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Influence of dispersion forces on phase equilibria between thin liquid films and their vapour

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Abstract

Heat transfer and nucleation processes in nucleate boiling strongly depend on the phase equilibrium at the liquid–vapour interface. In a certain region between heated wall and a vapour bubble where a thin liquid film is adsorbed, phase equilibria are considerably influenced by dispersion forces acting on the liquid film. As shown in the paper in such systems the chemical potential, decisive for phase equilibria between liquid films and their vapour, contains an additional term for the action of dispersion forces, and differs from the chemical potential of dispersion-free systems, though their chemical potential is usually taken in the literature for systems with dispersion forces. With the aid of the chemical potential the Kelvin equations for the pressures at the liquid–vapour interface were derived. It turned out that the Gibbs assumption of a geometrical interface between extremely thin liquid films in equilibrium with its vapour does not hold. Instead, following the ideas of van der Waals junior, the small but finite transition interlayer between both phases had to be introduced.

As numerical examples illustrate, the dispersion forces considerably influence the pressures at the liquid–vapour interface. In nucleate boiling processes the driving pressure difference for evaporation undergoes a maximum within a tiny area underneath vapour bubbles. As could be shown the maximum driving pressure difference between gas-side interface and gas-core is a considerable fraction of the vapour pressure itself and contributes significantly to the high heat fluxes in nucleate boiling.

Keywords: Microscale heat transfer; Thin liquid films; Dispersion forces; Kelvin equation; Thin film chemical potential

1. Introduction

Microscale heat and mass transfer in nucleate boiling strongly depends on vapour–liquid phase equilibria of a thin liquid film adsorbed between the heated wall and the vapour bubble as first pointed out by Stephan and Hammer [1]. As an example, in Fig. 1 the curved line represents the interface between a vapour bubble and the liquid layer at a heated wall. In the so-called macro-region the interface has an almost constant curvature K corresponding to the bubble radius r_B, $K = 2/r_B$. In the micro-region the curvature of the interface sharply turns and ends in a non-evaporating liquid film adsorbed at the wall, the curvature being there $K = 0$. In this adsorbed film, in the so-called adhesion zone between wall and liquid film, attractive forces inhibit evaporation. In the micro-region between macro-region and the adsorbed film the curvature of the liquid–vapour interface undergoes a steep maximum, which for example for refrigerant R114 of 0.247 MPa boiling at a wall superheated by 5 K, amounts to $K_{max} \approx 10^7$ m^{-1}. The curvature varies over a small distance of about 0.1 μm between that of the adsorbed film $K = 0$, the maximum value $K_{max} \approx 10^7$ m^{-1} in the micro-region and an almost constant value $K \approx 10^3$ m^{-1} in the macro-region, thus leading to extremely high capillary forces, a strong liquid flow towards the interface, and hence in the thin liquid film to extreme high heat fluxes of up to 10^7 W/m^2 [1–6].

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Nomenclature

A	Hamaker constant (J)
A_{disp}	dispersion constant (J) $= A/6\pi$
E	energy (J)
e_η	unit vector in direction η
F_{disp}	dispersion force (N)
$\overline{F}_{\mathrm{disp}}$	molar dispersion force ($\mathrm{N\,mol^{-1}}$)
f	body force per volume ($\mathrm{N\,m^{-3}}$), condensation coefficient (–)
f^*	body force per mass ($\mathrm{N\,kg^{-1}}$)
g	gravity ($\mathrm{m\,s^{-2}}$)
H	height (m)
K	curvature ($\mathrm{m^{-1}}$)
L	length (m)
M	molar mass ($\mathrm{kg\,kmol^{-1}}$)
N_{A}	Avogadro number ($\mathrm{mol^{-1}}$)
n	mole number (mol)
p	pressure ($\mathrm{N\,m^{-2}}$)
$\dot{q}$	heat flux ($\mathrm{W\,m^{-2}}$)
R	gas constant ($\mathrm{J\,kg^{-1}\,K^{-1}}$)
R_{m}	universal gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
r	radius, radial co-ordinate (m)
S	entropy ($\mathrm{J\,K^{-1}}$)
$\overline{S}$	molar entropy ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
T	Temperature (K)
V	volume ($\mathrm{m^3}$)
$\overline{V}$	molar volume ($\mathrm{m^3\,mol^{-1}}$)
W	work (N)
w	interaction pair potential (J)
ξ	co-ordinate (m)
η	co-ordinate (m)
ρ	density ($\mathrm{kg\,m^{-3}}$)
ρ_1, ρ_2	number density ($\mathrm{m^{-3}}$) of species 1 and 2
μ	chemical potential ($\mathrm{J\,mol^{-1}}$)
σ	surface tension ($\mathrm{N\,m^{-1}}$)
δ	film thickness (m)

Subscripts

ad	adsorption
B	bubble
disp	dispersion
G	gas
hydr	hydrodynamical
L	Liquid
mic	micro-region
Ph	at interface
Ph, L	on liquid side of the interface
Ph, G	on gas side of the interface
SL	interaction of solid with liquid
S, L, G	interaction of solid with gas across liquid
S, Lσ, G	interaction of solid with gas across liquid and σ-phase
S, L, σG	interaction of solid with σ- and gas-phase across liquid
sat	saturation
W	wall
η	in direction η
σ	interface between liquid and gas

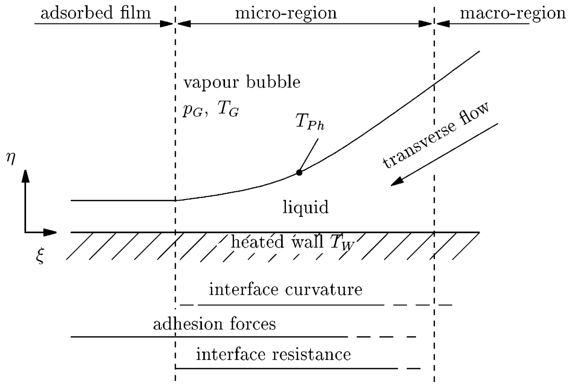

Fig. 1. Liquid film between vapour bubble and heated wall: (—) region of strong influence and (- - -) region of weak influence.

Phase equilibria at the liquid–vapour interface are different from those at plane interfaces free of dispersion forces for three reasons:

(i) The capillary forces due to the strong change in curvature in the micro-region also enhance the interface temperature T_{Ph}. The superheat over saturation temperature of a plane interface necessary for evaporation of the curved interface increases with capillary pressure.

(ii) Because of the thin liquid film in the micro-region the temperature drop $T_{\mathrm{W}} - T_{\mathrm{Ph}}$ between wall and gas–liquid interface can be as small or even smaller than the temperature drop $T_{\mathrm{Ph}} - T_{\mathrm{G}}$ between gas–liquid interface and gas-core. The molecular kinetic resistance at the liquid–vapour interface has to be taken into account.

(iii) In the adhesion zone and the micro-region long range interaction forces, so called dispersion forces, between solid wall and the molecules of the thin liquid film rise the temperature T_{Ph} at the interface.

Because of the variation of curvature $K(\xi)$ and film thickness $\delta(\xi)$ the interface temperature T_{Ph} is not constant but a function of the radial co-ordinate ξ. We can

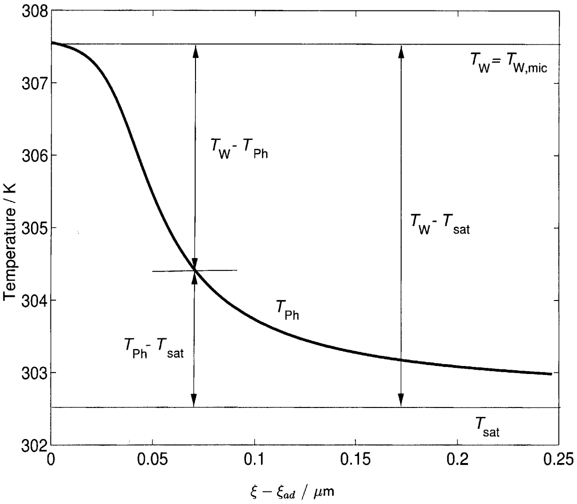

Fig. 2. Temperature differences in the micro-region, R114 at $p_{sat} = 0.247$ MPa, $T_{sat} = 302.63$ K, $T_W = 307.63$ K.

therefore state, as shown in Fig. 2, that the temperature drop $T_{Ph} - T_{sat}$ is considerable, and thus the driving temperature difference $T_W - T_{Ph}$ for heat transfer is smaller than $T_W - T_{sat}$ of a plane film, when the dispersion forces and intermolecular resistance are negligible. The smaller temperature difference $T_W - T_{Ph}$ compared to $T_W - T_{sat}$ reduces the heat flux. This reduction in the micro-region, however, is partly compensated by the much smaller thermal resistance of the thin liquid film.

Basic and pioneering theoretical and experimental studies of evaporating thin liquid films were mainly performed by Wayner and coworkers. A concise review of their research is given by Wayner [7,8]. As shown by them the assumption of a constant interface temperature T_{Ph} and also a constant curvature $K = \text{const}$ in the micro-region does not hold.

It is obvious that the liquid–vapour phase change is of fundamental interest and of practical significance in nucleate boiling heat transfer.

A useful tool for the study of phase equilibria is the Kelvin equation, which shall be presented here for pure substances. Its derivation is usually based on the assumption of a fluid with ideal vapour and an incompressible liquid phase. Intermolecular forces between solid and liquid are not taken into account. In our case we also assume an ideal vapour and an incompressible liquid. However, because of the presence of dispersion forces the intermolecular forces between solid and liquid must be taken into account. They add to the capillary forces. Furthermore the temperature rises at the liquid–vapour interface because of the molecular kinetic resistance. Both effects cause a shift in the chemical potential, which shall be discussed in this paper. Then, with the aid of the Kelvin equation, deduced from the chemical potential, the variation of pressures in the liquid and vapour phase, as they occur in nucleate boiling when vapour bubbles exist at solid walls, will be studied.

2. The nature of dispersion forces

The adhesion or dispersion forces between the solid wall and the liquid film can be attractive or repulsive. As long range forces they can be effective from distances of interatomic spacing in the liquid film of about 0.2 nm to distances of some 10 nm. As Israelachvili [9] pointed out they are quantum mechanical in origin, and are present even if molecules are non-polar. Though the time average dipole of these molecules vanishes there exists a finite dipole moment given by the instantaneous position of the electron around the protons. These instantaneous dipoles generate an electric field inducing a dipole moment in any nearly neutral atoms giving rise to an instantaneous attractive force between the atoms. The time average of this force is finite. Attractive forces mainly determine the boiling point and the heat of vaporisation of a substance, hence their importance when studying boiling processes.

Dispersion forces were intensively studied by Israelachvili [9] and in earlier papers by Derjaguin [10–12], who developed a model to convert these forces into a liquid pressure. The dispersion forces lead to an additional pressure p_{disp} in the liquid film, which under the assumption of an interaction pair potential $w = -C/r^n$ with coefficient C describing the interaction between two molecules and for example $n = 6$ for van der Waals forces becomes [9]

$$p_{disp} = A_{disp}/\eta^3, \tag{1}$$

where η is the distance between a certain position within the liquid and an infinitely extended solid surface. The dispersion constant describing the interaction between two bodies 1 and 2 is defined as

$$A_{disp} = \pi C \rho_1 \rho_2 / 6. \tag{2}$$

ρ_1 and ρ_2 are the number densities of molecules in the interacting bodies, and coefficient C describes the interaction between the atoms in the bodies. Instead of the dispersion constant A_{disp} the Hamaker constant A, after Hamaker [13], who did earlier studies to explore the forces between macroscopic bodies, is often used in the literature,

$$A = 6\pi A_{disp}. \tag{3}$$

As shown by Lifshitz [14], Hamaker constants of van der Waals forces and hence dispersion constants can be calculated from bulk properties such as dielectric constants and refractive indices. The essential equations are reviewed in the book of Israelachvili [9].

3. The chemical potential of a system with dispersion forces

With the aid of dispersion forces we can now proceed to determine the chemical potential of a homogeneous bulk phase, for instance the liquid phase in Fig. 3. In all the literature known to the author, it is taken from the Gibbs–Duhem equation

$$\mathrm{d}\mu = -\overline{S}\,\mathrm{d}T + \overline{V}\,\mathrm{d}p, \quad \text{or from}$$
$$\mathrm{d}\mu = -\overline{S}\,\mathrm{d}T + \overline{V}\,\mathrm{d}p + M\vec{g}\,\mathrm{d}r$$

if gravity is not negligible. Quantities with an overbar represent molar quantities: $\overline{S}(p,T)$ are the molar entropy and $\overline{V}(p,T)$ the molar volume. If the above equations for the chemical potential were correct then according to the thermal equation of state $\overline{V}(p,T)$ or $p = p(\rho, T)$ where ρ is the density, for an incompressible fluid the pressure inside the fluid would only be a function of temperature. This is correct when dispersion forces are absent, but does not hold when they are not negligible. As we saw before, Eq. (1) then the dispersion pressure becomes important, depending on the distance between fluid and the solid surface. We should therefore expect $p = p(\rho, T, \vec{r})$, where $\vec{r}$ stands for the distance, and hence a chemical potential $\mu = \mu(p, T, \vec{r})$ and not $\mu = \mu(p, T)$ as in the above equation.

In order to derive the correct chemical potential of the liquid phase we start from the Gibbs function

$$E = E(S, V, \vec{r}, n) \tag{4}$$

with entropy S, volume V, co-ordinate $\vec{r}$ in the liquid and the mole number n. From Eq. (4) we obtain

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V - \vec{F}_{\mathrm{disp}}\mathrm{d}\vec{r} + \mu\,\mathrm{d}n \tag{5}$$

with

$$\vec{F}_{\mathrm{disp}} := -(\partial E/\partial \vec{r})_{\mathrm{S,V,n}} = \vec{F}_{\mathrm{disp}}(S, V, \vec{r}, n).$$

Temperature T, pressure p, and chemical potential μ are defined as partial derivatives of E, $T = \partial E/\partial S$, $p = -\partial E/\partial V$, $\mu = \partial E/\partial n$, but now depend on S, V, $\vec{r}$, n. Strictly speaking, $\vec{F}_{\mathrm{disp}}$ stands here for all forces acting on the system. For reasons of simplicity we disregard all other forces except for the dispersion forces as the most important forces for evaporation of thin liquid films.

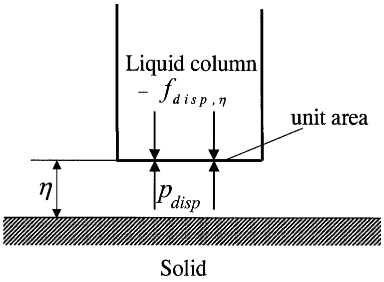

Fig. 3. Dispersion forces acting on a liquid volume of unit area.

Because the Gibbs function E, Eq. (4), is a homogeneous function of first order in the variables S, V, n its Euler-equation reads

$$E = TS - pV + \mu n. \tag{6}$$

From this we have

$$\mathrm{d}E = T\,\mathrm{d}S + S\,\mathrm{d}T - p\,\mathrm{d}V - V\,\mathrm{d}p + \mu\,\mathrm{d}n + n\,\mathrm{d}\mu.$$

Together with Eq. (5) we obtain the Gibbs–Duhem equation

$$S\,\mathrm{d}T - V\,\mathrm{d}p + \vec{F}_{\mathrm{disp}}\mathrm{d}\vec{r} + n\,\mathrm{d}\mu = 0. \tag{7}$$

The chemical potential $\mu(T, p, \vec{r})$ of the pure liquid therefore is given by

$$\mathrm{d}\mu = -\overline{S}\,\mathrm{d}T + \overline{V}\,\mathrm{d}p - \vec{\overline{F}}_{\mathrm{disp}}\mathrm{d}\vec{r}, \tag{8}$$

where $\overline{S}$, $\overline{V}$ and $\vec{\overline{F}}_{\mathrm{disp}}$ again represent molar quantities.

4. Dispersion forces and phase equilibria

Different from the chemical potential $\mathrm{d}\mu = -\overline{S}\,\mathrm{d}T + \overline{V}\,\mathrm{d}p$ in the absence of dispersion forces, Eq. (8) contains the term $\vec{\overline{F}}_{\mathrm{disp}}\,\mathrm{d}\vec{r}$ of the molar dispersion force $\vec{\overline{F}}_{\mathrm{disp}}$. Its quantity can be derived from the interaction energy of dispersion. In the case of two planar surfaces at a distance $\vec{r} = \eta e_\eta$ apart, one of unit area and infinite depth, for example a liquid and the other infinitely large, for example a solid wall, we have, as shown by Israelachvili [9, p. 158], the dispersion energy,

$$W(\eta) = -\pi C \rho_1 \rho_2 / 12\eta^2, \tag{9}$$

where C comes from the interaction pair potential $w = -C/r^n$ with $n = 6$, and ρ_1, ρ_2 again are the number densities of solid and liquid. The dispersion force $f_{\mathrm{disp},\eta}$ per unit surface is given by

$$f_{\mathrm{disp},\eta}(\eta) = -\frac{\partial W}{\partial \eta} = -\pi C \rho_1 \rho_2 / 6\eta^3 = -A_{\mathrm{disp}}/\eta^3. \tag{10}$$

The dispersion force $f_{\mathrm{disp},\eta}$ (η) between two bodies, for example a solid wall and a liquid, as shown in Fig. 3 is the resultant of all body forces due to dispersion acting on the liquid column and directed against the co-ordinate η. Because of the equilibrium of all forces acting on the liquid column at rest the force $f_{\mathrm{disp},\eta}$ is balanced by an external pressure, the so-called dispersion pressure defined as

$$p_{\mathrm{disp}} := -f_{\mathrm{disp},\eta} = A_{\mathrm{disp}}/\eta^3. \tag{11}$$

The dispersion pressure acts in a similar way as the hydrostatic pressure p_{hydr}. Both pressures balance out body forces, the dispersion pressure those of molecular origin, the hydrostatic pressure those of gravity.

However, different from the hydrostatic pressure which decreases linearly with height η according to $\partial p_{\mathrm{hydr}}/\partial\eta = -\rho_{\mathrm{L}} g$, the dispersion pressure decreases much faster with $1/\eta^3$ as can be seen from Eq. (11), and we have $\partial p_{\mathrm{disp}}/\partial\eta = -\pi C\rho_1\rho_2/2\eta^4$. The dispersion pressure tends to zero mostly after distances η above 100 nm, depending on the substances involved.

We consider now the momentum balance of a fluid volume element $\mathrm{d}V = A\,\mathrm{d}\eta$, where A is the surface area, replacing the unit area of Fig. 3. The momentum balance reads

$$\rho_{\mathrm{L}} f^*_{\mathrm{disp},\eta} = \frac{\partial p_{\mathrm{disp}}}{\partial\eta}, \tag{12}$$

where $f^*_{\mathrm{disp},\eta}$ stands for the body force per mass (SI-unit N/kg) acting on the volume element. Because of

$$\int_V \rho_{\mathrm{L}} f^*_{\mathrm{disp},\eta}\,\mathrm{d}\eta = \int_V (\partial p_{\mathrm{disp}}/\partial\eta)\,\mathrm{d}\eta = \int_A p_{\mathrm{disp}}\,\mathrm{d}A$$

in the limit $V \to 0$ the volume integral disappears much faster than the surface integral, we have in any cross section $\int_A p_{\mathrm{disp}}\,\mathrm{d}A = 0$. Dispersion forces in any cross section are opposed to each other and cancel. They behave in the same way as hydrostatic forces which also cancel over a surface.

With Eq. (11) we obtain

$$f^*_{\mathrm{disp},\eta} = v_{\mathrm{L}} \frac{\partial p_{\mathrm{disp}}}{\partial\eta} = -v_{\mathrm{L}} \frac{3A_{\mathrm{disp}}}{\eta^4}. \tag{13}$$

The molar body force $\overline{F}_{\mathrm{disp},\eta}$ (SI-unit N/mol) is

$$\overline{F}_{\mathrm{disp},\eta} = \overline{V}_{\mathrm{L}} \frac{\partial p_{\mathrm{disp}}}{\partial\eta} = -\overline{V}_{\mathrm{L}} \frac{3A_{\mathrm{disp}}}{\eta^4}. \tag{14}$$

From this we obtain

$$\overline{F}_{\mathrm{disp},\eta}\,\mathrm{d}\eta = \overline{V}_{\mathrm{L}} \frac{\partial p_{\mathrm{disp}}}{\partial\eta}\,\mathrm{d}\eta = \overline{V}_{\mathrm{L}}\,\mathrm{d}p_{\mathrm{disp}}. \tag{15}$$

Keeping in mind that $A_{\mathrm{disp}} = \pi C\rho_1\rho_2/6$ contains in the case of a liquid–solid interaction the liquid number density $\rho_1 = \rho_{\mathrm{L}} = \mathrm{d}N_{\mathrm{L}}/\mathrm{d}V_{\mathrm{L}} = N_A\,\mathrm{d}n_{\mathrm{L}}/\mathrm{d}V_{\mathrm{L}} = N_A/\overline{V}_{\mathrm{L}}$ with the Avogadro number N_{A} and the solid number density ρ_2 the molar body force can be rewritten

$$\overline{F}_{\mathrm{disp},\eta} = -\frac{\pi C N_{\mathrm{A}} \rho_2}{2\eta^4}. \tag{16}$$

If gravity plays a role in addition to the dispersion forces the momentum balance becomes $\rho_{\mathrm{L}} f_\eta = \rho_{\mathrm{L}}(f_{\mathrm{g},\eta} + f^*_{\mathrm{disp},\eta}) = \partial p_{\mathrm{L}}/\partial\eta$ with gravity $f_{g,\eta} = -g$ and $f^*_{\mathrm{disp},\eta}$ from Eq. (13). In the liquid film $0 \leqslant \eta \leqslant \delta$ gravity is however mostly negligible as we can see from the ratio of dispersion forces and gravity

$$\frac{f^*_{\mathrm{disp},\eta}}{f_{\mathrm{g},\eta}} = \frac{v_{\mathrm{L}}\pi C\rho_1\rho_2}{2\eta^4 g} = \frac{3A_{\mathrm{disp}}}{\eta^4\rho_{\mathrm{L}} g} \geqslant \frac{3A_{\mathrm{disp}}}{\delta^4\rho_{\mathrm{L}} g} \cong 3.6 \times 10^7.$$

As an example we used herein the values $A_{\mathrm{disp}} = 8.69 \times 10^{-21}$ J for solid–liquid interaction, $\rho_{\mathrm{L}} = 1441$ kg/m^3, film thickness $\eta = \delta = 15$ nm for refrigerant R114 at saturation pressure of 0.247 MPa corresponding to a saturation temperature of 302.63 K.

4.1. The Young–Laplace equation

The assumptions made in our model are

- The gaseous phase obeys the equation of state of an ideal gas. Then interactions between gas-molecules disappear.
- The system studied here consists of a solid wall wetted by an extremely thin liquid film in equilibrium with its vapour phase. Because of the thin liquid film we cannot a priori accept the Gibbs assumption according to which the interlayer between gas and liquid is a geometrical surface. Its thickness can be of the same order as that of the liquid film.

Molecular dynamics simulation [15] of the liquid–vapour interface of a Lennard-Jones fluid with real gaseous phases has indeed shown that the thickness of the interlayer is of the order of a few Nanometers. When the gaseous phase may be considered as ideal the interfacial thickness comes close to 1 nm. Of the same order of magnitude are liquid films in the micro-region, so that the Gibbs-assumption according to which the thickness of the interlayer is negligible compared to that of the liquid film, at least in some parts of the micro-region does not hold.

In order to derive the Young–Laplace equation describing the mechanical equilibrium in such a system we consider, as shown in Fig. 4a, two homogeneous bulk phases consisting of liquid L and gas G, connected by an interface layer σ, having for the sake of simplicity the form of a circular cylindrical shell element of arc length $r\,\mathrm{d}\varphi$, depth L and of thickness Δr. Then the forces σL exerted by surface tension σ act upon the side edges of depth L. Their resultant is given by $\mathrm{d}F_{\mathrm{R}} = \sigma L\,\mathrm{d}\varphi$. Also of importance are the forces resulting from gas and liquid pressures and from dispersion. The force balance is given by

$$p_{\mathrm{L}} \cdot (r + \Delta r) \cdot \mathrm{d}\varphi L + \mathrm{d}F_{\mathrm{R}} = p_{\mathrm{G}} r\,\mathrm{d}\varphi L + \mathrm{d}F_{\mathrm{disp}}. \tag{17}$$

The dispersion forces act as body forces upon the cylindrical shell, and are equal to the difference

$$\mathrm{d}F_{\mathrm{disp}} = (p_{\mathrm{disp,Ph,L}} - p_{\mathrm{disp,Ph,G}}) r\,\mathrm{d}\varphi L$$

of the dispersion pressure forces on both sides of the interface. With this the force balance reads

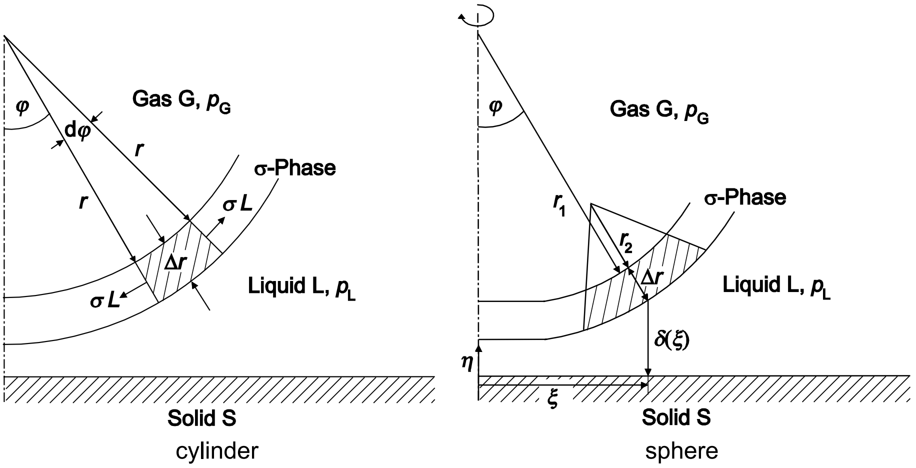

Fig. 4. Mechanical equilibrium between liquid L, gas G and σ-phase: (a) cylinder and (b) main curvatures r_1, r_2.

$$p_L \cdot (r + \Delta r) \cdot d\varphi L + \sigma d\varphi L = p_G r d\varphi L + (p_{\mathrm{disp,Ph,L}} - p_{\mathrm{disp,Ph,G}}) r d\varphi L,$$

or because of $\Delta r \ll r$,

$$p_L + \frac{\sigma}{r} = p_G + p_{\mathrm{disp,Ph,L}} - p_{\mathrm{disp,Ph,G}}. \tag{18}$$

For a surface with mean curvature $K = 1/r_1 + 1/r_2$, as shown in Fig. 4b, the equivalent balance reads

$$p_L + \sigma K = p_G + p_{\mathrm{disp,Ph,L}} - p_{\mathrm{disp,Ph,G}}. \tag{19}$$

This is the Young–Laplace equation for a system with dispersion forces. For a Gibbs interface, because of $\Delta r = 0$ and hence $p_{\mathrm{disp,Ph,L}} = p_{\mathrm{dispPh,G}}$ converts into the well known form of the Young–Laplace equation for a system without dispersion forces $p_L + \sigma K = p_G$.

It is noteworthy that in all references known to the author Eq. (19) is pretended to write

$$p_L + \sigma K = p_G - p_{\mathrm{disp}}.$$

Different from Eq. (19) the dispersion pressure does not disappear at a Gibbs interface.

In Eq. (19) the location of $p_{\mathrm{dispPh,L}}$ in cylinder co-ordinates is at position φ, $r_1 + \Delta r$ or in Cartesian co-ordinates at ξ, δ (see Fig. 4b). The cylinder co-ordinates of $p_{\mathrm{disp,Ph,G}}$ are φ, r_1 and its Cartesian co-ordinates $\xi - \Delta r_1 \sin\varphi$, $\delta + \Delta r \cos\varphi$. With this the dispersion pressures in the Cartesian co-ordinate system are

$$p_{\mathrm{disp,Ph,L}} = A_{\mathrm{disp,Ph,L}}/\delta^3 \quad \text{and} \quad p_{\mathrm{disp,Ph,G}} = A_{\mathrm{disp,Ph,G}}/(\delta + \Delta r \cos\varphi)^3. \tag{20}$$

The dispersion force leading to the pressure $p_{\mathrm{disp,Ph,L}}$ is caused by the interaction of the solid wall S with the σ- and the gas-phase G across the liquid film L. Following the notation of Israelachvili [9] the corresponding dispersion constant for the interaction can be written $A_{\mathrm{disp,Ph,L}} = A_{\mathrm{S,L,\sigma G}}/6\pi$. For the interaction of the solid wall S with the gas G across the liquid L and the σ-phase we have $A_{\mathrm{disp,Ph,G}} = A_{\mathrm{S,L\sigma,G}}/6\pi$. Approximate combining rules for the Hamaker constants were given for example by Israelachvili [9] and can be written in the following form

$$A_{\mathrm{disp,Ph,L}} 6\pi = A_{\mathrm{S,L,\sigma G}} \approx \left(\sqrt{A_{\mathrm{SS}}} - \sqrt{A_{\mathrm{LL}}}\right)\left(\sqrt{A_{\mathrm{\sigma G,\sigma G}}} - \sqrt{A_{\mathrm{LL}}}\right) \tag{21}$$

and

$$A_{\mathrm{disp,Ph,G}} 6\pi = A_{\mathrm{S,L\sigma,G}} \approx \left(\sqrt{A_{\mathrm{SS}}} - \sqrt{A_{\mathrm{L\sigma,L\sigma}}}\right)\left(\sqrt{A_{\mathrm{GG}}} - \sqrt{A_{\mathrm{L\sigma,L\sigma}}}\right). \tag{22}$$

Herein the Hamaker constants A_{ii} are those of two dielectric or electrically non-conducting media i interacting across vacuum. They are given by the Lifshitz theory see [9, Eq. (11.14)]

$$A_{\mathrm{ii}} = \frac{3}{4} kT \left(\frac{\varepsilon_i - 1}{\varepsilon_i + 1}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_i^2 - 1)^2}{(n_i^2 + 1)^{3/2}}, \tag{23}$$

where ε_i is the dielectric constant of medium i, n_i its refractive index in the visible, k is the Boltzmann constant, h the Planck constant and ν_e the Plasma frequency of the free electron. In nucleate boiling processes the solid wall is mostly a metal. For two metals interacting across vacuum the Hamaker constant is $A_{\mathrm{SS}} \approx 4 \times 10^{-19}$ J [9]. The Hamaker constants $A_{\mathrm{S,L,\sigma G}}$ and $A_{\mathrm{S,L\sigma,G}}$ are both negative, because of $A_{\mathrm{SS}} \succ A_{\mathrm{L\sigma,L\sigma}} \succ A_{\mathrm{LL}}$, $A_{\mathrm{LL}} \succ A_{\mathrm{\sigma G,\sigma G}}$ and $A_{\mathrm{GG}} \approx 0$. The negative sign is in agreement with the usually adopted sign convention according to which attractive forces are negative and repulsive forces positive. As follows then from the definition Eq. (11), dispersion pressures due to attractive forces are positive and those due to repulsive forces negative. The interaction forces between a solid wall and a wetting liquid surpass those between solid wall and gas- or σ-phase. The gas- and σ-phase are kept away from the solid wall through the liquid, an effect which is reflected in negative values of the Hamaker constants $A_{\mathrm{S,L},\sigma\mathrm{G}}$ and $A_{\mathrm{S,L}\sigma,\mathrm{G}}$.

4.2. The Kelvin equation

With Eq. (15) the chemical potential Eq. (8) of a system with dispersion forces can be written

$$\mathrm{d}\mu = -\overline{S}\,\mathrm{d}T + \overline{V}\,\mathrm{d}p - \overline{V}\,\mathrm{d}p_{\mathrm{disp}}. \tag{24}$$

Hence the chemical potential is $\mu = \mu(T, p, p_{\mathrm{disp}})$. Strictly speaking a gravity term $M\vec{g}\,\mathrm{d}\vec{r}$ should also appear in Eq. (24). As we are interested in phase equilibria this term appears, however, in the chemical potential of all phases in equilibrium and therefore cancels. We can leave it out here.

We consider now (Fig. 5) an element $\mathrm{d}\xi$ of a curved liquid film L of thickness $\delta(\xi)$ in phase equilibrium with its vapour G and the σ-phase between liquid and vapour. The temperature at the interfaces and in the σ-phase be $T_{\mathrm{Ph}}(\xi)$, the liquid-side pressure $p_{\mathrm{Ph,L}}$ and the gas-side pressure $p_{\mathrm{Ph,G}}$ Phase equilibrium requires

$$\mu_{\mathrm{L}}(T_{\mathrm{Ph}}, p_{\mathrm{Ph,L}}, \eta = \delta) = \mu_{\mathrm{G}}(T_{\mathrm{Ph}}, p_{\mathrm{Ph,G}}, \eta = \delta + \Delta r\cos\varphi). \tag{25}$$

The condition for phase equilibrium at temperature T_{Ph} of the same substance if it had a plane interface and if dispersion forces were negligible would be

$$\mu_{\mathrm{L}}(T_{\mathrm{Ph}}, p_{\mathrm{sat}}, \eta \to \infty) = \mu_{\mathrm{G}}(T_{\mathrm{Ph}}, p_{\mathrm{sat}}, \eta \to \infty). \tag{26}$$

From that follows $p_{\mathrm{sat}} = p_{\mathrm{sat}}(T_{\mathrm{Ph}})$. From Eqs. (25) and (26) we obtain

$$\begin{aligned}&\mu_{\mathrm{L}}(T_{\mathrm{Ph}}, p_{\mathrm{Ph,L}}, \eta = \delta) - \mu_{\mathrm{L}}(T_{\mathrm{Ph}}, p_{\mathrm{sat}}, \eta \to \infty)\\ &\quad = \mu_{\mathrm{G}}(T_{\mathrm{Ph}}, p_{\mathrm{Ph,G}}, \eta = \delta + \Delta r\cos\varphi)\\ &\qquad - \mu_{\mathrm{G}}(T_{\mathrm{Ph}}, p_{\mathrm{sat}}, \eta \to \infty)\end{aligned}$$

and hence from Eq. (24) for a given interface temperature T_{Ph}:

$$\begin{aligned}&\int_{p_{\mathrm{sat}}}^{p_{\mathrm{Ph,L}}} \overline{V}_{\mathrm{L}}\,\mathrm{d}p - \int_{\eta\to\infty}^{\delta} \overline{V}_{\mathrm{L}}\,\mathrm{d}p_{\mathrm{disp}}\\ &\quad = \int_{p_{\mathrm{sat}}}^{p_{\mathrm{Ph,G}}} \overline{V}_{\mathrm{G}}\,\mathrm{d}p - \int_{\eta\to\infty}^{\delta+\Delta r\cos\varphi} \overline{V}_{\mathrm{G}}\,\mathrm{d}p_{\mathrm{disp}}.\end{aligned}$$

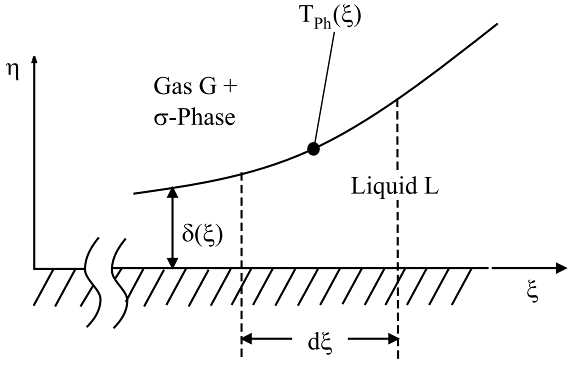

Fig. 5. Local phase equilibrium between liquid L with gas G and σ-phase.

Assuming the liquid and the gas to be incompressible, we obtain

$$\begin{aligned}&\overline{V}_{\mathrm{L}}(p_{\mathrm{Ph,L}} - p_{\mathrm{sat}}) - \overline{V}_{\mathrm{L}}p_{\mathrm{disp,Ph,L}}\\ &\quad = \overline{V}_{\mathrm{G}}(p_{\mathrm{Ph,G}} - p_{\mathrm{sat}}) - \overline{V}_{\mathrm{G}}p_{\mathrm{disp,Ph,G}}.\end{aligned} \tag{27}$$

The pressures $p_{\mathrm{Ph,L}}$ at the liquid interface and $p_{\mathrm{Ph,G}}$ at the vapour interface are connected by Eq. (19), in which the interface pressures $p_{\mathrm{Ph,L}}$ and $p_{\mathrm{Ph,G}}$ now replace the pressures p_{L} and p_{G} of the homogeneous phases. Elimination of $p_{\mathrm{Ph,L}}$ in Eq. (27) and introducing the density ρ instead of the molar volume $\overline{V} = M/\rho$ with molar mass M, we obtain the Kelvin equation for the gas-side pressure

$$p_{\mathrm{Ph,G}} = p_{\mathrm{sat}}(T_{\mathrm{Ph}}) - \frac{\rho_{\mathrm{G}}}{\rho_{\mathrm{L}} - \rho_{\mathrm{G}}}\sigma K + p_{\mathrm{disp,Ph,G}}. \tag{28}$$

Correspondingly, elimination of $p_{\mathrm{Ph,G}}$ in Eq. (27) yields the Kelvin equation for the liquid-side pressure

$$p_{\mathrm{Ph,L}} = p_{\mathrm{sat}}(T_{\mathrm{Ph}}) - \frac{\rho_{\mathrm{L}}}{\rho_{\mathrm{L}} - \rho_{\mathrm{G}}}\sigma K + p_{\mathrm{disp,Ph,L}}. \tag{29}$$

It should be noted that the dispersion pressures $p_{\mathrm{disp,Ph,G}}$ and $p_{\mathrm{disp,Ph,L}}$ on both sides of the σ-interface are negative for a wetting liquid, as stated before.

The Kelvin equations, Eqs. (28) and (29), hold for local equilibrium of any evaporating system independently if it is open or closed. For a spherical bubble (closed system) of constant curvature K in a liquid far-off from the solid wall we obtain the well known relations

$$p_{\mathrm{Ph,G}} = p_{\mathrm{sat}}(T_{\mathrm{Ph}}) - \frac{\rho_{\mathrm{G}}}{\rho_{\mathrm{L}} - \rho_{\mathrm{G}}}\sigma K \tag{30}$$

and

$$p_{\mathrm{Ph,L}} = p_{\mathrm{sat}}(T_{\mathrm{Ph}}) - \frac{\rho_{\mathrm{L}}}{\rho_{\mathrm{L}} - \rho_{\mathrm{G}}}\sigma K. \tag{31}$$

The liquid pressure $p_{\mathrm{Ph,L}}$ and the gas pressure $p_{\mathrm{Ph,G}}$ at the temperature T_{Ph} are lower than the saturation pressure $T_{\mathrm{sat}}(T_{\mathrm{Ph}})$, Fig. 6. For a given saturation temperature T_{sat} the liquid must be superheated by $\Delta T = T_{\mathrm{Ph}} - T_{\mathrm{sat}}$ for vapour bubbles to exist.

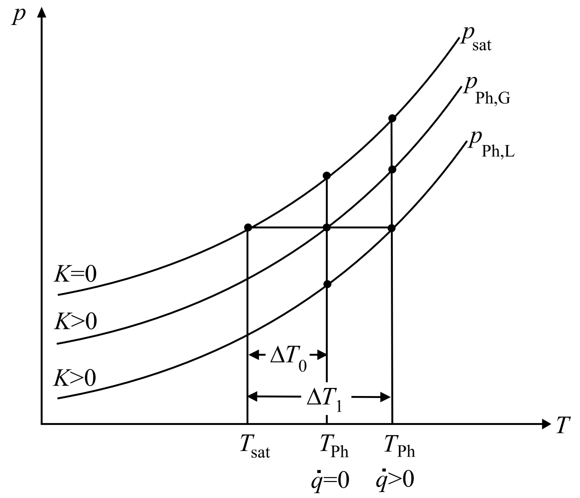

Fig. 6. Liquid and vapour pressure for spherical bubble, curvature K.

5. Gas and liquid pressures apart from the interface

If evaporation occurs, the gas pressure p_G and the liquid pressure p_L apart from the curved interface δ, Fig. 1, differ from the interface pressures $p_{\text{Ph,L}}$ and $p_{\text{Ph,G}}$. In the bulk of the gas, because of the intermolecular forces, the gas pressure p_G is slightly lower than the interfacial pressure $p_{\text{Ph,G}}$, the difference $p_{\text{Ph,G}} - p_G$ being the driving force for evaporation. As follows from the kinetic theory of gases we have (see for example [16]):

$$p_{\text{Ph,G}} - p_G = \dot{q}\,\frac{2-f}{2f}\,\frac{[2\pi R T_{\text{sat}}(p_G)]^{1/2}}{\Delta h_V}, \tag{32}$$

with the heat flux $\dot{q}$, the condensation coefficient f and the enthalpy of evaporation Δh_V. Only for vanishing heat fluxes $\dot{q} = 0$, we have $p_{\text{Ph,G}} = p_G$. In the micro-region, where heat fluxes are very high and of the order 10^7 W/m^2 the pressure difference $p_{\text{Ph,G}} - p_G$ is not negligible as the following example in Section 6.2 shows.

With the aid of the Kelvin equation (28), together with Eq. (24) we also obtain the pressure $p_L(\xi,\eta)$ in the liquid film. Proceeding from the interface $\eta = \delta(\xi)$ where we have $p_{\text{Ph,L}} = p_{\text{Ph,L}}(\xi, \eta = \delta)$ in the direction η and neglecting gravity in the very thin liquid film, we have

$$p_L(\xi,\eta) - p_{\text{Ph,L}} = \int_{\xi,\eta=\delta}^{\xi,\eta} \frac{\partial p_L}{\partial \eta}\,\partial\eta = \int_{\xi,\eta=\delta}^{\xi,\eta} \frac{\partial p_{\text{disp}}}{\partial \eta}\,\partial\eta.$$

With Eq. (11) we find

$$p_L(\xi,\eta) = p_{\text{Ph,L}} + \frac{A_{\text{disp,SL}}}{\eta^3} - \frac{A_{\text{disp,SL}}}{\delta^3}. \tag{33}$$

The difference of the two dispersion pressures describes the pressure increase inside the liquid because of the action of dispersion forces on the liquid column of height $\delta - \eta$. $A_{\text{disp,SL}}$ is the dispersion constant for the solid–liquid interaction upon this liquid column. As follows from the combining rules [9] we have

$$A_{\text{disp,SL}} 6\pi = A_{\text{SL}} = \sqrt{A_{\text{SS}} A_{\text{LL}}},$$

which is positive for the wetting liquids considered here.

Combining Eq. (33) with Eqs. (20) and (29) yields the pressure distribution in the liquid film

$$p_L(\xi,\eta) = p_{\text{sat}}(T_{\text{Ph}}) - \frac{\rho_L}{\rho_L - \rho_G}\sigma K + \frac{A_{\text{disp,Ph,L}}}{\delta^3} + \frac{A_{\text{disp,SL}}}{\eta^3} - \frac{A_{\text{disp,SL}}}{\delta^3}, \tag{34}$$

whereas the dispersion constant $A_{\text{disp,SL}}$ is positive, $A_{\text{disp,Ph,L}}$ is negative as follows from Eq. (21).

6. Application examples

6.1. The spreading of thin liquid films at a vertical wall

As an example for the application of the previous equations we consider a liquid that fully wets and spontaneously spreads on a surface, as shown in Fig. 7. Near the vertical wall a thin film forms above the intrinsic meniscus. The intrinsic meniscus is that part of the meniscus so far away from the solid wall that dispersion between solid and liquid become negligible. We want to determine the film thickness δ as function of liquid height H.

At a given position η inside the liquid film the pressure decreases with height ξ according to

$$p_L(\xi,\eta) - p_L(\xi_0,\eta) = -\rho_L g(\xi - \xi_0). \tag{35}$$

As Fig. 7 shows the wall distance is $\eta = \delta(\xi)$ and hence from Eq. (34) under the assumption that we are in the

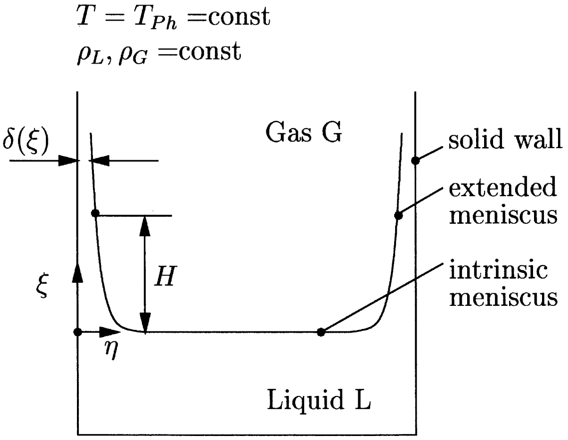

Fig. 7. Wetting liquid in contact with solid wall.

region of the extended meniscus where the curvature is negligible:

$$p_\mathrm{L}(\xi,\eta) = p_\mathrm{L}(\xi,\eta=\delta) = p_\mathrm{sat}(T_\mathrm{Ph}(\xi)) + \frac{A_\mathrm{disp,Ph,L}}{\delta^3}. \qquad (36)$$

As position ξ_0 we choose in Eq. (34) that of the intrinsic meniscus so that the dispersion pressure is negligible, $\delta = \delta(\xi_0) \to \infty$. Then, because of $\eta = \delta(\xi)$ the liquid pressure at position ξ_0 is

$$p_\mathrm{L}(\xi_0,\eta) = p_\mathrm{L}(\xi_0,\eta=\delta) = p_\mathrm{sat}(T_\mathrm{Ph}(\xi_0)) + \frac{A_\mathrm{disp,SL}}{\delta^3}. \qquad (37)$$

Because of $A_\mathrm{disp,Ph,L} \prec 0$ and $A_\mathrm{disp,SL} \succ 0$, under isothermal conditions $T_\mathrm{Ph}(\xi) = T_\mathrm{Ph}(\xi_0)$ the upper pressure $p_\mathrm{L}(\xi,\eta=\delta)$, Eq. (36), is smaller than the bottom pressure $p_\mathrm{L}(\xi_0,\eta=\delta)$, Eq. (37). The pressure difference is balanced out by the hydrostatic pressure of the climbing liquid film. Cooling of the upper part of the liquid film or heating of the bottom part leads to an increase of the pressure difference and thus to thicker liquid films at the same position ξ.

With Eqs. (36) and (37), we find from Eq. (35) under the assumption of isothermal conditions the film thickness δ as function of the liquid height $H = \xi - \xi_0$:

$$\delta = \left(\frac{A_\mathrm{disp,SL} - A_\mathrm{disp,Ph,L}}{\rho_\mathrm{L} g H}\right)^{1/3}. \qquad (38)$$

In all the literature known to the author we find instead $\delta = (A/(\rho_\mathrm{L} g H))^{1/3}$ wherein A in terms of our nomenclature is either taken as $A_\mathrm{disp,SL}$ or as $-A_\mathrm{disp,S,L,G}$.

The dispersion forces support a thin liquid film against gravity above the intrinsic meniscus. For refrigerant R114 we obtain with $A_\mathrm{disp,SL} = 6.78 \times 10^{-21}$ J, $A_\mathrm{disp,Ph,L} = -3.39 \times 10^{-21}$ J, $T_\mathrm{Ph} = 302.63$ K at $p_\mathrm{sat}(T_\mathrm{Ph}) = 0.247$ MPa and $\rho_\mathrm{L} = 1440.8$ kg/m^3 a film thickness of $\delta = 8.96 \times 10^{-9}$ m$^{4/3}$/H$^{1/3}$. At a height of 0.1 m the film thickness is $\delta = 1.98 \times 10^{-8}$ m $= 19.8$ nm, the bottom dispersion pressure is $p_\mathrm{disp,SL} = A_\mathrm{disp,SL}/\delta^3 = 873$ Pa, and the upper dispersion pressure $p_\mathrm{disp,Ph,L} = A_\mathrm{disp,Ph,L}/\delta^3 = -437$ Pa.

As another example we consider the spreading of a thin liquid film of ^{4}Helium along a vertical CaF$_2$-wall. With $A_\mathrm{disp,SL} = 3.39 \times 10^{-22}$ J, $A_\mathrm{disp,Ph,G} = -2.3 \times 10^{-22}$ J for a temperature of 1.38 K we find from Eq. (38) with $\rho_\mathrm{L} = 145$ kg/m^3 a film thickness $\delta = 15.9$ nm at a height of $H = 0.1$ m, and $\delta = 3.4$ nm at $H = 10$ m, slightly different from the value $\delta = 2.8$ nm determined by Sabisky and Anderson [17] from their experiments. At $H = 0.01$ m they obtained $\delta = 21.5$ nm instead of $\delta = 34$ nm from Eq. (38). As pointed out by Israelachvili [9] such a deviation might be due to retardation effects observed for liquid films thicker than 6 nm and neglected in our analysis. As we can see from Eqs. (36) and (37) temperature differences between bottom and upper part of the film in the experiment might also cause deviations.

6.2. Liquid and vapour pressure at the interface of vapour bubbles in nucleate boiling

As a further example we consider a vapour bubble of R114 at a given time t during nucleate boiling on a copper wall. At this time the curvature of the bubble cap shall be $K_\mathrm{cap} = 2 \times 10^4$ m^{-1} corresponding to a cap diameter of 0.2 mm. The outside liquid pressure is assumed to be 0.2470 MPa, corresponding to a saturation temperature of 302.63 K. The wall temperature shall be $\Delta T = 4.96$ K higher, $T_\mathrm{W} = 307.59$ K. For this example pressure and temperature at a liquid–vapour interface had to be determined by solving the balance equations of mass, momentum and energy. Details of the numerical solution are given elsewhere [5]. As a result the liquid pressure and vapour pressure $p_\mathrm{Ph,L}$, $p_\mathrm{Ph,G}$ were obtained using the previous equations.

Fig. 8 shows the variation of these pressures as a function of the radial co-ordinate ξ. As we can see the interface liquid pressure $p_\mathrm{Ph,L}$ decrease from 0.2470 MPa at large values ξ to about 0.1 MPa towards the bubble centre because of the strong change of curvature. The liquid pressure $p_\mathrm{Ph,L}$ undergoes a minimum because the large curvature change in the micro-region first leads to a decrease of the pressure. For small values $\xi - \xi_\mathrm{ad}$ close to the zone where the liquid film is adsorbed and where the curvature approaches zero, see Fig. 1, the dispersion forces cause an enhancement of liquid pressure. Under the assumption of a Gibbs interface, $\Delta r = 0$, it ends up in the adsorbed zone with a value of 0.24721 MPa, slightly above the outside liquid pressure of 0.2470 MPa. The thickness of the adsorbed liquid area was determined to $\delta_\mathrm{ad} = 4.85$ nm. If we assume instead a σ-phase

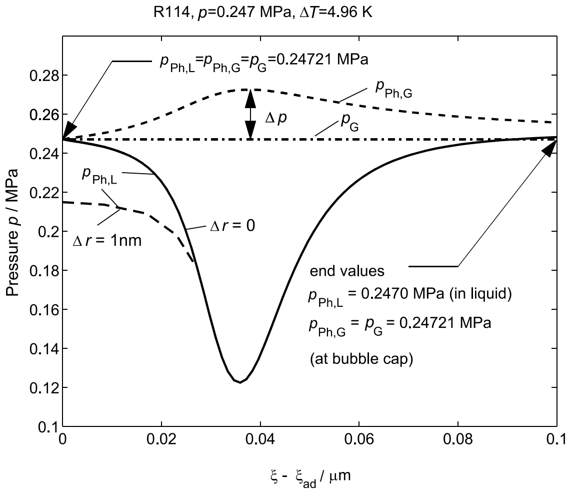

Fig. 8. Liquid and vapour pressure $p_\mathrm{Ph,L}$, $p_\mathrm{Ph,G}$ along the interface.

of thickness $\Delta r = 1$ nm we obtain $\delta_{\mathrm{ad}} = 3.6$ nm, a liquid pressure in the adsorbed zone of $p_{\mathrm{Ph,L}} = 0.2144$ MPa, whereas the gas pressure is as before $p_{\mathrm{Ph,G}} = 0.24721$ MPa. The liquid pressure differs from that obtained under the assumption of a Gibbs interface and clearly indicates that such an assumption leads to erroneous results when liquid films near the solid wall are extremely thin.

The strong curvature of the interface is maintained on the vapour side by a strong increase of pressure as the curve for $p_{\mathrm{Ph,G}}$ in Fig. 8 indicates. It approaches slightly different end values in the adsorption zone and at the bubble cap, where the pressure is a little lower due to the small hydrostatic pressure drop.

Though the liquid pressure $p_{\mathrm{Ph,L}} = p_{\mathrm{L}}(\xi, \eta = \delta)$ decreases with sufficiently small values $\xi - \xi_{\mathrm{ad}}$, liquid is nevertheless flowing from the outside region towards the interface, because $p_{\mathrm{L}}(\xi, \eta)$ at different positions η parallel to the wall decreases towards the bubble centre as shown in Fig. 9. In this figure under the assumption of a Gibbs interface, $\Delta r = 0$, the pressure p_{L} inside the liquid film is plotted for different values η as a function of the radial co-ordinate $\xi - \xi_{\mathrm{ad}}$. Close to the wall at $\eta = \delta_{\mathrm{ad}}$ we observe a steep pressure gradient $\partial p_{\mathrm{L}}/\partial \xi$, whereas farther away, for instance at position $\eta = 3\delta_{\mathrm{ad}}$, the gradient $\partial p_{\mathrm{L}}/\partial \xi$ becomes smaller. At the interface $\eta = \delta$ with pressure $p_{\mathrm{Ph,L}}$, dashed line in Fig. 9, the gradient $\partial p_{\mathrm{L}}/\partial \xi$, as the solid lines in Fig. 9 show, is still positive: Liquid is flowing towards the interface, even in the region where the interface pressure $p_{\mathrm{Ph,L}}$ decreases in the radial direction $\xi - \xi_{\mathrm{ad}}$. This becomes clearly visible in the upper part of Fig. 9 showing the velocity field inside the liquid film.

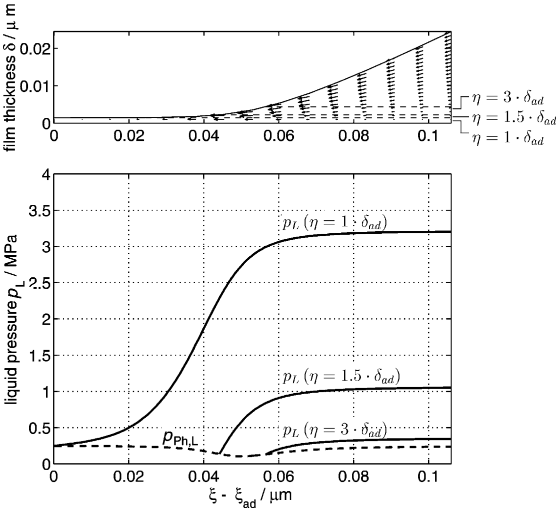

Fig. 9. Liquid pressure and flow pattern within the thin liquid film.

7. Concluding remarks

As shown before dispersion forces are of high importance in nucleate boiling heat transfer processes. They are long range interaction forces between the solid wall and the liquid film, and lower the pressure at the vapour liquid interface. The chemical potential of the liquid phase, decisive for phase equilibria is therefore different from that of a system where dispersion forces are negligible; it contains an additional term for the dispersion forces. The Kelvin-equation derived from the condition of equal chemical potentials for liquid and vapour delivers the pressures at the liquid–vapour interface. They depend on interface temperature T_{ph} curvature of the interface and the dispersion pressure. For a given interface temperature T_{ph} both pressures are lower than the saturation pressure $p_{\mathrm{sat}}(T_{\mathrm{Ph}})$ of a flat surface, free of dispersion forces, the reduction of the liquid pressure being much higher than that of the vapour pressure because of the higher liquid density. As a numerical example shows, the reduction of the liquid pressure at the interface can be of the order of half the saturation pressure $p_{\mathrm{sat}}(T_{\mathrm{Ph}})$. In contrast to this, the vapour pressure at the interface increases, but less than the liquid pressures decreases. The vapour pressure undergoes a maximum, because two effects overlap: The interface temperature T_{Ph} increases towards the bubble centre, thus causing an increase of vapour pressure, whereas the capillary and dispersion forces lead to a reduction of the vapour pressure.

A generalisation of these results for liquid and vapour interface pressure including dispersion forces with the aid of correlations seems at least at present impossible because of the many parameters involved.

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