting the phase equilibrium. In both cases the pressure lowering depends on the ratio $\rho_V/(\rho_L - \rho_V)$, which is not always true in the literature.

A remark seems in order concerning the potential difference $\Delta\phi$. Namely, while obtaining Eq. (3) from Eq. (2), the sum $p + \phi$ has been taken as constant throughout the phase. If this is not the case, this sum may be understood as a local quantity next to the interface, see Appendix A.

4. Equilibrium temperature of the interface

The equilibrium temperature T_V of a system exposed to an external action can readily be obtained by employing the Clausius–Clapeyron equation. Allowing a change of the vapour pressure p_V according to Eq. (17) from the initial pressure p_V at $T_{V\infty}$ to the final pressure p at the corresponding equilibrium temperature T_V (analogous to Fig. 2d), we first define a pressure difference Δp to be equilibrated by the temperature rise,

$$\Delta p = p - p_V = (p - p_{V\infty}) + (p_{V\infty} - p_V). \tag{22}$$

Involving Eq. (17) gives

$$\Delta p = (p - p_{V\infty}) + \frac{\rho_V}{\rho_L - \rho_V}(\sigma\kappa + \Delta\phi). \tag{23}$$

Then,

$$\frac{\mathrm{d}p}{\mathrm{d}T} \approx \frac{\Delta p}{T_{\mathrm{V}} - T_{\mathrm{V}\infty}} = \frac{\Delta h \rho_{\mathrm{L}} \rho_{\mathrm{V}}}{T_{\mathrm{V}\infty}(\rho_{\mathrm{L}} - \rho_{\mathrm{V}})}, \tag{24}$$

hence

$$T_{\mathrm{V}} = \left(1 + \left((p - p_{\mathrm{V}\infty}) + \frac{\rho_{\mathrm{V}}}{\rho_{\mathrm{L}} - \rho_{\mathrm{V}}}(\sigma\kappa + \Delta\phi)\right)\frac{\rho_{\mathrm{L}} - \rho_{\mathrm{V}}}{\rho_{\mathrm{L}}\rho_{\mathrm{V}}\Delta h}\right)T_{\mathrm{V}\infty}. \tag{25}$$

Choosing the pressure difference $p - p_{\mathrm{V}\infty}$, one defines a particular system and, for instance, with $p - p_{\mathrm{V}\infty} = 0$, one gets

$$T_{\mathrm{V}} = \left(1 + \frac{\sigma\kappa + \Delta\phi}{\rho_{\mathrm{L}}\Delta h}\right)T_{\mathrm{V}\infty}. \tag{26}$$

For $p - p_{\mathrm{V}\infty} = \sigma\kappa$, Eq. (25) becomes

$$T_{\mathrm{V}} = \left(1 + \left(\frac{\sigma\kappa}{\rho_{\mathrm{V}}} + \frac{\Delta\phi}{\rho_{\mathrm{L}}}\right)\frac{1}{\Delta h}\right)T_{\mathrm{V}\infty}. \tag{27}$$

Finally, for $p - p_{\mathrm{V}\infty} = \sigma\kappa + \Delta\phi$, we have

$$T_{\mathrm{V}} = \left(1 + \frac{\sigma\kappa + \Delta\phi}{\rho_{\mathrm{V}}\Delta h}\right)T_{\mathrm{V}\infty}. \tag{28}$$

Eqs. (26) and (27) have been derived earlier [12], taking $\Delta\phi$ to represent a wall action upon a liquid film. The former one gives the temperature rise required just to keep the pressure in the vapour phase at $p = p_{\mathrm{V}\infty}$, that is, to compensate the vapour pressure lowering due to $\sigma\kappa + \Delta\phi$; the corresponding interface has been termed *open*. Eq. (27) is valid for a closed interface (vapour bubble), if the pressure in the vapour obeys the classical Laplace equation (without $\Delta\phi$), while the vapour pressure is affected by the potential $\Delta\phi$. Finally, Eq. (28), also valid for a closed interface, consistently accounts for the effects of $\sigma\kappa$ and $\Delta\phi$.

As is evident from Eqs. (26) and (28), the temperature difference $T_{\mathrm{V}} - T_{\mathrm{V}\infty}$ is by the factor $\rho_{\mathrm{L}}/\rho_{\mathrm{V}}$ larger for a closed than for an open interface, other parameters being the same.

Setting in Eq. (27) or (28) $\Delta\phi = 0$, one obtains the well-known Thomson [2] equation [13],

$$T_{\mathrm{V}} = \left(1 + \frac{\sigma\kappa}{\rho_{\mathrm{V}}\Delta h}\right)T_{\mathrm{V}\infty}. \tag{29}$$

If a plane interface ($\kappa = 0$) is exposed to the potential $\Delta\phi$, Eq. (26) gives

$$T_{\mathrm{V}} = \left(1 + \frac{\Delta\phi}{\rho_{\mathrm{L}}\Delta h}\right)T_{\mathrm{V}\infty}. \tag{30}$$

The shape of this equation belongs basically to the family of J.J. Thomson's equations.

5. Origin of the potential difference

The potential difference $\Delta\phi$ can arise from different sources, for instance from an electric and/or a magnetic field. If dielectric fluid phases are exposed to an electric field, the free energy of the phases changes [14], giving

$$\Delta\phi = \frac{\varepsilon - 1}{8\pi}(\varepsilon E_{\mathrm{n}}^2 + E_{\mathrm{t}}^2) - \frac{1}{8\pi}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \rho_{\mathrm{L}} E^2, \tag{31}$$

where E denotes the field strength (E_{n}, E_{t} being the components orthogonal and tangential to the interface) and ε, the electrical permittivity of the L-phase, relative to that of free space ($\varepsilon_{\mathrm{V}} = 1$). In [14], Eq. (31) is given as a pressure difference.

Of much greater importance for the present considerations is the action of a wall upon the film, Fig. 2c. In this case, although in another form, the potential ϕ has been introduced at the same time as the capillary pressure $\sigma\kappa$ by Pierre Simon de Laplace [15]. He ascribed the interaction between the wall molecules and the fluid to a potential that is proportional to the densities of the bodies involved. Details concerning the interaction law remained unspecified, however. The difficulties concerning this point are best depicted by Clairaut's remark that as many interaction laws as is pleased could be formulated. In general, the potential action was considered sensitive only at insensitive (immeasurable) distance.

When dealing with thin films, the potential difference $\Delta\phi$ is discussed in terms of an experimentally accessible *pressure difference*. The latter has been the subject matter of several studies, see e.g. [1,2,16–21] for more recent references. According to Derjaguin [10] it may be seen as an *excess pressure* in a liquid film above that in the bulk phase, basically arising from molecular interactions of the film with its substrate; he termed this pressure difference *disjoining pressure*. [3] As illustrated in Appendix A for attraction between wall and fluid, the excess pressure is always positive; it increases with decreasing film thickness.

The different components of this pressure difference vary not only in magnitude from each other, but also qualitatively; some of them are even negative [1]. For a given wall–fluid pair the pressure difference depends in

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[2] J.J. Thomson, the discoverer of the electron. The name of another Thomson, William, perpetuated in the Kelvin temperature, is much more frequently encountered in area of this paper.

Alternative derivation and a comprehensive analysis of Eq. (29) can be found in the monograph by Defay et al. [9].

[3] Leger and Joanny [22] define the disjoining pressure as follows: "The disjoining pressure is the pressure that one has to impose on the film to prevent it from thickening."

a complex manner on the temperature. It affects the film equilibrium when the film interfaces (wall–fluid, fluid–fluid) come into mutual interactions, that is, when δ_I and δ_W overlap [12], Fig. 2c.

The contribution arising from molecular interactions (dispersion forces) for nonpolar substances with a solid wall is apparently much larger than the other ones. In this case, the potential difference $\Delta\phi$, written as a pressure difference Δp_ϕ, becomes

$$\Delta p_\phi = \frac{A}{\delta^3}, \tag{32}$$

where δ is the film thickness, Fig. 2c, and $A = A_0/(6\pi)$, A_0 being the Hamaker constant. This relationship may be used for planar films on very smooth substrates; according to Churaev [19], the film thickness δ should not exceed 12 nm.

The Hamaker constant is system-specific and depends, in addition, on the temperature; so, the Hamaker constant is actually not constant. Its magnitude for nonpolar liquids on quartz at room temperature is $A_0 \approx 1.3 \times 10^{-20}$ J, and on metallic substrates $A_0 \approx 15 \times 10^{-20}$ J. For details concerning this quantity, the reader may be referred to the monographs by Derjaguin et al. [1], and Israelachvili [2], a paper by Churaev [19], and a review by Israelachvili and Tabor [18], the latter discussing also the temperature effect on A_0.

For films of a thickness between 40 and 80 nm, instead of Eq. (32), the expression

$$\Delta p_\phi = \frac{B}{\delta^4}, \tag{33}$$

has been recommended [1,18,19], which, like Eq. (32), can be derived from the theory of dispersion forces. It describes well the experiments of Kussakov and Titijewskaja [23] with nonpolar liquids (*n*-decane, *n*-octane, *n*-heptane, *n*-hexane) on steel, lead glass, diamond, and quartz substrates. From these experiments, the value of B was found to be $B \approx (1.5\text{–}1.7) \times 10^{-28}$ J m, which is in agreement with the theory ($B \approx 1.6 \times 10^{-28}$ J m), see also [1,16,18]. At approximately $\delta \approx 20$ nm, Eqs. (32) and (33) deliver the same values for Δp_ϕ on metallic substrates.

In view of Eqs. (32) and (33) an interesting conclusion is obtained concerning the shape of a vapour bubble situated in the field of a wall action. Namely, from the thermal equilibrium requirement ($T_V = \text{const}$ over the bubble surface, Eq. (28)), it follows

$$\sigma\kappa + \Delta\phi = \sigma\kappa + \frac{A}{\delta^n} = \text{const.}, \quad \frac{\partial\kappa}{\partial\delta} \sim \frac{1}{\delta^{n+1}}, \tag{34}$$

and the curvature κ decreases with increasing δ for $n > 1$. Note that A/δ^n stands for either of Eqs. (32) and (33).

Summing up the contributions $\Delta\phi_k$ mentioned above gives

$$\Delta\phi = \frac{A}{\delta^n} + \frac{\varepsilon - 1}{8\pi}(\varepsilon E_n^2 + E_t^2) - \frac{1}{8\pi}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T \rho_L E^2. \tag{35}$$

By this equation the equilibrium temperature depends on the direction of the electric field with respect to the interface. The wall effect, originally formulated for a planar film, is approximately valid also for films of a varying thickness.

6. General discussion

6.1. Vapour pressure

The equations given above for the vapour pressures can be condensed to one single expression by integrating

$$d\mu_L = v_L\, dp_L = v_V\, dp_V, \tag{36}$$

from $\mu_L(p_{L\infty}, T_{L\infty})$ and $p_{V\infty}(T_{V\infty})$ to $\mu_L(p_L, T_{L\infty})$ and $p_V(T_{V\infty})$. Hence,

$$p_V = p_{V\infty} \exp\left(\frac{\Delta\mu_L}{\Re T_{V\infty}}\right), \tag{37}$$

for ideal vapour, where ($\Delta\mu_L = \Delta\mu_V$)

$$\begin{aligned}\Delta\mu_L &= \mu_L(p_L, T_{L\infty}) - \mu_L(p_{L\infty}, T_{L\infty}) \\ &\approx \left(\frac{\partial\mu_L}{\partial p_L}\right)_{T_{L\infty}} (p_L - p_{L\infty}).\end{aligned} \tag{38}$$

At small values of the quantity $\Delta\mu_L/(\Re T_{V\infty})$, Eq. (37) becomes

$$p_V = p_{V\infty}\left(1 + \frac{\Delta\mu_L}{\Re T_{V\infty}}\right) = p_{V\infty} + \frac{\Delta\mu_L}{v_V}. \tag{39}$$

Given the temperature $T_{V\infty}$, the difference of the chemical potentials governs alone the vapour pressure. Increase in μ_L ($\Delta\mu_L > 0$), whatever the cause, rises the vapour pressure and condensation is expected to occur. To prevent this process, the chemical potential μ_L is to be lowered at the same rate by a counteraction.

To illustrate the efficacy of Eq. (39), we denote again the initial pressure by $p_{V\infty} = p_{L\infty}$, corresponding to the potential $\mu_V(p_{V\infty}, T_{L\infty}) = \mu_L(p_{L\infty}, T_{L\infty})$, replace the pressure p_V in Eq. (4) by $p_{V\infty}$, getting

$$p_L - p_{V\infty} = p_L - p_{L\infty} = -(\sigma\kappa + \Delta\phi). \tag{40}$$

Combining with Eqs. (38) and (39) results in the above Eq. (16).

If the pressure in the phases is not homogeneous, but changes due to action of e.g. gravity, the well-known Gibbs equation,

$$\Delta\mu_L + gz = 0, \tag{41}$$

applies, giving

$$\mu_L(p_L, T_{L\infty}) = \mu_L(p_{L\infty}, T_{L\infty}) - gz, \tag{42}$$

with the distance z measured from the reference plane corresponding to $p_L = p_{L\infty}$. Introducing Eq. (41) in Eq. (37) results in the Laplace barometric formula.

Note that via the vapour pressure the chemical potential $\Delta\mu_L$ can readily be connected with the equilibrium temperature.

6.2. Simultaneous actions of gravity and potential

For phases exposed to simultaneous actions of curvature κ, gravity g, and potential ϕ, an extended capillarity equation can be deduced by writing Eq. (38) in the form

$$p_L = p_{L\infty} + \frac{\Delta\mu_L}{v_L}, \tag{43}$$

and combining with Eq. (39) to get

$$p_V - p_L = \left(\frac{1}{v_V} - \frac{1}{v_L}\right)\Delta\mu_L. \tag{44}$$

Substituting Eq. (41) in Eq. (44) and considering Eq. (4), one obtains

$$\sigma\kappa + \Delta\phi = (\rho_L - \rho_V)gz. \tag{45}$$

From this expression the height z of the liquid column in a capillary, or the height of a climbing film, can be calculated,

$$z = \frac{\sigma\kappa + \Delta\phi}{(\rho_L - \rho_V)g}. \tag{46}$$

With the exception of a relationship by Derjaguin [10], equations of the type of Eq. (46) reported in the literature ignore either the wall or the vapour effect. This equation reduces for $\Delta\phi = 0$ to the familiar expression for the height of a liquid column in a capillary tube. If the outer surface of the capillary is considered, the interface of the liquid film climbing up the tube is convex and its curvature negative, hence

$$z = \frac{\Delta\phi - \sigma\kappa}{(\rho_L - \rho_V)g}. \tag{47}$$

For the outer tube surface to become wetted, the wall attraction must overcome the Laplace pressure, $\Delta\phi - \sigma\kappa > 0$. Consequently, the wetted portion of the tube height is always larger inside than outside the tube. However, neglecting the wall thickness of the tube along with the film thickness, the difference Δz obtained from Eqs. (46) and (47),

$$\Delta z = \frac{2\sigma\kappa}{(\rho_L - \rho_V)g}, \tag{48}$$

measures the height of the internal film, formed above the meniscus, relative to the external film.

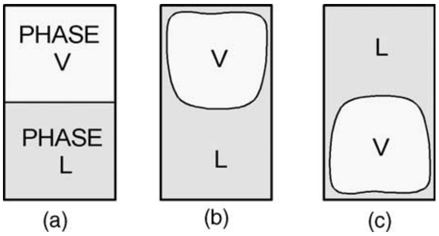

Fig. 3. Wetting of a wall by two rivalling liquid phases L and V: (a) equal wall action on the phases L and V, $\Delta\phi = \phi_L - \phi_V = 0$, (b) more dense phase L completely wets the wall, $\Delta\phi > 0$, and (c) less dense phase wets the wall, $\Delta\phi < 0$.

For $\Delta\phi + \sigma\kappa < 0$, vapour phase creeps between the liquid and wall thus forming a vapour film. Finally, for a planar interface, $\kappa = 0$, the potential difference $\Delta\phi$ governs alone the shape of the interface,

$$z = \frac{\Delta\phi}{(\rho_L - \rho_V)g} = \frac{A/\delta^n}{(\rho_L - \rho_V)g}. \tag{49}$$

Omitting the vapour density in Eq. (49) gives an expression frequently used in the literature for calculation of the height of climbing films.

For $\sigma\kappa + \Delta\phi > 0$, the height z in Eq. (46) tends to infinity at $\Delta\rho = \rho_L - \rho_V \to 0$. Therefore, it depends on $\Delta\phi$ only, whether a wall surface will become wetted by the fluid at its thermodynamic critical point ($\Delta\rho = 0$, $\sigma = 0$).

6.3. Immiscible liquid phases

An interesting picture is expected to establish with two liquid phases in the miscibility gap. Namely, if the densities of the phases are (nearly) equal and if $\sigma\kappa + \Delta\phi \neq 0$, the height z in Eq. (46) may become very large. In this case, favourably one of the phases will wet the container wall, thereby tending to enclose the other phase, Fig. 3. At very small density differences of the phases, it can become principally possible, that the phase of larger density forms a film at the top of the less dense phase, and vice versa, Fig. 3b and c. These phenomena have been observed by Moldover and Chan [24] with binary liquid mixtures and discussed by de Gennes [25] in terms of long-range molecular forces.

7. Conclusion

An external action upon the phases of a system, consisting at least of two phases, affects the phase equilibrium. Its effect can readily be taken into account by employing the familiar relationships of thermodynamics. This leads to the corresponding extensions of the common expressions. For instance, the isothermal change of the vapour pressure required to match an external action upon the system can be included into the classical Thomson (W. Thomson) equation. This equation was originally associated with the curvature of the interface without any external effect. The analogous is valid for the isobaric temperature rise according to the Thomson (J.J. Thomson) expression.

Although most of the results given in the paper are known from the literature, and several expressions can be deduced from the famous thought experiment by Thomson [11], illustrating the liquid rise in a capillary tube, the straightforwardness of the model adopted for the present derivations may serve to quickly survey the interactions associated with phase changes in thin films.

Appendix A

The aim is to illustrate the potential and pressure distributions in a fluid layer that is adhering to a wall surface. The wall is assumed to attract the fluid by a force obtainable from a potential field.

For a fluid at rest the Euler equation,

$$-\mathrm{grad}\, p + \rho \vec{f} = 0. \tag{A.1}$$

couples the pressure p and the density ρ with the force $\vec{f}$ per unit of mass.

Taking the force $\vec{f}$ to arise from a potential field

$$\vec{f} = -\mathrm{grad}\, \phi, \tag{A.2}$$

where ϕ denotes the potential energy per unit mass, and combining with Eq. (A.1) gives

$$\mathrm{grad}\, p + \rho\, \mathrm{grad}\, \phi = 0. \tag{A.3}$$

Involving the identity,

$$\mathrm{grad}\,(\rho\phi) = \rho\, \mathrm{grad}\, \phi + \phi\, \mathrm{grad}\, \rho, \tag{A.4}$$

multiplying by $\mathrm{d}\vec{r}$, where $\vec{r}$ is the radius vector, Fig. 4, Eq. (A.3) becomes

$$\mathrm{d}(p + \rho\phi) = \phi\, \mathrm{d}\rho, \tag{A.5}$$

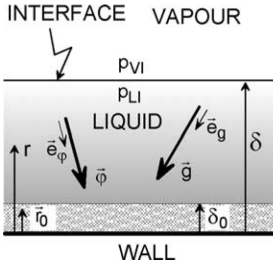

Fig. 4. Illustration supporting derivation of potential jump across the interface.

or

$$p + \rho\phi = \int \phi\, \mathrm{d}\rho + C, \tag{A.6}$$

with C as a constant.

Further treatment of Eq. (A.6) requires ρ in dependence of ϕ. However, taking ρ as constant, gives the basic equation of hydrostatics,

$$p + \rho\phi = p_0 + \rho\phi_0 = C, \tag{A.7}$$

where the index 0 indicates the reference quantities. This equation shows the sum of the pressure p and the energy density $\rho\phi$ arising from the potential field to be constant throughout the layer. We will return to this equation further below, particularly to the constant C.

To obtain the potential ϕ, Eq. (A.2) is multiplied by $\mathrm{d}\vec{r}$ and integrated,

$$\phi - \phi_0 = -\int_{\delta_0}^{r} \vec{f} \cdot \mathrm{d}\vec{r}. \tag{A.8}$$

The lower boundary is shown in Fig. 4 and its physical meaning is stated below.

Assuming the force to consist of different contributions, say, $\vec{g}$ and $\vec{\varphi}$, we can write

$$\vec{f} = \vec{g} + \vec{\varphi} = g\vec{e}_g + \varphi\vec{e}_\varphi, \tag{A.9}$$

where $\vec{e}_g$ and $\vec{e}_\varphi$ are the unit vectors, $g > 0$ and $\varphi > 0$ are the magnitudes of the force components. With Eq. (A.9) and $\mathrm{d}\vec{r} = \vec{r}_0\, \mathrm{d}r$, $\vec{r}_0$ being the unit vector, Eq. (A.8) becomes

$$\phi - \phi_0 = -\int_{\delta_0}^{r} (g\cos(\vec{e}_g, \vec{r}_0) + \varphi\cos(\vec{e}_\varphi, \vec{r}_0))\, \mathrm{d}r. \tag{A.10}$$

This equation should be applied to a fluid layer adhering to a horizontal wall, supposing

$$\cos(\vec{e}_g, \vec{r}_0) = \cos(\vec{e}_\varphi, \vec{r}_0) = -1. \tag{A.11}$$

By this condition, the forces $\vec{g}$ and $\vec{\varphi}$ are perpendicularly directed toward the wall, hence

$$\phi - \phi_0 = \int_{\delta_0}^{r} (g + \varphi)\, \mathrm{d}r, \tag{A.12}$$

and Eq. (A.7) becomes

$$p = p_0 - \rho\int_{\delta_0}^{r} (g + \varphi)\, \mathrm{d}r. \tag{A.13}$$

Since $(g + \varphi) > 0$ and $\mathrm{d}r > 0$, the integral is always positive, the pressure p thus decreases with increasing r.

If the forces $\vec{g}$ and $\vec{\varphi}$ counteract, instead of (A.11) we have

$$-\cos(\vec{e}_g, \vec{r}_0) = \cos(\vec{e}_\varphi, \vec{r}_0) = -1, \tag{A.14}$$

giving

$$\phi - \phi_0 = \int_{\delta_0}^{r} (\varphi - g)\, \mathrm{d}r, \tag{A.15}$$

$$p = p_0 - \rho \int_{\delta_0}^{r} (\varphi - g)\,\mathrm{d}r, \tag{A.16}$$

instead of (A.12) and (A.13).

Taking the quantity g to represent the acceleration due to gravity, Eqs. (A.12) and (A.13) describe the potential and pressure distributions in a fluid layer supported by a horizontal wall, while Eqs. (A.15) and (A.16) apply to a fluid layer adhering to the lower wall surface. For simplicity, however, the quantity g is omitted in the following.

To exemplify the effect of the force φ on the potential and pressure distributions, we assume this force to arise from the interactions between wall and fluid according to the ansatz

$$\varphi = \frac{n}{r^{n+1}} B, \quad B > 0, \ n > 0. \tag{A.17}$$

Then, Eq. (A.12) or (A.15) gives

$$\phi = \phi_0 + \left(\frac{1}{\delta_0^n} - \frac{1}{r^n} \right) B, \tag{A.18}$$

while the pressure p follows from Eq. (A.13) or (A.16),

$$p = p_0 - \left(\frac{1}{\delta_0^n} - \frac{1}{r^n} \right) \rho B. \tag{A.19}$$

As is evident from these equations, the potential decreases and the pressure increases when approaching the wall surface; the fluid is thus pressed against the wall.

The quantity δ_0 used above as the lower integration boundary can basically be specified arbitrarily, but it seems reasonable to define by δ_0 the region adjacent to the wall surface within which the fluid structure could be changed thus violating the common continuity hypothesis. The equations derived above are, therefore, valid for $r > \delta_0$ only.

In order to apply the results obtained so far to the vapour phase, the different phases will be discriminated by attaching indices to the phase-specific quantities. The index L is used for the liquid phase. Eqs. (A.18) and (A.19) thus read

$$\phi_{\mathrm{L}} = \phi_{\mathrm{L0}} + \left(\frac{1}{\delta_0^n} - \frac{1}{r^n} \right) B_{\mathrm{L}}, \tag{A.20}$$

$$p_{\mathrm{L}} = p_{\mathrm{L0}} - \left(\frac{1}{\delta_0^n} - \frac{1}{r^n} \right) \rho_{\mathrm{L}} B_{\mathrm{L}}. \tag{A.21}$$

Taking the ansatz (A.17) to also hold true for the vapour phase, we have

$$\phi_{\mathrm{V}} = \phi_{\mathrm{VI}} + \left(\frac{1}{\delta^n} - \frac{1}{r^n} \right) B_{\mathrm{V}}, \tag{A.22}$$

$$p_{\mathrm{V}} = p_{\mathrm{VI}} - \left(\frac{1}{\delta^n} - \frac{1}{r^n} \right) \rho_{\mathrm{V}} B_{\mathrm{V}}, \quad r > \delta, \tag{A.23}$$

where the index VI refers to the vapour at the interface.

Eqs. (A.20) and (A.22) are suitable to examine whether or not the wall effect leads to a potential jump across the interface. To achieve this, we set in Eq. (A.20) $r = \delta$, denote the corresponding potential by ϕ_{LI},

$$\phi_{\mathrm{LI}} = \phi_{\mathrm{L0}} + \left(\frac{1}{\delta_0^n} - \frac{1}{\delta^n} \right) B_{\mathrm{L}}, \tag{A.24}$$

and combine with (A.22), thus

$$\phi_{\mathrm{LI}} - \phi_{\mathrm{VI}} = \phi_{\mathrm{L0}} - \phi_{\mathrm{V}} + \left(\frac{1}{\delta_0^n} - \frac{1}{\delta^n} \right) B_{\mathrm{L}} + \left(\frac{1}{\delta^n} - \frac{1}{r^n} \right) B_{\mathrm{V}}. \tag{A.25}$$

Denoting by $\phi_{\mathrm{V}\infty}$ the potential of the vapour at infinity (both δ and r), Eq. (A.25) simplifies

$$\phi_{\mathrm{LI}} - \phi_{\mathrm{VI}} = \phi_{\mathrm{L0}} - \phi_{\mathrm{V}\infty} + \frac{B_{\mathrm{L}}}{\delta_0^n}. \tag{A.26}$$

Since for r, $\delta \to \infty$ the wall effect on the interface may be neglected ($\phi_{\mathrm{LI}} - \phi_{\mathrm{VI}} = 0$), Eq. (A.26) gives

$$\phi_{\mathrm{L0}} - \phi_{\mathrm{V}\infty} + \frac{B_{\mathrm{L}}}{\delta_0^n} = 0. \tag{A.27}$$

The quantities in this equation are independent of δ, its validity is therefore taken to be independent of the film thickness. Eqs. (A.25) and (A.27) then give

$$\Delta\phi_{\mathrm{I}} = \phi_{\mathrm{LI}} - \phi_{\mathrm{VI}} = \frac{B_{\mathrm{V}} - B_{\mathrm{L}}}{\delta^n} - \frac{B_{\mathrm{V}}}{r^n} \tag{A.28}$$

with the limits

$$\Delta\phi_{\mathrm{I}} = \phi_{\mathrm{LI}} - \phi_{\mathrm{VI}} = \frac{B_{\mathrm{V}} - B_{\mathrm{L}}}{\delta^n}, \quad r \to \infty, \tag{A.29}$$

$$\Delta\phi_{\mathrm{I}} = \phi_{\mathrm{LI}} - \phi_{\mathrm{VI}} = -\frac{B_{\mathrm{L}}}{\delta^n}, \quad r = \delta. \tag{A.30}$$

Analogous reasoning leads to the following relationships for the interfacial liquid pressure p_{LI}, the reference pressure p_{L0}, and the interfacial pressure jump Δp_{I},

$$p_{\mathrm{LI}} = p_{\mathrm{L0}} - \left(\frac{1}{\delta_0^n} - \frac{1}{\delta^n} \right) \rho_{\mathrm{L}} B_{\mathrm{L}}, \tag{A.31}$$

$$p_{\mathrm{L0}} = p_{\mathrm{V}\infty} + \frac{\rho_{\mathrm{L}} B_{\mathrm{L}}}{\delta_0^n}, \tag{A.32}$$

$$\Delta p_{\mathrm{I}} = p_{\mathrm{LI}} - p_{\mathrm{VI}} = \frac{\rho_{\mathrm{L}} B_{\mathrm{L}} - \rho_{\mathrm{V}} B_{\mathrm{V}}}{\delta^n} + \frac{\rho_{\mathrm{V}} B_{\mathrm{V}}}{r^n}. \tag{A.33}$$

The latter equation delivers

$$\Delta p_{\mathrm{I}} = p_{\mathrm{LI}} - p_{\mathrm{VI}} = \frac{\rho_{\mathrm{L}} B_{\mathrm{L}} - \rho_{\mathrm{V}} B_{\mathrm{V}}}{\delta^n}, \quad r \to \infty, \tag{A.34}$$

$$\Delta p_{\mathrm{I}} = p_{\mathrm{LI}} - p_{\mathrm{VI}} = \frac{\rho_{\mathrm{L}} B_{\mathrm{L}}}{\delta^n}, \quad r = \delta. \tag{A.35}$$

Since $\Delta\varphi_{\mathrm{I}}$ and Δp_{I} are local quantities, only Eqs. (A.30) and (A.35) possess physical significances concerning these jumps.

Prior to closing the considerations, let us return to Eq. (A.6). Being valid for the whole phase, it must also hold true for the phase boundary, the interface, hence

$$\left(p+\rho\phi-\int\phi\,\mathrm{d}\rho\right)_{\mathrm{LI}}=C_{\mathrm{LI}}, \tag{A.36}$$

$$\left(p+\rho\phi-\int\phi\,\mathrm{d}\rho\right)_{\mathrm{VI}}=C_{\mathrm{VI}}, \tag{A.37}$$

or

$$\left(p+\rho\phi-\int\phi\,\mathrm{d}\rho\right)_{\mathrm{VI}}-\left(p+\rho\phi-\int\phi\,\mathrm{d}\rho\right)_{\mathrm{LI}}=C_{\mathrm{VI}}-C_{\mathrm{LI}}. \tag{A.38}$$

Excluding other external actions on the phases and viewing the terms as energy densities, the energy jump across the interface can only arise from the shape of the interface. Taking the mass densities as constant and the interface as curved in a way that increases the energy in the vapour, we can write

$$(p+\rho\phi)_{\mathrm{VI}}-(p+\rho\phi)_{\mathrm{LI}}=\sigma\kappa, \tag{A.39}$$

where σ and κ are the free energy and the curvature of the interface, respectively. Replacing formally the product $\rho\phi$ by ϕ (energy per unit volume, e.g. in J/m^3) and omitting the index I, Eq. (39) becomes identical to Eq. (4) in this paper.

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