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## The equilibria of vapour–liquid systems revisited

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## Abstract

We study equilibrium conditions of liquid–vapour phase transitions for a single substance at constant temperature. The phase transitions are modelled by a classical sharp interface model with boundary contact energy.

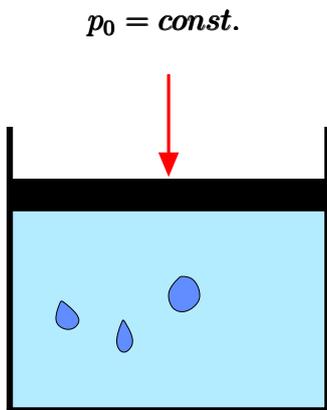
We revisit this old problem mainly for the following reasons. Equilibria in a two-phase system can be established either under fixed external pressure or under fixed total volume. These two different settings lead to distinct equilibria, a fact that is usually ignored in the literature. In nature and in most technical processes, the approach of a two-phase system to equilibrium runs at constant pressure, whereas mathematicians prefer to study processes in constant domains, i.e. at constant volume. Furthermore, in the literature the sharp interface of the liquid and the vapour phase is usually described by a surface with high symmetry like a plane interface or a radially symmetric interface which has the shape of the boundary of a ball.

In this paper we establish equilibrium conditions for pressure control as well as for volume control with arbitrary shapes of the interface. The results are derived by methods of differential geometry. Further, the common features and differences of pressure and volume control are worked out for some simple cases.

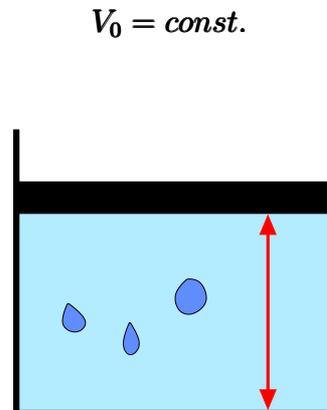
## 1 Introduction and setting of the problem

We study the equilibria of liquid–vapour phase transitions for a single substance. We suppose that the two-phase system is contained in a vessel at constant temperature  $T$  and that the total mass of the system is conserved. The phase transitions are described by the classical sharp interface model with boundary contact energy.

The aim of this work is to characterize the equilibrium conditions for the following two configurations, see Figures 1 and 2:



*Figure 1: Pressure control*



*Figure 2: Volume control*

- (i) The external pressure  $p_0$  is prescribed so that the indicated piston can move during the phase transitions.
- (ii) The piston is fixed so that the total volume  $V_0$  of the system is constant.

Equilibria in a two-phase system can be established either under fixed external pressure or under fixed total volume. These different settings lead to different equilibria, a fact that is usually ignored in the literature. In nature and in most technical processes, the approach of a two-phase system to equilibrium run at constant pressure. Examples are nucleation and evolution of liquid droplets in a cloud, or the settings in a cloud chamber, which are used to study homogeneous nucleation. On the other hand, mathematicians prefer to study processes in constant domains, i.e. at constant volume. Furthermore, the sharp interface of the liquid and the vapour phase is usually described either by a plane interface or by a radially symmetric interface which has the shape of the boundary of a ball. These two cases, however, are not appropriate to study phenomena where the interface of the two phases meets the piston or the fixed walls of the chambers in Figures 1 and 2.

The main focus of our work is to establish equilibrium conditions for *both* kind of settings with *arbitrary* shapes of the interface up to some technical assumptions. Our results are deduced by means of differential geometry. It will turn out that the necessary condition for phase equilibrium agrees for both cases, i.e. the continuity of the specific Gibbs free energies at the interface. Furthermore there results for both cases the same conditions for mechanical equilibrium across the interface, viz. the pressures in  $\Omega_L$ ,  $\Omega_V$  are related by the Young-Laplace law to the mean curvature of the interface. However, the contact angles only agree at the tight boundary of the vessel. Differences occur at the movable piston. For pressure control we receive that either the liquid phase or the vapour phase has contact with the piston whereas for volume control both phases may exist at the piston.

From the necessary conditions for equilibria we read off those points, where the available free energy has extrema. A determination of the nature of the extrema, i.e. whether they correspond to minima or to maxima leads to enormous differences for the cases of fixed pressure and fixed volume. For instance a droplet, i.e. a radially symmetric ball with liquid inside, cannot reach stable equilibrium in vapour at fixed pressure. This stands in contrast to the case of volume control. Here, it becomes possible to stabilize a droplet in equilibrium. The behaviour of a bubble, i.e. a radially symmetric ball with vapour, enclosed in the liquid phase is qualitatively the same. There is no stable bubble of finite size in a process where equilibrium has been reached at fixed pressure.

We like to mention that the described phenomena only regard the behaviour of a single substance. In a mixture of several different constituents, droplets or bubbles may also co-exist in equilibrium with the surrounding at fixed pressure. The most prominent example is fog, which represents water droplets in air. The main constituents of air are gaseous water, oxygen and nitrogen, and the two latter constituents may stabilize the droplets, see [Mue85].

Our work generalizes the classical equilibrium conditions in nucleation theory, see [Mue85],

as well as various equilibrium results with boundary contact energy concerning the sharp interface model, cf. [Fin86] and [LL97]. Analogous equilibrium considerations for the case that the sharp interface model is substituted by the corresponding phase field model, viz. the van der Waals–Cahn–Hilliard phase model, can be found in [DK].

The paper is organized as follows. In Section 2 and Section 3 we introduce some basics of thermodynamics and simple constitutive laws that describe the behaviour of vapour and liquid. Our main results are established in Section 4. We prove necessary equilibrium conditions for the two–phase system with arbitrary sharp interfaces. In Section 5 we study in detail the special case of ‘a droplet in vapour’. To this end we reduce the available free energy as a function of a single variable, so that it becomes an easy matter to illustrate the qualitative and quantitative behaviour of equilibria. Finally we have added an appendix in which we provide the necessary ingredients of differential geometry.

## 2 Global versions of the balance equations for energy and entropy

We consider the pressure and volume controlled systems of Figures 1 and 2. The interior  $\Omega$  of the vessel is divided into a vapour phase  $\Omega_V$  and a liquid phase  $\Omega_L$ . The two phases may be arbitrary up to the condition  $\Omega = \Omega_V \cup \Omega_L$ . Further we assume that the total mass is conserved and that the temperature  $T_0$  on the boundary  $\partial\Omega$  of the vessel is constant. Later on we will make the assumption that the temperature within the vessel is also constant and equal to  $T_0$ .

The global balance laws of total energy  $E$  and entropy  $S$  applied to the systems read

$$\frac{dE}{dt} = \dot{Q} + \oint_{\partial\Omega} \sigma^{ij} v^j da^i \quad \text{and} \quad \frac{dS}{dt} \geq \frac{\dot{Q}}{T_0}. \quad (1)$$

Equation (1)<sub>1</sub> represents the first law of thermodynamics. The quantity  $\dot{Q}$  denotes the heat power, that may flow in or out, and the surface integral gives the mechanical power due to stresses  $\sigma$  acting on the boundary of the vessel,  $\partial\Omega$ , which moves with the velocity  $v$ . Relation (1)<sub>2</sub> expresses Clausius version of the second law of thermodynamics. The growth of entropy is greater than the ratio of supplied heat and temperature in non–equilibrium whereas equality holds in equilibrium.

To determine the mechanical power we have to distinguish the cases pressure and volume control. If we prescribe the external pressure  $p_0$  then the total volume  $V$  of the vessel may change with time and can be calculated. On the other hand, if we fix the piston so that a time–independent total volume  $V_0$  is established, the external pressure may change with time and can be calculated. We have

$$\oint_{\partial\Omega} \sigma^{ij} v^j da^i = \begin{cases} -p_0 \frac{dV}{dt} & \text{fixed pressure.} \\ 0 & \text{fixed volume.} \end{cases} \quad \text{for}$$

Elimination of the heat power in (1)<sub>2</sub> by means of (1)<sub>1</sub> leads to the thermodynamic inequality

$$\frac{d\mathcal{A}}{dt} \leq 0 \quad \text{with} \quad \mathcal{A} := \begin{cases} E - T_0S + p_0V & \text{pressure control,} \\ E - T_0S & \text{volume control,} \end{cases} \quad (2)$$

where the quantity  $\mathcal{A}$  is called the *available free energy* or *availability*.

Recall, that the total energy  $E$  is given by the sum of internal energy  $U$  and the kinetic energy  $K$ , i.e.  $E=U+K$ . Consequently, if the temperature  $T$  in  $\Omega$  is constant with  $T = T_0$ , there appears the combination  $U - T_0S$  in (2), which represents the total free energy  $\Psi$  of the system. Thus we may express  $\mathcal{A}$  by

$$\mathcal{A} = \begin{cases} \Psi + p_0V & \text{pressure control.} \\ \Psi & \text{volume control.} \end{cases} \quad (3)$$

From (2) we conclude that for arbitrary thermodynamic processes in  $\Omega$  that run at constant outer temperature and constant total mass and which are either pressure or volume controlled, the corresponding availabilities must always decrease and assume their minimum in thermodynamic equilibrium.

## 3 Constitutive laws for vapour and liquid

### 3.1 General constitutive laws

The constitutive laws relate the temperature  $T$  and the mass density  $\rho$  to the pressure  $p$ , the specific internal energy  $u$  and the specific entropy  $s$ . We suppose the following dependence

$$p = \hat{p}(T, \rho), \quad u = \hat{u}(T, \rho), \quad s = \hat{s}(T, \rho). \quad (4)$$

These equations are not independent of each other, because of the Gibbs equation

$$Tds = du + p d\frac{1}{\rho}, \quad (5)$$

which allows us to establish equivalent forms for the specific free energy

$$\psi = u - Ts$$

and for the specific Gibbs free energy

$$g = \psi + \frac{p}{\rho}. \quad (6)$$

We obtain

$$d\psi = -sdT - pd\frac{1}{\rho} \quad \text{and} \quad dg = -sdT + \frac{1}{\rho}dp. \quad (7)$$

Moreover,

$$d(\rho\psi) = -\rho s dT + g d\rho. \quad (8)$$

These differential forms and the resulting integrability conditions simplify the exploitation of inequality (2). In particular, we receive for the Gibbs free energy and the pressure the formulas

$$g = \frac{\partial(\psi(T, \rho)\rho)}{\partial\rho} \quad \text{and} \quad p = \rho^2 \frac{\partial\psi(T, \rho)}{\partial\rho}. \quad (9)$$

### 3.2 Special constitutive laws

We describe the vapour phase as an ideal gas and the liquid phase as a compressible isotropic body. The pressure of the vapour  $p_V$  and of the liquid  $p_L$  are related to the corresponding mass densities  $\rho_V$ ,  $\rho_L$  and the temperature  $T$  by

$$p_V = \frac{kT}{m}\rho_V \quad \text{and} \quad p_L = p_L^R(T) + K_L(T)\left(\frac{\rho_L}{\rho_L^R(T)} - 1\right). \quad (10)$$

Here,  $k$  denotes the Boltzmann constant,  $m$  is the atomic mass,  $K_L$  is the compressibility of the liquid and  $p_L^R$  as well as  $\rho_L^R$  are reference values of the pressure and the density of liquid which will be chosen appropriately later on. It is also useful to introduce the corresponding reference values in the vapour phase, i.e.  $p_V^R(T) = kT/m\rho_V^R(T)$ .

In the following we will consider our systems at constant temperature  $T = T_0$ . Integration of (7) and (8) gives

(i) for the vapour phase:

$$(a) \quad \psi_V = \psi_V^R + \frac{p_V^R}{\rho_V^R} \log\left(\frac{\rho_V}{\rho_V^R}\right) \quad (11)$$

$$(b) \quad g_V = g_V^R + \frac{p_V^R}{\rho_V^R} \log\left(\frac{\rho_V}{\rho_V^R}\right) \quad \text{or equivalently,} \quad (12)$$

$$g_V = g_V^R + \frac{p_V^R}{\rho_V^R} \log\left(\frac{p_V}{p_V^R}\right) \quad (13)$$

$$(c) \quad \rho_V\psi_V = \rho_V^R\psi_V^R + g_V^R(\rho_V - \rho_V^R) + \frac{p_V^R}{\rho_V^R}\left(\rho_V \log\left(\frac{\rho_V}{\rho_V^R}\right) - \rho_V + \rho_V^R\right) \quad (14)$$

(ii) for the liquid phase:

$$(a) \quad \psi_L = \psi_L^R - \frac{K_L - p_L^R}{\rho_L^R} + \frac{K_L - p_L^R}{\rho_L} + \frac{K_L}{\rho_L^R} \log\left(\frac{\rho_L}{\rho_L^R}\right) \quad (15)$$

$$(b) \quad g_L = g_L^R + \frac{K_L}{\rho_L^R} \log\left(\frac{\rho_L}{\rho_L^R}\right) \quad \text{or equivalently,} \quad (16)$$

$$g_L = g_L^R + \frac{K_L}{\rho_L^R} \log\left(1 + \frac{p_L - p_L^R}{K_L}\right) \quad (17)$$

$$(c) \quad \rho_L \psi_L = \rho_L^R \psi_L^R + g_L^R (\rho_L - \rho_L^R) + \frac{K_L}{\rho_L^R} \left( \rho_L \log\left(\frac{\rho_L}{\rho_L^R}\right) - \rho_L + \rho_L^R \right) \quad (18)$$

In the literature the liquid phase is often considered as an incompressible body, which is described by the limit  $K_L \rightarrow \infty$ . In this case we obtain from (17) for the specific Gibbs energy

$$g_L = g_L^R + \frac{p_L - p_L^R}{\rho_L^R}. \quad (19)$$

However, the incompressible limit is only appropriate for the system under fixed external pressure, whereas it is not a suitable assumption for a system under fixed total volume because it may lead to large errors in that case.

## 4 The two-phase system with sharp interfaces

### 4.1 The sharp interface model

In the sharp interface model the available free energy

$$\mathcal{A} = \Psi + \begin{cases} p_0 V & \text{pressure control,} \\ 0 & \text{volume control,} \end{cases} \quad (20)$$

consists of the total free energy and a power term in the case of pressure control. The total free energy is described by three additive parts, viz.

$$\Psi = \Psi_L + \Psi_V + \Psi_I.$$

The bulk free energies of liquid and vapour are represented by the integral forms

$$\Psi_L = \int_{\Omega_L} \rho_L \psi_L(\rho_L) dx \quad \text{and} \quad \Psi_V = \int_{\Omega_V} \rho_V \psi_V(\rho_V) dx,$$

where we have dropped the dependence of the specific free energy on  $T$ , since we consider processes at constant temperature. We assume that  $\Omega_L \subseteq \Omega$  and  $\Omega_V \subseteq \Omega$  are domains

in  $\mathbb{R}^3$  with  $\bar{\Omega} = \bar{\Omega}_L \cup \bar{\Omega}_V$  and  $\Omega_L \cap \Omega_V = \emptyset$  such that  $\Omega$  is a Lipschitz domain. Here,  $\bar{G}$  means the closure of a set  $G$ . The densities  $\rho_L : \bar{\Omega}_L \rightarrow \mathbb{R}_+$  and  $\rho_V : \bar{\Omega}_V \rightarrow \mathbb{R}_+$  shall be continuous differentiable functions. In particular,  $\rho_L$  and  $\rho_V$  may be regarded as restrictions of  $C^1$ -functions with compact support in  $\mathbb{R}^3$ .

The interfacial free energy  $\Psi_I$  is subdivided into three parts

$$\Psi_I = \Psi_{I_{LV}} + \Psi_{I_{LW}} + \Psi_{I_{VW}}.$$

$\Psi_{I_{LV}}$ ,  $\Psi_{I_{VW}}$  and  $\Psi_{I_{LW}}$  are the interfacial energy of liquid–vapour, vapour–wall and liquid–wall, respectively. The interface  $I_{LV}$  is modeled by a finite union of orientable  $C^2$ -hypersurfaces with locally finite perimeter<sup>1</sup>. Further, we suppose that  $I_{LW} = \text{Int}(\partial\Omega \cap \partial\Omega_L)$  and  $I_{VW} = \text{Int}(\partial\Omega \cap \partial\Omega_V)$  can likewise be represented by a finite union of orientable  $C^2$ -hypersurfaces with locally finite perimeter. The symbol  $\text{Int}S$  stands for the interior of a hyperset  $S$ . Each interfacial energy is assumed to be proportional to the surface measure of the interface and the corresponding positive proportionality factor is called the surface tension. There results

$$\Psi_I = \Psi_{I_{LV}} + \Psi_{I_{LW}} + \Psi_{I_{VW}} = \sigma_{LV} \int_{I_{LV}} d\mathcal{H}^2 + \sigma_{LW} \int_{I_{LW}} d\mathcal{H}^2 + \sigma_{VW} \int_{I_{VW}} d\mathcal{H}^2,$$

where  $\mathcal{H}^n$  denotes the  $n$ -dimensional Hausdorff measure.

## 4.2 Necessary conditions for equilibrium

We derive the equilibria conditions by means of calculus of variations. The available free energy  $\mathcal{A}$  has the integral form

$$\begin{aligned} \mathcal{A} = & \int_{\Omega_L} \rho_L(x) \psi_L(\rho_L(x)) dx + \int_{\Omega_V} \rho_V(x) \psi_V(\rho_V(x)) dx + \sigma_{LV} \int_{I_{LV}} d\mathcal{H}^2 \\ & + \sigma_{LW} \int_{I_{LW}} d\mathcal{H}^2 + \sigma_{VW} \int_{I_{VW}} d\mathcal{H}^2 + \begin{cases} p_0 \int_{\Omega} dx & \text{pressure control.} \\ 0 & \text{for} \\ & \text{volume control.} \end{cases} \end{aligned}$$

Now we vary over the domains  $\Omega_L$ ,  $\Omega_V$  and the interface  $I_{LV}$ . We assume that  $\Omega = \Omega_L \cup \Omega_V \cup I_{LV}$  (coordinates denoted by  $x$ ) depends on a parameter  $t$ , which is mapped from the original domain  $\hat{\Omega} = \hat{\Omega}_V \cup \hat{\Omega}_L \cup \hat{I}_{LV}$  (coordinates denoted by  $\hat{x}$ ) by a  $C^1$ -diffeomorphism

$$x = T(\hat{x}, t) \quad \text{with} \quad \hat{x} = T(\hat{x}, 0).$$

We suppose that this transformation satisfies the prescribed assumptions of Section 4.1, i.e. the conditions on the domains  $\Omega_L$  and  $\Omega_V$ , the interfaces  $I_{LV}$ ,  $I_{LW}$  and  $I_{VW}$  and their

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<sup>1</sup>An open set with Lipschitz boundary has for instance locally finite perimeter, see [EL92] for more details.

corresponding boundaries.

Observe, that in the case of pressure control the domain  $\Omega$  may vary along the direction of the piston, whereas for volume control  $\Omega$  is mapped onto itself.

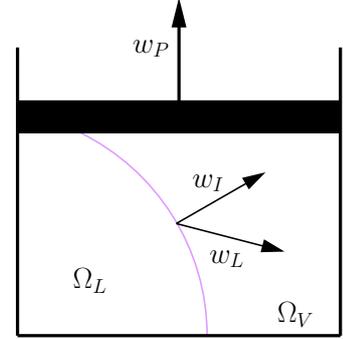
In both cases the mass densities fulfill the local balance of mass:

$$\frac{\partial \rho_L}{\partial t} + \operatorname{div}(\rho_L v_L) = 0, \quad (21)$$

$$\frac{\partial \rho_V}{\partial t} + \operatorname{div}(\rho_V v_V) = 0, \quad (22)$$

where  $v_L : \bar{\Omega}_L \rightarrow \mathbb{R}^3$  and  $v_V : \bar{\Omega}_V \rightarrow \mathbb{R}^3$  are the velocities of liquid and vapour, respectively. In order to determine the equilibrium conditions of the two systems we still have to introduce some notations, cf. Fig. 3:

- $\partial\Omega_L$ : boundary of liquid
- $\partial\Omega_V$ : boundary of vapour
- $I_P$ : surface of the piston
- $\nu$ : measure theoretic unit outer normal on  $\partial\Omega$
- $\nu_L$ : measure theoretic unit outer normal on  $\partial\Omega_L$
- $\nu_V$ : measure theoretic unit outer normal on  $\partial\Omega_V$
- $\nu_I$ : continuous measure theoretic unit normal field on  $I_{LV}$ , where we assume without loss of generality that  $\nu_I = \nu_L$  on  $I_{LV}$ .
- $w_P$ : velocity of the piston  $I_P$ ,  $w_P = \frac{\partial x}{\partial t}$  on  $I_P$ .
- $w_I$ : velocity of the interface  $I_{LV}$ ,  $w_I = \frac{\partial x}{\partial t}$  on  $I_{LV}$ .
- $w_L$ : velocity of  $\partial\Omega_L$ ,  $w_L = \frac{\partial x}{\partial t}$  on  $\partial\Omega_L$ .



**Figure 3:** Two-phase system

We also abbreviate

$$I_{LW_P} := I_P \cap \partial\Omega_L, \quad I_{VW_P} := I_P \cap \partial\Omega_V$$

as well as

$$v_{L,\nu} := v_L \cdot \nu_L, \quad v_{V,\nu} := v_V \cdot \nu_V, \quad w_{I,\nu} := w_I \cdot \nu_I, \quad w_{P,\nu} := w_P \cdot \nu, \quad w_{L,\nu} := w_L \cdot \nu_L.$$

The necessary equilibrium conditions are achieved by evaluating the total time derivative of  $\mathcal{A}$  and setting it to zero. To this end we consider the cases volume and pressure control separately.

### Pressure control:

The available free energy (20) takes on the form

$$\begin{aligned} \mathcal{A}(t) = & \int_{\Omega_L(t)} \rho_L(x, t) \psi_L(\rho_L(x, t)) dx + \int_{\Omega_V(t)} \rho_V(x, t) \psi_V(\rho_V(x, t)) dx \\ & + \sigma_{LV} \int_{I_{LV}(t)} d\mathcal{H}^2 + \sigma_{LW} \int_{I_{LW}(t)} d\mathcal{H}^2 + \sigma_{VW} \int_{I_{VW}(t)} d\mathcal{H}^2 + p_0 \left( \int_{\Omega_L(t)} dx + \int_{\Omega_V(t)} dx \right). \end{aligned} \quad (23)$$

Now, we compute for each term of (23) the time derivative. Due to (6), (9) and Reynold's transport we derive

$$\begin{aligned}
\frac{d\Psi_L}{dt} &= \int_{\Omega_L} \left( \frac{\partial(\rho_L \psi_L)}{\partial \rho_L} \frac{\partial \rho_L}{\partial t} + \operatorname{div}(\rho_L \psi_L w_L) \right) dx \\
&= \int_{\Omega_L} g_L \frac{\partial \rho_L}{\partial t} dx + \int_{\partial \Omega_L} g_L \rho_L w_{L,\nu} d\mathcal{H}^2 - \int_{\partial \Omega_L} p_L w_{L,\nu} d\mathcal{H}^2 \\
&= \int_{\Omega_L} \left( g_L \frac{\partial \rho_L}{\partial t} + \operatorname{div}(g_L \rho_L v_L) \right) dx + \int_{I_{LV}} g_L \rho_L (w_{I,\nu} - v_{L,\nu}) d\mathcal{H}^2 - \int_{\partial \Omega_L} p_L w_{L,\nu} d\mathcal{H}^2 \\
&\stackrel{(9),(21)}{=} \int_{\Omega_L} \frac{\partial p_L}{\partial x^k} v_L^k dx - \int_{I_{LV}} p_L w_{I,\nu} d\mathcal{H}^2 - \int_{I_{LW_P}} p_L w_{P,\nu} d\mathcal{H}^2 + \int_{I_{LV}} g_L \rho_L (w_{I,\nu} - v_{L,\nu}) d\mathcal{H}^2.
\end{aligned} \tag{24}$$

Similarly as before we compute

$$\frac{d\Psi_V}{dt} = \int_{\Omega_V} \frac{\partial p_V}{\partial x^k} v_V^k dx + \int_{I_{LV}} p_V w_{I,\nu} d\mathcal{H}^2 - \int_{I_{VW_P}} p_V w_{P,\nu} d\mathcal{H}^2 - \int_{I_{LV}} g_V \rho_V (w_{I,\nu} - v_{V,\nu}) d\mathcal{H}^2.$$

To the volume integrals of the latter expression in (23) we also apply Reynold's transport theorem. This gives

$$\frac{d}{dt} \left( \int_{\Omega_L} dx \right) = \int_{I_{LV}} w_{I,\nu} d\mathcal{H}^2 + \int_{I_{LW_P}} w_{P,\nu} d\mathcal{H}^2$$

as well as

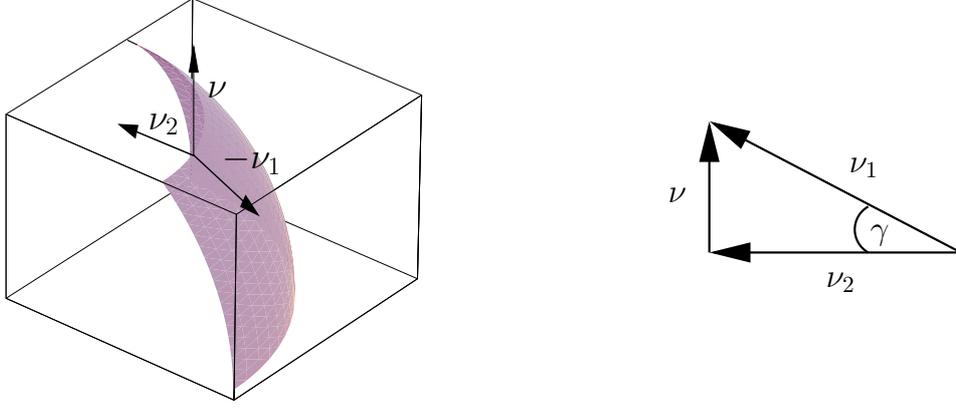
$$\frac{d}{dt} \left( \int_{\Omega_V} dx \right) = - \int_{I_{LV}} w_{I,\nu} d\mathcal{H}^2 + \int_{I_{VW_P}} w_{P,\nu} d\mathcal{H}^2.$$

Finally we compute the total derivatives of the interface integrals in (20). Here, we take advantage from Reynold's transport theorem for surface vectors, which is deduced in the appendix, cf. Theorem 2. We receive

- (i)  $\frac{d}{dt} \int_{I_{LV}} d\mathcal{H}^2 = \int_{\partial^* I_{LV}} w_I \nu_1 \sqrt{g} d\mathcal{H}^1 - \int_{I_{LV}} 2k_{M,I} w_{I,\nu} d\mathcal{H}^2$ , where  $\nu_1$  is the theoretic unit outer normal on  $\partial^* I_{LV}$  in the tangent plane of  $I_{LV}$  and  $k_{M,I}$  is the mean curvature of  $I_{LV}$ .
- (ii)  $\frac{d}{dt} \int_{I_{LW}} d\mathcal{H}^2 = \int_{\partial^* I_{LW}} w_I \nu_2 \sqrt{g} d\mathcal{H}^1 - \int_{I_{LW_P}} 2k_{M,P} w_{P,\nu} d\mathcal{H}^2$ , where  $\nu_2$  is the theoretic unit outer normal on  $\partial^* I_{LW}$  in the tangent plane of  $I_{LW}$  and  $k_{M,P}$  is the mean curvature of  $I_P$ .
- (iii)  $\frac{d}{dt} \int_{I_{VW}} d\mathcal{H}^2 = - \int_{\partial^* I_{VW}} w_I \nu_2 \sqrt{g} d\mathcal{H}^1 - \int_{I_{VW_P}} 2k_{M,P} w_{P,\nu} d\mathcal{H}^2$ .

Observe,

$$\nu_1 = \cos \gamma \nu_2 + \sin \gamma \nu, \quad \gamma : \text{contact angle of } \partial\Omega \text{ and } I_{LV}, \text{ see Fig. 4.}$$



**Figure 4:** Normal and tangential vectors of the interface  $I_{LV}$

We may now summarize the intermediate steps to obtain

$$\begin{aligned} \frac{d\mathcal{A}}{dt} = & \int_{\Omega_L} \frac{\partial p_L}{\partial x^k} v_L^k dx + \int_{\Omega_V} \frac{\partial p_V}{\partial x^k} v_V^k dx + \int_{I_{VW_p}} (p_0 - p_V - 2\sigma_{VW} k_{M,P}) w_{P,\nu} d\mathcal{H}^2 + \\ & \int_{I_{LW_p}} (p_0 - p_L - 2\sigma_{LW} k_{M,P}) w_{P,\nu} d\mathcal{H}^2 + \int_{I_{LV}} (-p_L + p_V - 2\sigma_{LV} k_{M,I}) w_{I,\nu} d\mathcal{H}^2 + \\ & \int_{I_{LV}} (g_L - g_V) \rho_L (w_{I,\nu} - v_{L,\nu}) d\mathcal{H}^2 + (\cos \gamma \sigma_{LV} - \sigma_{LW} + \sigma_{VW}) \int_{\partial^* I_{LV}} w_I \nu_2 \sqrt{g} d\mathcal{H}^1 + \\ & \sin \gamma \sigma_{LV} \int_{\partial^* I_{LV}} w_I \nu \sqrt{g} d\mathcal{H}^1. \end{aligned}$$

Observe, the right hand side of this equation is linear in  $v_L$ ,  $v_V$ ,  $w_P$  and  $w_I$  which may be arbitrarily chosen. In consequence, each integral expression has to vanish. Thus we end up with the following necessary conditions for equilibrium:

*Mechanical conditions:*

- (i)  $p_V = \text{locally const. in } \Omega_V$  and  $p_L = \text{locally const. in } \Omega_L$
- (ii)  $\gamma = 0$  on  $I_P$ , since  $\sin \gamma \int_{\partial^* I_{LV}} w_I \nu \sqrt{g} d\mathcal{H}^1 = 0$  has to be satisfied.  
 $\implies I_P = I_{LW_p}$  or  $I_P = I_{VW_p}$   
 $\implies p_V = p_0 - 2\sigma_{VW} k_{M,P}$  on  $I_p$  or  $p_L = p_0 - 2\sigma_{LW} k_{M,P}$  on  $I_p$
- (iii)  $p_V - p_L = 2\sigma_{LV} k_{M,I}$  on  $I_{LV}$
- (iv)  $\cos \gamma = \frac{\sigma_{LW} - \sigma_{VW}}{\sigma_{LV}}$  on  $\partial^* I_{LV}$

*Phase condition:*

$$g_L = g_V \quad \text{on } I_{LV}$$

**Volume control:**

In the case of fixed total volume we have for the available free energy the representation

$$\begin{aligned} \mathcal{A}(t) = & \int_{\Omega_L(t)} \rho_L(x, t) \psi_L(\rho_L(x, t)) dx + \int_{\Omega_V(t)} \rho_V(x, t) \psi_V(\rho_V(x, t)) dx \\ & + \sigma_{LV} \int_{I_{LV}(t)} d\mathcal{H}^2 + \sigma_{LW} \int_{I_{LW}(t)} d\mathcal{H}^2 + \sigma_{VW} \int_{I_{VW}(t)} d\mathcal{H}^2 \end{aligned} \quad (25)$$

with  $\Omega_L(t) \cup \Omega_V(t) \cup I_{LV}(t) = \Omega = \text{const.}$ . The total derivative of  $\mathcal{A}$  can be computed analogously to the case of pressure control. In fact, the formulas even simplify since we do not have contributions of the surface terms at the piston. We derive

$$\begin{aligned} \frac{d\mathcal{A}}{dt} = & \int_{\Omega_L} \frac{\partial p_L}{\partial x^k} v_L^k dx + \int_{\Omega_V} \frac{\partial p_V}{\partial x^k} v_V^k dx + \int_{I_{LV}} (-p_L + p_V - 2\sigma_{LV} k_{M,I}) w_{I,\nu} d\mathcal{H}^2 + \\ & \int_{I_{LV}} (g_L - g_V) \rho_L (w_{I,\nu} - v_{L,\nu}) d\mathcal{H}^2 + (\cos \gamma \sigma_{LV} - \sigma_{LW} + \sigma_{VW}) \int_{\partial^* I_{LV}} w_I \nu_2 \sqrt{g} d\mathcal{H}^1. \end{aligned} \quad (26)$$

Thus we obtain the following necessary conditions for equilibrium.

*Mechanical conditions:*

- (i)  $p_V = \text{locally const. in } \Omega_V$       and       $p_L = \text{locally const. in } \Omega_L$
- (ii)  $p_V - p_L = 2\sigma_{LV} k_{M,I}$  on  $I_{LV}$
- (iii)  $\cos \gamma = \frac{\sigma_{LW} - \sigma_{VW}}{\sigma_{LV}}$  on  $\partial^* I_{LV}$
- (iv)  $V_0 = V_L + V_V$

*Phase condition:*

$$g_L = g_V \quad \text{on } I_{LV}$$

Let us compare the results of volume control and pressure control. For both cases we obtain the same condition for phase equilibrium, i.e. the continuity of the specific Gibbs free energies at the interface  $I_{LV}$ . The mechanical conditions for the pressures  $p_L$  and  $p_V$  in  $\Omega_L$ ,  $\Omega_V$  and on the interface  $I_{LV}$  also agree for volume control as well as for pressure control. The jump condition for the pressures  $p_L$  and  $p_V$  on  $I_{LV}$  represents the classical Laplace law, where the higher pressure is inside the enclosed phase. The fact that the higher pressure is always inside the enclosed phase can be extracted from the definition of the mean curvature which is linear in the normal field  $\nu_I = \nu_L$ . The formula for the contact angle  $\gamma$  only coincides for volume and pressure control on the fixed boundary of the vessel. Differences occur at the movable piston. For pressure control we conclude

that either the liquid phase or the vapour phase has contact with the piston  $I_P$ . Further we obtain an analogous jump condition for the pressure on  $I_P$  as on the interface  $I_{LV}$ . The corresponding outer condition for volume control states that the total volume  $V_0$  is constant.

### 4.3 Plane interface

The case  $k_{M,I} \equiv 0$  on the liquid-vapour interface characterizes a two-phase system with a plane interface. In this case the necessary conditions for equilibrium imply that not only the specific Gibbs free energies but also the pressures are continuous across the interface:

$$\bar{p} := p_V = p_L \quad \text{and} \quad g_V(T, p_V) = g_L(T, p_L). \quad (27)$$

The pressure  $\bar{p}$  is called the vapour pressure, that may be calculated from (27)<sub>2</sub> as a function of temperature. By means of the constitutive laws (10)<sub>1</sub> and (10)<sub>2</sub> we can then compute the corresponding mass densities  $\bar{\rho}_L(T)$  and  $\bar{\rho}_V(T)$ .

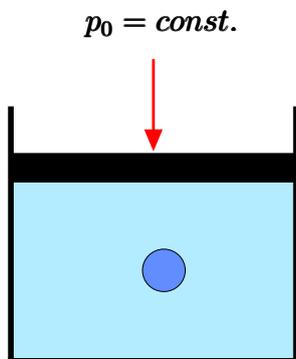
In our further considerations we will use the thermodynamic state determined by (27) as the reference state, i.e. we set in (11)–(19)

$$p_L^R = p_V^R = \bar{p}(T), \quad \rho_L^R = \bar{\rho}_L(T), \quad \rho_V^R = \bar{\rho}_V(T), \quad g_L^R = g_V^R = \bar{g}(T). \quad (28)$$

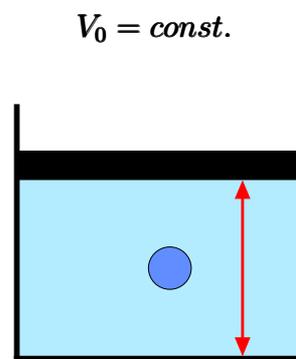
## 5 Droplet–vapour and bubble–liquid systems

### 5.1 Necessary Conditions for equilibrium

In this paragraph we consider equilibrium conditions for the special situation that we have either a single droplet in vapour or a single bubble in liquid at constant temperature  $T = T_0$ , cf. Figures 5 and 6. We assume that droplet and bubble have spherical symmetry.



*Figure 5: Pressure control*



*Figure 6: Volume control*

As a consequence of the results of Section 4 we suppose that the phases are homogeneous in  $\Omega_L$  and  $\Omega_V$ . Then the thermodynamic fields may only change across the interface  $I_{LV}$ . Thus the bulk free energies can be written as *mass*  $\times$  *specific free energy* and the interfacial energy as *surface tension*  $\times$  *surface area of the interface*. In consequence,

$$\Psi = \Psi_L + \Psi_V + \Psi_I = m_L \psi_L \left( T, \frac{m_L}{V_L} \right) + m_V \psi_V \left( T, \frac{m_V}{V_V} \right) + \sigma(T) 4\pi \left( \frac{3}{4\pi} \right)^{2/3} V_L^{2/3}. \quad (29)$$

If we denote by  $\alpha$  the number of atoms in the droplet and in the bubble, respectively, and by  $m$  and  $N_0$  as before the molecular mass and the total number of atoms of the system, we obtain for a single droplet in vapour

$$\Psi = m\alpha \psi_L \left( T, \frac{m\alpha}{V_L} \right) + m(N_0 - \alpha) \psi_V \left( T, \frac{m(N_0 - \alpha)}{V_V} \right) + \sigma(T) 4\pi \left( \frac{3}{4\pi} \right)^{2/3} V_L^{2/3} \quad (30)$$

and for a bubble in liquid

$$\Psi = m(N_0 - \alpha) \psi_L \left( T, \frac{m(N_0 - \alpha)}{V_L} \right) + m\alpha \psi_V \left( T, \frac{m\alpha}{V_V} \right) + \sigma(T) 4\pi \left( \frac{3}{4\pi} \right)^{2/3} V_V^{2/3}. \quad (31)$$

A comparison of (30) and (31) shows that the bubble–liquid system can be treated similarly to the droplet–vapour system. We just have to switch  $V_V$  and  $V_L$ . Therefore we want to restrict the study of equilibrium conditions to the cases

- i) a single droplet in vapour under fixed pressure and
- ii) a single droplet in vapour under fixed volume.

To i) The available free energy  $\mathcal{A}$  in (3) may be written as a function of the three variables  $V_L$ ,  $V_V$  and  $\alpha$ . We have

$$\begin{aligned} \mathcal{A}(V_L, V_V, \alpha) = m\alpha \psi_L \left( T, \frac{m\alpha}{V_L} \right) + m(N_0 - \alpha) \psi_V \left( T, \frac{m(N_0 - \alpha)}{V_V} \right) + \\ \sigma(T) 4\pi \left( \frac{3}{4\pi} \right)^{2/3} V_L^{2/3} + p_0(V_L + V_V). \end{aligned} \quad (32)$$

Next we calculate the first derivatives of  $\mathcal{A}$  with respect to these variables and set the resulting equations equal to zero. There result by means of (6)

$$p_L = p_V + \frac{2\sigma}{r}, \quad p_V = p_0 \quad \text{and} \quad g_L = g_V, \quad (33)$$

where  $r = \left( \frac{3}{4\pi} V_L \right)^{1/3}$ .

To ii) Here, the available free energy  $\mathcal{A}$  may be represented in contrast to the case above as a function of the two variables  $V_L$  and  $\alpha$  since we have the condition  $V_0 = V_L + V_V = \text{const.}$ . Thus we receive for the available free energy

$$\mathcal{A}(V_L, \alpha) = m\alpha \psi_L \left( T, \frac{m\alpha}{V_L} \right) + m(N_0 - \alpha) \psi_V \left( T, \frac{m(N_0 - \alpha)}{V_0 - V_L} \right) + \sigma(T) 4\pi \left( \frac{3}{4\pi} \right)^{2/3} V_L^{2/3} \quad (34)$$

the following conditions at critical points

$$p_L = p_V + \frac{2\sigma}{r} \quad \text{and} \quad g_L = g_V \quad \text{with} \quad V_0 = V_L + V_L, \quad (35)$$

where  $r = \left(\frac{3}{4\pi}V_L\right)^{1/3}$ .

## 5.2 Reduction of $\mathcal{A}$ to a function of a single variable

### Part 1: Derivation

The fact that mechanical equilibrium is much faster approached than phase equilibrium simplifies the exploitation of the necessary conditions for equilibrium and in particular the identification of the nature of the extrema. Taking care of mechanical equilibrium we may reduce the available free energy  $\mathcal{A}$  of (32) and (34) to a function of a single variable.

(i) Fixed pressure:

$$\begin{aligned} \mathcal{A} &\stackrel{(33),(6)}{=} m(N_0 - \alpha)g_V(T, p_0) + m\alpha g_L\left(T, p_0 + \frac{2\sigma(T)}{r}\right) + \sigma(T)\frac{4\pi}{3}r^2. \\ &\stackrel{(13),(17)}{=} mN_0 g_V(T, p_0) + m\alpha \left( \frac{K_L(T)}{\bar{\rho}} \log\left(1 + \frac{p_0 + \frac{2\sigma(T)}{r} - \bar{p}}{K_L(T)}\right) - \frac{kT}{m} \log\left(\frac{p_0}{\bar{p}}\right) \right) \\ &\quad + \sigma(T)\frac{4\pi}{3}r^2 \end{aligned} \quad (36)$$

We observe that  $\mathcal{A}$  becomes a function of the single variable  $r$  if we express  $\alpha$  as a function of  $r$ :

$$\alpha = \frac{1}{m} \frac{4\pi}{3} r^3 \rho_L = \frac{1}{m} \frac{4\pi}{3} \bar{\rho}_L \left( \left(1 + \frac{p_0 - \bar{p}}{K_L}\right) r^3 + \frac{2\sigma(T)}{K_L} r^2 \right). \quad (37)$$

(ii) Fixed volume:

$$\begin{aligned} \mathcal{A} &\stackrel{(35),(6)}{=} m\alpha g_L\left(T, p_V + \frac{2\sigma(T)}{r}\right) + m(N_0 - \alpha)g_V(T, p_V) + \sigma(T)\frac{4\pi}{3}r^2 - p_V V_0 \\ &\stackrel{(13),(17)}{=} mN_0 g_V(T, p_0) + m\alpha \left( \frac{K_L(T)}{\bar{\rho}} \log\left(1 + \frac{p_0 + \frac{2\sigma(T)}{r} - \bar{p}}{K_L(T)}\right) - \frac{kT}{m} \log\left(\frac{p_0}{\bar{p}}\right) \right) \\ &\quad + \sigma(T)\frac{4\pi}{3}r^2 - p_V V_0. \end{aligned} \quad (38)$$

Proceeding as in the case of fixed pressure we write

$$\alpha = \frac{1}{m} \frac{4\pi}{3} r^3 \rho_L = \frac{1}{m} \frac{4\pi}{3} r^3 \bar{\rho}_L \left( 1 + \frac{p_V + \frac{2\sigma}{r} - \bar{p}}{K_L} \right) \quad (39)$$

and observe that  $\alpha$  now depends on  $r$  and  $p_V$ . Therefore we need an additional relation in order to eliminate  $p_V$  which is based on the conservation of mass. We have

$$\begin{aligned} mN_0 &= m(\alpha + (N_0 - \alpha)) \\ &= \frac{4\pi}{3}r^3\rho_L + \left(V_0 - \frac{4\pi}{3}r^3\right)\rho_V \\ &= \frac{4\pi}{3}r^3\bar{\rho}_L \left(1 + \frac{p_V + \frac{2\sigma}{r} - \bar{p}}{K_L}\right) + \left(V_0 - \frac{4\pi}{3}r^3\right)\bar{\rho}_V\frac{p_V}{\bar{p}}. \end{aligned}$$

In consequence, we can express  $p_V$  as a function of  $r$ :

$$p_V = \bar{p} \frac{mN_0 - \frac{4\pi}{3}r^3\frac{\bar{\rho}_L}{K_L(T)}(K_L(T) + \frac{2\sigma(T)}{r} - \bar{p})}{\bar{\rho}_V(V_0 - \frac{4\pi}{3}r^3) + \frac{\bar{p}}{K_L(T)}\bar{\rho}_L\frac{4\pi}{3}r^3} \quad (40)$$

This shows that we can also write  $\mathcal{A}$  as a function of the single variable  $r$  in the volume controlled case.

Note that the assumption of an incompressible liquid, i.e.  $K_L \rightarrow \infty$ , becomes a non-valid approximation if the droplet volume  $\frac{4\pi}{3}r^3$  approaches the total volume  $V_0$  of the system.

## 5.3 Reduction of $\mathcal{A}$ to a function of a single variable

### Part 2: Summary of results in dimensionless quantities

#### 5.3.1 Introduction of dimensionless quantities

Next we write the available free energies of (36) and (38) as a function of dimensionless quantities. Therefore we utilize the following dimensionless notations

$$p \rightarrow \hat{p} = \frac{p}{\bar{p}(T)}, \quad \rho \rightarrow \hat{\rho} = \frac{\rho}{\bar{\rho}_V(T)}, \quad V \rightarrow \hat{V} = \frac{V\bar{\rho}_V(T)}{mN_0}, \quad \mathcal{A} \rightarrow \hat{\mathcal{A}} = \frac{\mathcal{A} - mN_0g_V(T, p_0)}{N_0kT} \quad (41)$$

and  $\hat{K}_L(T) := K_L/\bar{p}(T)$ . Moreover, we define the atomic phase fraction

$$z = \frac{\alpha}{N_0} \in [0, 1] \quad (42)$$

and for systems with fixed total volume  $V_0$  we introduce the volumetric phase fraction

$$\varphi = \frac{V_L}{V_0} \in [0, 1]. \quad (43)$$

For further considerations it is useful to introduce a constant  $c$ , so that we may write

$$\frac{2\sigma}{\bar{p}r} = c\hat{V}^{-1/3} \quad \text{and} \quad \frac{\sigma 4\pi r^2}{3N_0kT} = \frac{1}{2}c\hat{V}^{2/3} \quad \text{with} \quad c = \frac{2\sigma}{\bar{p}} \left(\frac{4\pi}{3} \frac{\bar{\rho}_V}{mN_0}\right)^{1/3}. \quad (44)$$

### 5.3.2 Droplet–vapour system under fixed pressure

We now express the dimensionless available free energy  $\hat{\mathcal{A}}$  as function of the dimensionless droplet volume  $\hat{V}_L$ . For this purpose we represent  $z$  as a function of  $\hat{V}_L$

$$z(\hat{V}_L) = \hat{\rho}_L \left( \left( 1 + \frac{\hat{p}_0 - 1}{\hat{K}_L} \right) \hat{V}_L + \frac{c}{\hat{K}_L} \hat{V}_L^{2/3} \right) \quad (45)$$

and receive

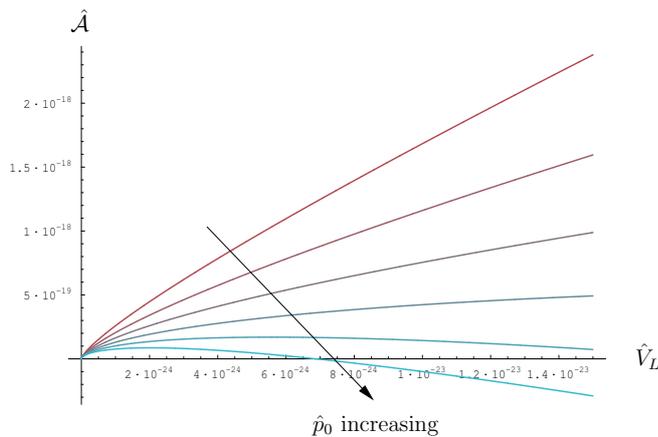
$$\hat{\mathcal{A}}(\hat{V}_L) = z(\hat{V}_L) \left( \frac{\hat{K}_L}{\hat{\rho}_L} \log \left( 1 + \frac{\hat{p}_0 - 1}{\hat{K}_L} + \frac{c}{\hat{K}_L} \hat{V}_L^{-1/3} \right) - \log(\hat{p}_0) \right) + \frac{1}{2} c \hat{V}_L^{2/3}. \quad (46)$$

Let us also consider the limiting case  $\hat{K}_L \rightarrow \infty$ . It treats the liquid as an incompressible body which is for the droplet–vapour configuration under fixed pressure a suitable assumption. Then the available free energy simplifies to

$$\hat{\mathcal{A}}_{\hat{K}_L \rightarrow \infty}(\hat{V}_L) = \hat{\rho}_L \left( \frac{\hat{p}_0 - 1}{\hat{\rho}_L} - \log(\hat{p}_0) \right) \hat{V}_L + \frac{3}{2} c \hat{V}_L^{2/3}. \quad (47)$$

In the literature one usually finds  $\hat{\mathcal{A}}_{\hat{K}_L \rightarrow \infty}$  without the term  $(\hat{p}_0 - 1)/\hat{\rho}_L$ , which is only appropriate if  $\hat{\rho}_L \gg 1$ . If  $\hat{p}_0 > 1$  then the available free energy  $\hat{\mathcal{A}}$  assumes a maximum at  $\hat{V}_L^C \in (0, 1/\hat{\rho}_L)$  between the two end point minima at  $\hat{V}_L = 0$  and  $\hat{V}_L = 1/\hat{\rho}_L$ .

$\hat{V}_L^C$  is the so-called critical volume which gives the location of the nucleation barrier. The interpretation is as follows: A droplet which appears by fluctuation with initial volume  $\hat{V}_L < \hat{V}_L^C$  disappears again, whereas it grows for  $\hat{V}_L > \hat{V}_L^C$  further on. For  $p_0 < 1$ , in contrast, the only minimum is at  $\hat{V}_L = 0$ . This means that only the vapour phase is stable. We infer that a droplet within vapour cannot be stable under fixed external pressure.



**Figure 7:** Available free energy  $\hat{\mathcal{A}}$

Figure 7 illustrates the available free energy  $\hat{\mathcal{A}}$  for the external pressures  $p_{0,i} = i \hat{p}/5$ ,  $i \in \{3, 4, 5, 6, 7, 8\}$ . For the numerical computation we have used the following material data for water:

$m = 2.988997 \cdot 10^{-26} kg$  (molecular mass)

$N_0 = 6.0 \cdot 10^{21}$  (total number of molecules)

$T_0 = 275.15K$  with the corresponding data

$$\bar{p} = 710 \frac{N}{m^2}, \quad \bar{\rho}_V = 0.0056 \frac{kg}{m^3}, \quad \bar{\rho}_L = 1000 \frac{kg}{m^3}, \quad \sigma = 7.5 \cdot 10^{-2} \frac{N}{m}, \quad K_L = 1.98926 \cdot 10^9 \frac{N}{m^2}.$$

### 5.3.3 Droplet–vapour system under fixed volume

In this case we represent the available free energy as a function of the volumetric phase fraction  $\varphi$ .

For reasons of more clarity we express at first the pressure of the vapour phase and the atomic phase fraction by  $\varphi$ . Owing to (39) and (40) we compute

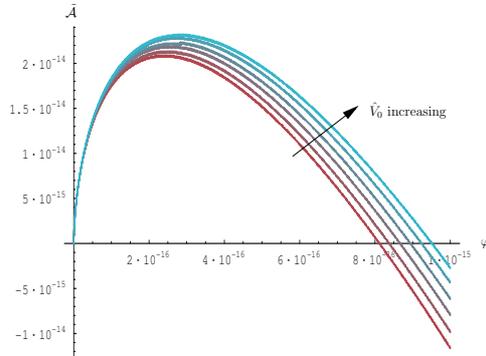
$$\hat{p}_V(\varphi) = \frac{\frac{\hat{K}_L}{\hat{V}_0} - \hat{\rho}_L(\hat{K}_L - 1)\varphi - \hat{\rho}_L c \hat{V}_0^{-1/3} \varphi^{2/3}}{\hat{K}_L(1 - \varphi) + \hat{\rho}_L \varphi} \quad (48)$$

and

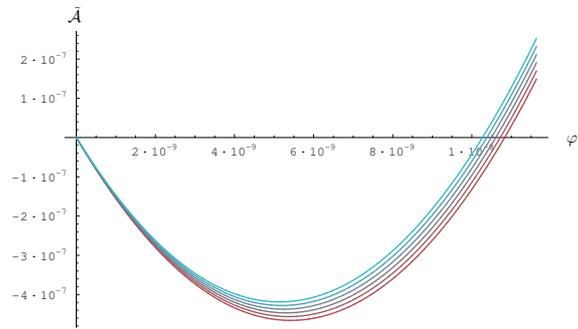
$$z(\varphi) = \hat{V}_0 \hat{\rho}_L \left( \left(1 - \frac{1}{\hat{K}_L}\right) \varphi + \frac{\hat{p}_V(\varphi)}{\hat{K}_L} \varphi + \frac{c}{\hat{K}_L} \hat{V}_0^{-1/3} \varphi^{2/3} \right). \quad (49)$$

Thus  $\hat{\mathcal{A}}$  can be written in the form

$$\hat{\mathcal{A}}(\varphi) = (1 - z(\varphi)) \log(\hat{p}_V(\varphi)) + z(\varphi) \frac{\hat{K}_L}{\hat{\rho}_L} \log \left( 1 + \frac{\hat{p}_V(\varphi) + c \hat{V}_0^{-1/3} \varphi^{-1/3} - 1}{\hat{K}_L} \right) + \frac{c}{2} \hat{V}_0^{2/3} \varphi^{2/3} - \hat{p}_V(\varphi) \hat{V}_0. \quad (50)$$



**Figure 8:** Available free energy  $\hat{\mathcal{A}}$  for small values of  $\varphi$

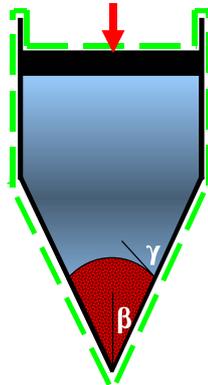


**Figure 9:** Figure 8 on a larger scale

Under fixed volume it becomes now possible to stabilize a droplet. For an appropriate choice of the total volume  $\hat{V}_0$ , the available free energy assumes a local interior maximum and a local interior minimum. For the calculation of the available free energy  $\hat{\mathcal{A}}$  we take the same material data as in the case of pressure control. Since the maximum and the minimum occur on different scales we plot  $\tilde{\mathcal{A}}(\varphi) = \hat{\mathcal{A}}(\varphi) - \hat{\mathcal{A}}(10^{-20})$  in the Figures 8 and 9 for the total volumes  $\hat{V}_{0,i} = (0.999 + i 0.001) m N_0 / \bar{\rho}_V$ ,  $i \in \{3, 4, 5, 6, 7, 8\}$ .

### 5.3.4 Remark on heterogeneous nucleation

Finally we study heterogenous nucleation of a droplet where the contact angle between the liquid and the wall of the pressure vessel comes into play. In this case the simplest setting is a system under fixed volume and we consider the device which is depicted in Figure 10. The droplet is located in the apex with cone angle  $\beta$ , and the contact angle between the droplet and the wall is denoted by  $\gamma$ . We assume as before that mechanical equilibrium is much faster established as phase equilibrium, which reduces the available free energy to a function of a single variable. For simplicity we furthermore assume that the interface between droplet and vapour is a portion of a sphere with radius  $r$ . Relying on the results from Section 4.2 we find that the pressures  $p_V$  and  $p_L$  in vapour and liquid are constant, and that they are related by  $p_L - p_V = 2\sigma/r$ .



*Figure 10: droplet on the wall of the vessel*

Recall that we have three contributions to the interfacial free energy, viz.

$$\Psi_I = \sigma_{LV}\mathcal{O}_{LV} + \sigma_{LW}\mathcal{O}_{LW} + \sigma_{VW}\mathcal{O}_{VW}. \quad (51)$$

We now introduce for the indicated two-phase system the total external surface  $\mathcal{O} = \mathcal{O}_{VW} + \mathcal{O}_{LW}$ . In the case of fixed total volume, also the total external surface is fixed, so that in the following we may ignore the constant term  $\sigma_{VW}\mathcal{O}$ , and after introducing the mechanical equilibrium conditions of volume control, cf. Section 4.2, we obtain with  $\sigma \equiv \sigma_{LV}$

$$\Psi_I = \sigma(\mathcal{O}_{LV} + \cos(\gamma)\mathcal{O}_{LW}). \quad (52)$$

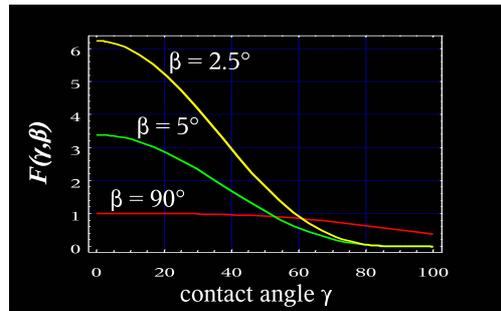
The calculation of the surface term within the bracket and of the volume  $V_L$  of the droplet by means of some trigonometric identities yields

$$\mathcal{O}_{LV} + \cos(\gamma)\mathcal{O}_{LW} = 4\pi r^2 F(\gamma, \beta), \quad V_L = \frac{4\pi}{3} r^3 F(\gamma, \beta), \quad (53)$$

where the common factor is a function of the contact angle and cone angle which reads

$$F(\gamma, \beta) = \frac{1}{2}(1 - \sin(\gamma - \beta)) + \frac{1}{4} \cos(\gamma) \frac{\cos(\gamma - \beta)^2}{\sin(\beta)}. \quad (54)$$

Thus with respect to homogeneous nucleation, the interfacial free energy and the volume of the droplet, which is proportional to the number of droplet particles, is changed by the factor  $F(\gamma, \beta)$ . Its behaviour is illustrated in the following graph that shows  $F$  for three cone angles as a function of the contact angle.



*Figure 11:  $F$  for different cone angles*

We observe that ranges exist where  $F < 1$ , and in these cases the interfacial free energy and the number of droplet particles, which are necessary to form a critical droplet, may be apparently reduced. If we meet these cases heterogeneous nucleation sets in before homogeneous nucleation takes place.

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## 6 Appendix

In this appendix we provide the necessary notations and auxiliary theorems of differential geometry for Section 5. The main objective is to transfer the well-known transport theorem to surface functions in a version which we could not find in the literature.

### 6.1 Gaussian description of surfaces

Let  $D \subset \mathbb{R}^2$  be a domain and let  $x : D \rightarrow \mathbb{R}^3$  be a function represented by

$$x = (x^1, x^2, x^3) = (\hat{x}^1(u^1, u^2), \hat{x}^2(u^1, u^2), \hat{x}^3(u^1, u^2)), \quad (u^1, u^2) \in D.$$

Then the range of  $x$  is called a *surface*  $I$  and  $u = (u^1, u^2)$  are the *Gaussian* surface parameters. A surface  $I$  is said to be a  $C^2$ -surface if  $x$  is twice differentiable and  $x_{u^1} := \left(\frac{\partial x^1}{\partial u^1}, \frac{\partial x^2}{\partial u^1}, \frac{\partial x^3}{\partial u^1}\right)$  and  $x_{u^2} := \left(\frac{\partial x^1}{\partial u^2}, \frac{\partial x^2}{\partial u^2}, \frac{\partial x^3}{\partial u^2}\right)$  fulfill the condition  $x_{u^1} \times x_{u^2} \neq 0$  in  $D$ .

In this study we consider  $C^2$ -surfaces  $I_t$  depending on the parameter  $t$ , which in our case represents the time. We assume that  $I_t : [0, \infty) \times D \rightarrow \mathbb{R}^3$  is a  $C^2$ -surface which is also continuous differentiable in  $t$  and has a parametrization of the form

$$x = \hat{x}(t, u) = (\hat{x}^1(t, u^1, u^2), \hat{x}^2(t, u^1, u^2), \hat{x}^3(t, u^1, u^2)), \quad (t, u^1, u^2) \in [0, \infty) \times D.$$

To each surface point  $x$  we define the tangential vectors, the metric tensor and the unit normal vector, respectively, by

$$\tau_\alpha = \frac{\partial \hat{x}}{\partial u^\alpha}, \quad g_{\alpha\beta} = \tau_\alpha \cdot \tau_\beta, \quad \nu = \frac{\tau_1 \times \tau_2}{\sqrt{g}} = \left( \frac{\varepsilon^{ijk} \tau_1^j \tau_2^k}{\sqrt{g}} \right)_{i=1,2,3}, \quad \alpha, \beta \in \{1, 2\}, \quad (55)$$

where  $g := \det(g_{\alpha\beta})$  and  $\varepsilon^{ijk}$  denotes the Levi-Civita-symbol. Here, we used the Einstein's sum convention.

The spatial derivative of  $\tau_\gamma$ ,  $\gamma \in \{1, 2\}$ , may be decomposed with respect to tangential and normal components, i.e.

$$\frac{\partial \tau_\alpha}{\partial u^\beta} = \Gamma_{\alpha\beta}^\gamma \tau_\gamma + b_{\alpha\beta} \nu \quad \text{with} \quad \Gamma_{\alpha\beta}^\gamma = g^{\gamma\delta} \frac{\partial \tau_\alpha^i}{\partial u^\beta} \tau_\delta^i \quad \text{and} \quad b_{\alpha\beta} = \frac{\partial \tau_\alpha^i}{\partial u^\beta} \nu^i,$$

where  $\Gamma_{\alpha\beta}^\gamma$  and  $b_{\alpha\beta}$  are the Christoffel symbols and the curvature tensor, respectively.

The spatial derivative of the normal vector  $\nu$  can be expressed as follows

$$\frac{\partial \nu}{\partial u^\beta} = -g^{\alpha\gamma} b_{\alpha\beta} \tau_\gamma.$$

Next we define the speed  $w$  of a surface point  $x$  and its decomposition into tangential and normal parts by

$$w = \frac{\partial \hat{x}}{\partial t} = w_\tau^\alpha \tau_\alpha + w_\nu \nu.$$

A simple calculation of the spatial derivative of  $w$  yields

$$\frac{\partial w}{\partial u^\alpha} = (w_{\tau;\alpha}^\beta - w_\nu g^{\beta\gamma} b_{\gamma\alpha}) \tau_\beta + \left( \frac{\partial w_\nu}{\partial u^\alpha} + w_\tau^\beta b_{\beta\alpha} \right) \nu.$$

Here, the semicolon stands for the covariant derivative, e.g.  $w_{\tau;\alpha}^\beta = \frac{\partial w_\tau^\beta}{\partial u^\alpha} + \Gamma_{\gamma\alpha}^\beta w_\tau^\gamma$ . Later on we need the time derivatives of the metric tensor and of the normal vector. Both can be computed in a similar manner. We deduce

$$\frac{\partial g_{\alpha\beta}}{\partial t} = w_{\tau;\alpha}^\gamma g_{\gamma\beta} + w_{\tau;\beta}^\gamma g_{\gamma\alpha} - 4w_\nu k_M g_{\alpha\beta} \quad \text{and} \quad \frac{\partial \nu}{\partial t} = - \left( \frac{\partial w_\nu}{\partial u^\alpha} + w_\tau^\beta b_{\alpha\beta} \right) g^{\alpha\delta} \tau_\delta, \quad (56)$$

where  $k_M = \frac{1}{2} b_{\alpha\beta} g^{\alpha\beta}$  is the mean curvature.

## 6.2 Stokes' theorem and the transport theorem for surface functions

The intention of this section is to evaluate Stokes' theorem and the transport theorem for surface functions, which are vector fields of the type  $\Phi = \varphi^\alpha(u^1, u^2) \tau_\alpha$ .

Our starting point is the generalized version of Stokes' theorem, cf. [EL92] p. 209.

Let  $I \subset \mathbb{R}^2$  be an orientated<sup>2</sup>  $C^2$ -surface with locally finite perimeter. Then

$$\int_I (\nabla \times \zeta)^i \nu^i d\mathcal{H}^2 = \oint_{\partial^* I} \zeta^i \nu^i d\mathcal{H}^1 \quad (57)$$

for all  $\zeta \in C_c^1(\mathbb{R}^2, \mathbb{R}^3)$ , where  $\mathcal{H}^n$  stands for the  $n$ -dimensional Hausdorff measure,  $\partial^* I$  denotes the reduced boundary of  $I$ ,  $l := \nu \times \nu_I$  and  $\nu_I$  is the unique measure theoretic unit outer normal on  $\partial I$ .

After a straightforward calculation we receive for the left hand side of (57)

$$\int_I (\nabla \times \Phi)^i \nu^i d\mathcal{H}^2 = \int_I \varepsilon^{ijk} \nabla_j \Phi^k \frac{1}{\sqrt{g}} \varepsilon^{irs} \tau_1^r \tau_2^s d\mathcal{H}^2 = \int_I \frac{1}{\sqrt{g}} (g_{2\alpha} \varphi_{;1}^\alpha - g_{1\alpha} \varphi_{;2}^\alpha) d\mathcal{H}^2. \quad (58)$$

The antisymmetric matrix

$$\varepsilon^{\alpha\beta} := \varepsilon_{\alpha\beta} := \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad (59)$$

fulfills the relations

$$\varepsilon^{\alpha\beta} = -\varepsilon^{\beta\alpha} \quad \text{and} \quad \varepsilon^{\alpha\gamma} \varepsilon_{\gamma\beta} = -\delta_\beta^\alpha. \quad (60)$$

This allows us to rewrite (58) in the form

$$\int_I (\nabla \times \Phi)^i \nu^i d\mathcal{H}^2 = \int_I \frac{-1}{\sqrt{g}} \varepsilon^{\alpha\beta} g_{\alpha\gamma} \varphi_{;\beta}^\gamma d\mathcal{H}^2 = \int_I \psi_{;\alpha}^\alpha d\mathcal{H}^2, \quad (61)$$

---

<sup>2</sup>A surface  $I$  is called an orientated surface if for  $I$  a continuous unit normal field  $\nu$  exists.

where the newly introduced quantity is defined by

$$\psi^\alpha = \frac{-1}{\sqrt{g}} \varepsilon^{\alpha\beta} g_{\beta\gamma} \varphi^\gamma. \quad (62)$$

Next we express the integrand of the right hand side of (57) by  $\psi^\alpha$ . We obtain

$$\zeta^i l^i = \varphi^\alpha \tau_\alpha^i l^i = -\sqrt{g} g^{\alpha\beta} \varepsilon_{\beta\gamma} \psi^\gamma \tau_\alpha^i l^i = \psi^\gamma e_\gamma \quad \text{with} \quad e_\gamma = -\sqrt{g} \varepsilon_{\delta\gamma} g^{\alpha\delta} \tau_\alpha^i l^i. \quad (63)$$

Using the representation  $l^i = m^\alpha \tau_\alpha^i$  we easily verify

$$l^i (e^\gamma \tau_\gamma^i) = \sqrt{g} \varepsilon_{\alpha\beta} m^\alpha m^\beta = 0. \quad (64)$$

This implies that the unit surface vector  $n = e^\gamma \tau_\gamma / \sqrt{g}$  lies in the tangential plane of  $I$  perpendicular to  $\partial I$ . Moreover,  $n$  points out of the surface  $I$ .

Consequently, by inserting (61) and (63) into Stokes' theorem (57), we obtain for surface vectors the relation

$$\int_I \psi_{;\alpha}^\alpha d\mathcal{H}^2 = \int_{\partial^* I} \psi^\alpha e_\alpha d\mathcal{H}^1. \quad (65)$$

In particular, if we set  $\Psi = \psi^\alpha \tau_\alpha$  we receive

$$\int_I \psi_{;\alpha}^\alpha d\mathcal{H}^2 = \int_{\partial^* I} \Psi^i n^i \sqrt{g} d\mathcal{H}^1. \quad (66)$$

Hence we have proved the following version of Stokes' theorem for surface vectors.

**Theorem 1** *Let  $I \subset \mathbb{R}^2$  be an orientated  $C^2$ -surface with locally finite perimeter. Then*

$$\int_I \psi_{;\alpha}^\alpha d\mathcal{H}^2 = \int_{\partial^* I} \Psi^i n^i \sqrt{g} d\mathcal{H}^1 \quad (67)$$

for all  $\Psi \in C_c^1(\mathbb{R}^2, \mathbb{R}^3)$  of the form  $\Psi|_D = \psi^\alpha(u^1, u^2) \tau_\alpha$ , where the same notations and definitions are used as above.

Next, we would like to state the transport theorem for surface functions.

**Theorem 2** *Let  $I_t : [0, t_f] \times D \rightarrow \mathbb{R}^3$ ,  $0 < t_f < \infty$ , be an evolving  $C^2$ -surface with locally finite perimeter. Then*

$$\frac{d}{dt} \int_{I_t} F(t, u) d\mathcal{H}^2 = \int_{I_t} \left( \frac{\partial F}{\partial t} + (w_{\tau;\alpha}^\alpha - 2k_M w_\nu) F \right) d\mathcal{H}^2 \quad (68)$$

for all  $F \in C_c^1([0, t_f] \times \mathbb{R}^2, \mathbb{R}^3)$  with the representation  $F|_D = f^\alpha(t, u^1, u^2) \tau_\alpha$ .

In particular, for  $F \equiv 1$

$$\frac{d}{dt} \int_{I_t} d\mathcal{H}^2 = \int_{\partial^* I_t} w^i n^i \sqrt{g} d\mathcal{H}^1 - \int_{I_t} 2k_M w_\nu d\mathcal{H}^2. \quad (69)$$

Here, the previous notations and definitions are also taken.

*Sketch of the proof:* We start with the identity

$$\frac{d}{dt} \int_{I_t} F(t, u) d\mathcal{H}^2 = \int_D \left( \frac{\partial(F\sqrt{g})}{\partial t} \right) du^1 du^2$$

and proceed by means of the product rule and the identity

$$\frac{\partial\sqrt{g}}{\partial t} = \frac{1}{2\sqrt{g}} g g^{\alpha\beta} \frac{\partial g_{\alpha\beta}}{\partial t}.$$

For the time-derivative of the metric tensor we insert relation (56) and attain finally formula (68).

If  $F \equiv 1$  we may transform the term with the covariant derivative of (68) by Stokes' theorem for surface vectors. There results

$$\frac{d}{dt} \int_{I_t} d\mathcal{H}^2 = \int_{\partial^* I_t} w^i n^i \sqrt{g} d\mathcal{H}^1 - \int_{I_t} 2k_M w_\nu d\mathcal{H}^2.$$

■

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