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The sharp interface limit of the van der Waals–Cahn–Hilliard phase model for fixed and time dependent domains

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Abstract. We first study the thermodynamic consistency of phase field models which include gradient terms of the density ρ in the free energy function, such as the van der Waals–Cahn–Hilliard model. It is well–known that the entropy inequality admits gradient and higher order gradient terms of ρ in the free energy function only if either the energy flux or the entropy flux is represented by a non-classical form. We identify a non-classical entropy flux, which is not restricted to isothermal processes, so that gradient contributions are possible. In particular, the compatibility of the van der Waals–Cahn–Hilliard model and the Korteweg stress tensor with the newly introduced entropy flux is shown.

Then we investigate the equilibria of liquid–vapour phase transitions of a single substance at constant temperature and relate the sharp interface model of classical thermodynamics to the van der Waals–Cahn–Hilliard phase field model. For two reasons we reconsider this old problem. 1. Equilibria in a two–phase system can be established either under fixed total volume of the system or under fixed external pressure. The latter case implies that the domain of the two–phase system varies. This situation does not seem to be treated in the mathematical literature. However, in nature most processes involving phase transitions run at constant pressure. 2. Thermodynamics provides for a single substance two jump conditions at the sharp interface, viz. the continuity of the specific Gibbs free energies of the adjacent phases and the discontinuity of the corresponding pressures, which is balanced by the mean curvature. From the existing studies on rigorous sharp interface limits one can only extract the first condition for the leading order term. For that reason we prove an asymptotic expansion of the density ρ that yields both conditions up to the first order. The results are based on local energy estimates and uniform convergence results of ρ.

Keywords and phrases: Van der Waals-Cahn-Hilliard theory, phase transitions, two-phase fluid, asymptotic expansion, local energy estimates, mechanical and phase equilibria, Gibbs-Thompson relation, surface tension, curvature, perimeter, minimal area, entropy, thermodynamic consistency.

AMS classification: 82B26, 49Q05, 35R35.

1 Introduction

One aim of this study is to show the thermodynamic consistency of the van der Waals–Cahn–Hilliard phase field theory. It is well–known that the entropy inequality allows the appearance of $\nabla\rho$ and higher order gradient terms of ρ in the free energy function only if either the energy flux or the entropy flux is represented by a non-classical form. The various contributions to the balance of internal energy are in principle directly measurable, whereas the entropy flux is not accessible to direct measurements. For this reason we prefer to preserve the classical form of the energy balance. We introduce a non-classical entropy flux, which is not restricted to isothermal processes, so that gradient contributions in the free energy become possible. Within this setting the van der Waals–Cahn–Hilliard phase model and the Korteweg stress tensor are thermodynamically consistent.

Then we consider the equilibrium behaviour of liquid–vapour phase transitions of a single substance with conserved total mass m. The two–phase system is contained in a vessel with interior Ω, where the regions of the vapour phase Ω_V and the liquid phase Ω_L may be arbitrary up to the conditions $\Omega = \Omega_L \cup \Omega_V \cup I$ and $\Omega_L \cap \Omega_V = \emptyset$, $I := \partial\Omega_L \cap \partial\Omega_V \cap \Omega$. The aim is to establish the equilibrium conditions of the following two systems for which liquid droplets in a gas phase may serve as an example to illustrate the outcome of the experiments.

(i) The total volume V_0 of the device is fixed, see Figure 1.

(ii) The external pressure p_0 is prescribed so that the indicated piston can move during the phase transition, see Figure 2.

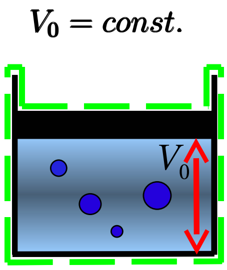

Figure 1: *Volume control*

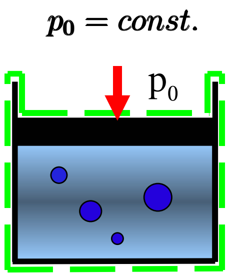

Figure 2: *Pressure control*

In case (i), where the approach to equilibrium runs at constant volume of the vessel, i.e. with fixed piston, it becomes possible to stabilize a droplet of finite radius in equilibrium. This stands in contrast to case (ii). Here, if the external pressure on the piston is fixed, a droplet cannot reach stable equilibrium. More precisely, there exists a critical radius, which is determined by temperature and pressure, so that the droplet vanishes if its initial radius is smaller. If the process starts with a radius larger than the critical point, then the liquid phase remains in equilibrium exclusively.

Liquid–vapour phase transitions are usually described by two different models. The *sharp interface model* treats the free boundary between two adjacent phases by conditions across the boundary explicitly. In this case the interface forms a hypersurface where certain jump conditions have to be satisfied. The *phase field model* avoids discontinuities. The spatial transition between two phases has a thin but finite width. In this region functions change smoothly with respect to spatial variables. The information of the boundary conditions of the sharp interface model are described by partial differential equations. If the regions of the two adjacent phases are large compared to the width of the interface, then the sharp interface model may be regarded as the limit of the phase field model.

Many physical and technical processes, for example the evolution of clouds, usually run at constant pressure but not at constant volume. However, in the mathematical literature phase field models like the Waals–Cahn–Hilliard model are usually studied for time–independent domains. Therefore we revisit liquid–vapour phase transitions of a single substance to include time–dependent domains and to extend the van der Waals–Cahn–Hilliard phase field theory to the following further aspect, that was not recognized up to now.

Within the sharp interface model the equilibria of a simple liquid–vapour system are given by two conditions that must hold across the interface, cf. [DK]. The first condition describes phase equilibrium at the interface and states the continuity of the specific Gibbs free energies of the adjacent phases. The second condition characterizes interfacial mechanical equilibrium. It relates the difference of the pressures between the two phases to the mean curvature of the interface. A careful study of the existing rigorous convergence results of the van der Waals–Cahn–Hilliard phase model to its sharp interface limit has revealed that the phase equilibrium condition can only be extracted for the leading order term of the mass density ρ. Furthermore, the condition for mechanical equilibrium is missing. In this study we achieve both conditions up to the first order for global minimizers. To this end we establish an explicit representation of ρ up to the first order by means of local energy estimates and uniform convergence results for ρ.

The paper is organized as follows. Section 2.1 provides the necessary constituents of thermodynamics. In Section 2.2 we introduce a non–classical entropy flux and show the thermodynamic consistency of the van der Waals–Cahn–Hilliard phase field model and the Korteweg stress tensor. Then we focus on equilibrium conditions for the van der Waals–Cahn–Hilliard phase field model. Section 3 starts with some assumptions and preliminary results of this model. After that we prove an asymptotic expansion of the mass density ρ from which we deduce the equilibrium conditions for global minimizers in the sharp limit of the van der Waals–Cahn–Hilliard phase field model.

2 On the thermodynamic consistency of the van der Waals–Cahn–Hilliard theory

2.1 Basics of thermodynamics

2.1.1 The decrease of the available free energy $\mathcal{A}$

We consider the volume and pressure controlled systems in Figures 1 and 2. We assume that the temperature T_0 on the boundary Ω of the vessel is constant but make no assumptions on the temperature T within the vessel.
The global balance laws of total energy E and entropy S applied to the systems read

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

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 σ acting on the boundary of the vessel, $\partial\Omega$, which moves with the velocity υ. Equality in $(1)_2$ holds in equilibrium.

To determine the mechanical power we have to distinguish the cases pressure and volume control. There results

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

Elimination of the heat power in relation $(1)_2$ by means of $(1)_1$ leads to the thermodynamic inequality

$$\frac{d\mathcal{A}}{dt} \leq 0, \quad \text{where} \quad \mathcal{A} := \begin{cases} E - TS & & \text{fixed volume.} \\ & \text{for} & \\ E - TS + p_0 V & & \text{fixed pressure.} \end{cases} \tag{2}$$

The newly defined quantity $\mathcal{A}$ is called the *available free energy* or *availability*.
We recall that the total energy E is given by the sum of internal energy U and kinetic energy K, viz. $E = K + U$. The combination $U - TS$ denotes the free energy Ψ of the system.
We conclude that for arbitrary thermodynamic processes in Ω, that run at constant outer temperature and constant total mass and are either pressure or volume controlled, the corresponding availabilities must always decrease and assume their minima in thermodynamic equilibrium.

2.1.2 Decomposition of $\mathcal{A}$ for the sharp interface model

In the sharp interface model the interior Ω of the vessel is decomposed into two separate regions Ω_V and Ω_L, occupied by vapour (V) and liquid (L), respectively. Correspondingly, the total volume V of the system is divided into the volumes V_V and V_L. The total free energy however consists of three additive parts, viz. $\Psi = \Psi_V + \Psi_L + \Psi_I$, where the third contribution represents the interfacial free energy. If we neglect the kinetic energy then the available free energy $\mathcal{A}$ in (2) may be written in the form

$$\mathcal{A}(\rho_L, \rho_V, \mathcal{O}, T) = \Psi_V(\rho_V, T) + \Psi_L(\rho_L, T) + \Psi_I(\mathcal{O}, T) \qquad \text{fixed volume,} \tag{3}$$

and

$$\mathcal{A}(\rho_L, \rho_V, \mathcal{O}, V, T) = \Psi_V(\rho_V, T) + \Psi_L(\rho_L, T) + \Psi_I(\mathcal{O}, T) + p_0 V \quad \text{fixed pressure,} \tag{4}$$

where ρ_L and ρ_V are the densities of liquid and vapour. The interfacial free energy Ψ_I is assumed to be proportional to the surface area $\mathcal{O}$ of the interface I and the positive proportionality factor is called surface tension $\sigma(T)$, i.e. $\Psi_I(\mathcal{O}, T) = \sigma(T)\,\mathcal{O}$.

2.1.3 Decomposition of $\mathcal{A}$ for the phase field model

Within the phase field model the spatial distribution of the coexisting liquid and vapour phases are indicated by the field of the mass density ρ. In this case there is a single specific free energy $\hat{\psi}$ and the available free energy reads

$$\mathcal{A}(\rho, T) = \begin{cases} \displaystyle\int_\Omega \rho(x)\hat{\psi}(\rho(x), T)dx & \text{fixed volume.} \\ & \text{for} \\ \displaystyle\int_\Omega \big(\rho(x)\hat{\psi}(\rho(x), T) + p_0\big)dx & \text{fixed pressure.} \end{cases} \tag{5}$$

2.1.4 Constitutive laws within the sharp interface model

The constitutive laws relate the mass density ρ and the temperature T to the pressure p, the specific internal energy u and the specific entropy s.
In the sharp interface model we assume that there are different constitutive laws for liquid and vapour, but they all have the simple general form

$$p_L = \hat{p}_L(\rho_L, T), \quad u_L = \hat{u}_L(\rho_L, T), \quad s_L = \hat{s}_L(\rho_L, T), \tag{6}$$

$$p_V = \hat{p}_V(\rho_V, T), \quad u_V = \hat{u}_V(\rho_V, T), \quad s_V = \hat{s}_V(\rho_V, T). \tag{7}$$

These relations are not independent of each other, because there holds the Gibbs equation

$$Tds = du + pd\frac{1}{\rho}, \tag{8}$$

from which we can deduce equivalent forms for the specific free energy $\psi = u - Ts$ and the specific Gibbs free energy $g = \psi + p/\rho$, viz.

$$d\psi = -sdT - pd\frac{1}{\rho}, \quad dg = -sdT + \frac{1}{\rho}dp, \quad d\rho\psi = -\rho sdT + gd\rho, \tag{9}$$

see for example [Mue85]. These differential forms and the resulting integrability conditions simplify the exploitation of (3) and (4) considerably.

2.1.5 Constitutive laws within the van der Waals–Cahn–Hilliard phase field model

It was van der Waals in the year 1895 who related the interfacial contribution to the free energy to long range interactions of the molecules. He motivated the following form of the free energy density that appears in (5):

$$\rho\hat{\psi} = \rho\psi(\rho, T) + \frac{\varepsilon^2}{2}|\nabla\rho|^2 \tag{10}$$

The quantity ε is a material parameter that may depend on the temperature, and in some limiting case it can be related to the surface tension of the sharp interface model.

In Section 2.2 it will be shown that the local part $\rho\psi(T, \rho)$ of (10) satisfies the Gibbs equation of the sharp interface model. Note that the specific entropy, the specific Gibbs free energy and the pressure that appear in (9) result exclusively from the local contribution of these quantities. In particular, the pressure in (9) is only the local part of the stress tensor σ_K that reads

$$\sigma_K^{ij} = -\frac{\partial(\rho\hat{\psi})}{\partial(\nabla_j\rho)}\frac{\partial\rho}{\partial x^i} + \Big(\rho\hat{\psi} - \rho\frac{\partial(\rho\hat{\psi})}{\partial\rho} + \rho\frac{\partial}{\partial x^k}\frac{\partial(\rho\hat{\psi})}{\partial(\nabla_k\rho)} + \rho\frac{\partial\rho\hat{\psi}}{\partial(\nabla_k\rho)}T\frac{\partial(1/T)}{\partial x^k}\Big)\delta^{ij}.$$

2.2 Introduction of the entropy flux and the thermodynamic consistency of the van der Waals–Cahn–Hilliard phase model

In this section we show the compatibility of the van der Waals–Cahn–Hilliard model and the Korteweg stress tensor with the local version of the the second law of thermodynamics, i.e. to the local entropy inequality. We do not restrict the consistency problem to isothermal processes and we also consider the flow field.

2.2.1 Variables

The basic variables that determine the local thermodynamic state of a fluid are the following fields which depend on time $t \geq 0$ and space $x \in \Omega \subset \mathbb{R}^n$:

$$\rho : \text{ mass density}, \qquad \rho\upsilon : \text{ momentum density}, \qquad \rho u : \text{ internal energy density}, \tag{11}$$

where υ denotes the velocity of the fluid and u is the specific internal energy.
The objective of thermodynamics of a given substance is the modelling of a system of PDEs that describes the evolution of these fields for given initial and boundary data.

2.2.2 Equations of balance

The PDE–system relies on the equations of balance for mass, momentum and internal energy. These read without external sources

$$\begin{aligned}
&\frac{\partial\rho}{\partial t} + \frac{\partial(\rho\upsilon^k)}{\partial x^k} = 0\,,\\
&\frac{\partial(\rho\upsilon^i)}{\partial t} + \frac{\partial(\rho\upsilon^i\upsilon^k - \sigma^{ik})}{\partial x^k} = 0\,,\\
&\frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho u\upsilon^k + q^k)}{\partial x^k} = \sigma^{ik}\frac{\partial\upsilon^i}{\partial x^k},
\end{aligned}\tag{12}$$

where the Einstein's sum convention is used.
This is not a closed system for the variables, because there appear the stress tensor σ^{ik} and the heat flux q^k, which must be related to the variables by constitutive laws.

2.2.3 Constitutive laws

We consider a heat conducting fluid of Navier-Stokes type that is capable to undergo liquid–vapour phase changes. In the isothermal case such a fluid is called Navier-Stokes-Korteweg fluid. We assume that the stress can be additively decomposed according to

$$\sigma^{ik} = \sigma^{ik}_{NS} + \sigma^{ik}_{K}, \tag{13}$$

where σ^{ik}_{NS} denotes the Navier-Stokes stress and σ^{ik}_{K} is called Korteweg stress that takes care for possible phase transitions. The Navier-Stokes stress has the classical form

$$\sigma^{ik}_{NS} = \Big(\lambda + \frac{2}{3}\mu\Big)\frac{\partial \upsilon^j}{\partial x^j}\delta^{ik} + \mu\Big(\frac{\partial \upsilon^i}{\partial x^k} + \frac{\partial \upsilon^k}{\partial x^i} - \frac{2}{3}\frac{\partial \upsilon^j}{\partial x^j}\delta^{ik}\Big). \tag{14}$$

However we allow that the bulk viscosity $\lambda \geq -2/3\mu$ and the shear viscosity $\mu \geq 0$ may depend on ρu, ρ and $\nabla\rho$. The Korteweg stress may be given by a function

$$\sigma^{ik}_{K} = \sigma^{ik}_{K}(\rho u, \nabla\rho u, \rho, \nabla\rho, \nabla\nabla\rho). \tag{15}$$

Later on we will observe that this function can be derived from a scalar potential that depends on ρu, ρ and $\nabla\rho$. Concerning the heat flux we allow a constitutive function that has the general form

$$q^k = q^k(\rho u, \nabla\rho u, \rho, \nabla\rho, \nabla\nabla\rho). \tag{16}$$

It will turn out that this function can be consistently reduced to the simple Fourier law, which states that the heat flux is proportional to the temperature gradient.

2.2.4 Entropy principle

In the following we use the local version of the entropy principle in order to restrict the generality of the constitutive laws. To this end we represent the entropy principle by four axioms:

- There exists an entropy density/entropy flux pair $(\rho s, \varphi^k)$ that satisfies an equation of balance:

  $$\frac{\partial(\rho s)}{\partial t} + \frac{\partial(\rho s \upsilon^k + \varphi^k)}{\partial x^k} = \zeta. \tag{17}$$

  The quantity s is called specific entropy density and ζ is the entropy production.

- The entropy density/entropy flux pair is related to the variables by constitutive laws. We assume that their general form is represented by

  $$\rho s = h(\rho u, \rho, \nabla\rho) \quad \text{and} \quad \varphi^k = \varphi^k(\rho u, \nabla\rho u, \rho, \nabla\rho, \mathrm{div}\upsilon). \tag{18}$$

- Every solution of the field equations that is inserted into (18) and (17) must yield a non-negative entropy production:

  $$\zeta \geq 0, \tag{19}$$

  where equality determines the possible equilibria.

- The absolute temperature T is defined by

$$T = \Big(\frac{\partial h}{\partial \rho u}\Big)^{-1}. \tag{20}$$

Note, that the introduced constitutive model does not rely on Truesdell's principle of equipresence which starts with the same set of dependencies in all constitutive functions. Here we will exclusively establish consistency of the heat conducting Navier-Stokes-Korteweg fluid with the local version of the second law of thermodynamics. The strategy, which is described below, can be extended to the more general case with straightforward but cumbersome involved calculations.

2.2.5 Exploitation of the entropy principle

In order to exploit the entropy principle we write the entropy production in the form

$$\zeta = \frac{\partial(\rho s)}{\partial t} + \upsilon^k \frac{\partial \rho s}{\partial x^k} + \rho s \frac{\partial \upsilon^k}{\partial x^k} + \frac{\partial \varphi^k}{\partial x^k}. \tag{21}$$

At first we calculate $\partial(\rho s)/\partial t$. From the constitutive function $(18)_1$ we get

$$\frac{\partial(\rho s)}{\partial t} = \frac{\partial h}{\partial(\rho u)}\frac{\partial(\rho u)}{\partial t} + \frac{\partial h}{\partial \rho}\frac{\partial \rho}{\partial t} + \frac{\partial h}{\partial(\nabla_k \rho)}\frac{\partial^2 \rho}{\partial t \partial x^k}. \tag{22}$$

Correspondingly we determine $\partial(\rho s)/\partial x^k$. Next we plug in equation (22) any solution of the field equations (12) that may be established as follows. We form

$$\begin{aligned}
\frac{\partial \rho}{\partial t} &= -\upsilon^j \frac{\partial \rho}{\partial x^j} - \rho \frac{\partial \upsilon^j}{\partial x^j}\ , \\
\frac{\partial^2 \rho}{\partial t \partial x^k} &= -\frac{\partial \upsilon^j}{\partial x^k}\frac{\partial \rho}{\partial x^j} - \upsilon^j \frac{\partial^2 \rho}{\partial x^j \partial x^k} - \frac{\partial \rho}{\partial x^k}\frac{\partial \upsilon^j}{\partial x^j} - \rho \frac{\partial^2 \upsilon^j}{\partial x^j \partial x^k}\ , \\
\frac{\partial(\rho u)}{\partial t} &= -\upsilon^j \frac{\partial(\rho u)}{\partial x^j} - \rho u \frac{\partial \upsilon^j}{\partial x^j} - \frac{\partial q^j}{\partial x^j} + \sigma^{ij}\frac{\partial \upsilon^i}{\partial x^j}\ .
\end{aligned} \tag{23}$$

If we now eliminate $\partial(\rho s)/\partial t$ in the entropy production by means of (22) and (23) we observe that the three terms in (23), which are linear in the velocity, cancel with the corresponding terms $\upsilon^k \partial(\rho s)/\partial x^k$. Thus we obtain after some rearrangements

$$\begin{aligned}
\zeta = &\frac{\partial}{\partial x^k}\Big(\varphi^k - \frac{q^k}{T}\Big) + q^k \frac{\partial 1/T}{\partial x^k} + \\
&\Big(\frac{1}{T}\sigma^{ij} + \Big(h - \rho\frac{\partial h}{\partial \rho} - \frac{\rho u}{T}\Big)\delta^{ij}\Big)\frac{\partial \upsilon^i}{\partial x^j} + \\
&-\frac{\partial h}{\partial(\nabla_k \rho)}\frac{\partial \rho}{\partial x^k}\frac{\partial \upsilon^j}{\partial x^j} - \frac{\partial h}{\partial(\nabla_k \rho)}\frac{\partial \rho}{\partial x^j}\frac{\partial \upsilon^j}{\partial x^k} - \rho \frac{\partial h}{\partial(\nabla_k \rho)}\frac{\partial^2 \upsilon^j}{\partial x^j \partial x^k} \geq 0.
\end{aligned} \tag{24}$$

Next we introduce the two identities

$$\frac{\partial h}{\partial(\nabla_k \rho)}\frac{\partial \rho}{\partial x^k}\frac{\partial \upsilon^j}{\partial x^j} = \frac{\partial}{\partial x^k}\Big(\rho \frac{\partial h}{\partial(\nabla_k \rho)}\Big)\frac{\partial \upsilon^j}{\partial x^j} - \rho \frac{\partial}{\partial x^k}\Big(\frac{\partial h}{\partial(\nabla_k \rho)}\Big)\frac{\partial \upsilon^j}{\partial x^j}$$

and

$$\rho \frac{\partial h}{\partial(\nabla_k \rho)} \frac{\partial^2 v^j}{\partial x^j \partial x^k} = \frac{\partial}{\partial x^k}\Big(\rho \frac{\partial h}{\partial(\nabla_k \rho)} \frac{\partial v^j}{\partial x^j}\Big) - \frac{\partial}{\partial x^k}\Big(\rho \frac{\partial h}{\partial(\nabla_k \rho)}\Big) \frac{\partial v^j}{\partial x^j}$$

to simplify the second and third term of the last line in (24). Then the entropy production can be rewritten in the form

$$\begin{aligned}
\zeta = &\frac{\partial}{\partial x^k}\Big(\varphi^k - \frac{q^k}{T} - \rho \frac{\partial h}{\partial(\nabla_k \rho)} \frac{\partial v^j}{\partial x^j}\Big) \\
&+\Big(\frac{1}{T}\sigma_K^{ij} - \frac{\partial h}{\partial(\nabla_j \rho)} \frac{\partial \rho}{\partial x^i} + \Big(h - \rho \frac{\partial h}{\partial \rho} - \frac{\rho u}{T} + \rho \frac{\partial}{\partial x^k} \frac{\partial h}{\partial(\nabla_k \rho)}\Big)\delta^{ij}\Big) \frac{\partial v^i}{\partial x^j} \\
&+q^k \frac{\partial 1/T}{\partial x^k} + \frac{1}{T}\Bigg(\Big(\lambda + \frac{2}{3}\mu\Big)\Big(\frac{\partial v^j}{\partial x^j}\Big)^2 + 2\mu \frac{\partial v^{<i}}{\partial x^{j>}} \frac{\partial v^{<i}}{\partial x^{j>}}\Bigg) \geq 0 \ ,
\end{aligned} \tag{25}$$

where $\frac{v^{<i}}{\partial x^{j>}} = \frac{\partial v^i}{\partial x_j} - \frac{1}{3}\frac{\partial v^k}{\partial x_k}\delta^{ij}$ is the deviator. The first term on the right hand side drops out if we take for the entropy flux

$$\varphi^k = \frac{q^k}{T} + \rho \frac{\partial h}{\partial(\nabla_k \rho)} \frac{\partial v^j}{\partial x^j}. \tag{26}$$

This is a natural choice because it generalizes the classical form q^k/T in the most simple way. The bracket in the second term of (25) has to vanish since the velocity gradient can be chosen arbitrarily. Thus the entropy principle implies the following representation of the Korteweg stress:

$$\sigma_K^{ij} = T \frac{\partial h}{\partial(\nabla_j \rho)} \frac{\partial \rho}{\partial x^i} - \Bigg(Th - \rho T \frac{\partial h}{\partial \rho} - \rho u + \rho T \frac{\partial}{\partial x^k} \frac{\partial h}{\partial(\nabla_k \rho)}\Bigg)\delta^{ij}. \tag{27}$$

There remains the third term in (25) as the final representation of the entropy production:

$$\zeta = q^k \frac{\partial 1/T}{\partial x^k} + \frac{1}{T}\Bigg(\Big(\lambda + \frac{2}{3}\mu\Big)\Big(\frac{\partial v^j}{\partial x^j}\Big)^2 + 2\mu \frac{\partial v^{<i}}{\partial x^{j>}} \frac{\partial v^{<i}}{\partial x^{j>}}\Bigg) \geq 0 \tag{28}$$

We observe that the entropy production assumes the classical form with three contributions due to heat conduction, bulk viscosity and shear viscosity. The two latter contributions in (28) are obviously non–negative. Thus the non–negativity of the entropy production due to heat conduction can be easily established by assuming

$$q^k = -\kappa \frac{\partial T}{\partial x^k} = -\kappa \frac{\partial}{\partial x^k}\Big(\frac{\partial h}{\partial \rho u}\Big)^{-1} \quad \text{with} \quad \kappa > 0. \tag{29}$$

This is the classical version of Fouriers law. However, the heat conductivity may depend on ρu, ρ and $\nabla \rho$ like the viscosities.

2.2.6 Introduction of the free energy

The choice of the internal energy density as a basic variable instead of the temperature is best suited to exploit the entropy principle. However, as far as experiments and calculations of the constitutive functions, that rely on statistical mechanics, are concerned, it is much more appropriate to substitute the internal energy density by the temperature as a basic variable. To this end we write the entropy function as

$$\rho s = \hat{h}(T, \rho, \nabla\rho) \quad \text{with} \;\; \rho u = \hat{e}(T, \rho, \nabla\rho). \tag{30}$$

It is now an easy matter to express the function h and its derivatives by the free energy density $\rho\hat{\psi} \equiv \hat{e}(T, \rho, \nabla\rho) - T\hat{h}(T, \rho, \nabla\rho)$, because we have the relations

$$T\frac{\partial h}{\partial(\rho u)} = 1, \quad T\frac{\partial h}{\partial \rho} = -\frac{\partial(\rho\hat{\psi})}{\partial\rho}, \quad T\frac{\partial h}{\partial(\nabla\rho)} = -\frac{\partial(\rho\hat{\psi})}{\partial(\nabla\rho)}. \tag{31}$$

The first expression is part of the entropy principle and the other equations can be shown by applying the total differential to (30).
Thus the Korteweg stress assumes the form

$$\sigma_K^{ij} = -\frac{\partial(\rho\hat{\psi})}{\partial(\nabla_j\rho)}\frac{\partial\rho}{\partial x^i} + \Big(\rho\hat{\psi} - \rho\frac{\partial(\rho\hat{\psi})}{\partial\rho} + \rho\frac{\partial}{\partial x^k}\frac{\partial(\rho\hat{\psi})}{\partial(\nabla_k\rho)} + \rho\frac{\partial\rho\hat{\psi}}{\partial(\nabla_k\rho)}T\frac{\partial(1/T)}{\partial x^k}\Big)\delta^{ij}. \tag{32}$$

3 Equilibria of the van der Waals–Cahn–Hilliard phase field model

The aim of this section is to establish the equilibrium conditions for the volume and pressure controlled systems of Section 1 in the theory of van der Waals–Cahn–Hilliard. We will show rigorously that for isothermal processes the same thermodynamic equilibrium conditions can be obtained from the van der Waals–Cahn–Hilliard phase field model for $\varepsilon \to 0$ as in the sharp interface model. For this reason we summarize at first briefly the necessary conditions for equilibrium within the sharp interface model.

Since we consider from now on only isothermal processes, we will drop the dependence of the temperature T in our further considerations.

3.1 Necessary conditions for equilibrium within the sharp interface model

Necessary conditions for extremal points of $\mathcal{A}$ within the sharp interface model are achieved in [DK]. There it was shown that extremal points have to satisfy the following properties:

(i) The densities ρ_L and ρ_V are constant.

(ii) The specific Gibbs free energies are equal, i.e. $g_L(p_L) = g_V(p_V)$.

(iii) The difference of the pressures p_L and p_V satisfies the jump condition

$$p_V - p_L = (n-1)\sigma k_m, \qquad n \text{ dimension of the space.}$$

Here, k_m denotes the (constant) mean curvature of the interface I which is given by the sum of the principle curvatures divided by $(n-1)$, i.e. $k_m = \mathrm{div}_I \nu/(n-1)$, where the unit normal ν of the interface points into the direction of the liquid phase.

Note, this implies in particular that for a two–phase system the pressure of the enclosed phase is always higher than the pressure of the surrounding phase.

(iv) For *pressure control* the relation $p_V = p_0$ has to be satisfied. The corresponding condition for *volume control* is $V_0 = V_L + V_V$.

(v) A minimum point of $\mathcal{A}$ has minimal area in the following sense. If $\hat{V}_L$ and $\hat{V}_V$ are the volumes of the liquid and vapour phases of a minimum point with the densities $\hat{\rho}_L$ and $\hat{\rho}_V$ such that $\hat{V}_L\hat{\rho}_L + \hat{V}_V\hat{\rho}_V = m$, then the corresponding interface $\hat{I}$ has minimal surface area among all surfaces I separating two phases with the volumes $\hat{V}_L$ and $\hat{V}_V$. In addition, $\hat{I}$ meets the boundary of the vessel orthogonally.

3.2 Necessary conditions for equilibrium within the van der Waals–Cahn–Hilliard phase field model

To establish the thermodynamic equilibrium conditions for the van der Waals–Cahn–Hilliard phase field model we have to study two variational problems as $\varepsilon \to 0$ which we consider for reasons of generality in $\mathbb{R}^n$, $n \geq 2$.

(P1) Variational problem for volume control:
Minimize

$$\mathcal{A}_\varepsilon(\rho) = \int_\Omega \Big(\frac{\varepsilon^2}{2}|\nabla\rho(x)|^2 + \rho(x)\psi(\rho(x))\Big)dx, \quad \rho \in H^1(\Omega), \quad \Omega: \textit{ bounded domain,}$$

subject to $\int_\Omega \rho(x)dx = m$.

The variational problem for pressure control has the additional term p_0 times the volume of Ω, where now the volume may vary but is bounded from below and above by some constants.

(P2) Variational problem for pressure control:
Minimize

$$\mathcal{A}_\varepsilon(\rho,\Omega) = \int_\Omega \Big(\frac{\varepsilon^2}{2}|\nabla\rho(x)|^2 + \rho\psi(\rho(x))\Big)dx + p_0|\Omega|, \quad \rho \in H^1(\Omega), \qquad \Omega: \textit{ bounded domain,} \quad |\Omega| \in [C_1, C_2],$$

subject to $\int_\Omega \rho(x)dx = m$*, where* $|\cdot|$ *is the* n*–dimensional Lebesgue measure and* $C_1, C_2 > 0$ *are some constants.*

In our study we will mainly focus on variational problem (P1) since (P2) can be treated very easily. The necessary information on the equilibrium conditions will be established by studying the asymptotic behaviour of global minimizers ρ_ε as $\varepsilon \to 0$.

3.3 Some historical remarks on the van der Waals–Cahn–Hilliard phase model and new results

Variational problem (P1) is well–known and goes back to van der Waals [Van1893] as already mentioned earlier. In the year 1958 Cahn & Hilliard [CH58] apparently unaware of van der Waals theory rederived it. They obtained many important aspects concerning the interfacial energy between phases. Since then gradient theories have been used to analyze physical phenomena like phase transitions in pure substances, spinodal decomposition or coarsening phenomena. As a matter of fact there exists a huge amount of work in the mathematical literature on various generalizations and related problems to the van der Waals–Cahn–Hilliard phase theory. Therefore we can only point out a tiny selection of authors in connection to our work.
Fundamental properties of local minimizers of (P1) in higher dimensions like existence, smoothness and boundedness were studied by Gurtin and Matano [GM88]. Modica [Mod87] proved that the limit of a sequence of global minimizers of (P1) (on passing to a subsequence) as $\varepsilon \to 0$ is a two–valued function a.e. which minimizes the perimeter of the interface between the two phases. His considerations are based on various properties of functions of bounded variation and sets of finite perimeter. Sternberg [St88] obtained nearly the same results using the technique of $\Gamma-$convergence. The asymptotic behaviour of the Lagrange multiplier was investigated by Luckhaus & Modica [LM89]. Critical points of the energy functional $\mathcal{A}_\varepsilon$ of (P1) including those which are non energy minimizing were explored by Hutchinson & Tonegawa [HT00]. They showed that for those points the interface is close to a hypersurface with mean curvature zero if no Lagrange multiplier is present and with locally constant mean curvature in general. Niethammer [Nie95] investigated variational problem $(P1)$ in the class of radially symmetric functions. For this class of functions she got existence and uniqueness results of radially symmetric stationary points using the method of matched asymptotic expansion.

3.4 Assumptions

To make notations more convenient we use for variational problem (P1) the following abbreviations:

(A1) $\Omega \subset \mathbb{R}^n$, $n \geq 2$, is a bounded domain with a Lipschitz boundary.

(A2) The free energy $\rho\psi(\rho) \in C^2(t_0, t_1)$, $t_0, t_1 \in [-\infty, \infty]$, has a standard W–shape with two non–degenerate minima and a local maximum, see Fig. 3.

(A3) The total mass $m \in \mathbb{R}$ fulfills the inequality $\alpha|\Omega| \leq m \leq \beta|\Omega|$, where α and β denote the points of the density which satisfy the Maxwell conditions, cf. (34) and (35).

(A4) $\{\varepsilon_k\}_{k\in\mathbb{N}}$, $\varepsilon_k > 0$, is a sequence with $\lim_{k\to\infty} \varepsilon_k = 0$ such that the corresponding sequence $\{\rho_{\varepsilon_k}\}_{k\in\mathbb{N}}$ of global minimizers of variational problem (P1) converges to $\rho_0(x) \in \{\alpha, \beta\}$ for a.e. $x \in \Omega$ as $k \to \infty$.

Further, if (A4) is fulfilled we define $A = \{x \in \Omega : \rho_0(x) = \alpha\}$. $\overline{A}$ stands for the topological closure of A and $\mathring{A}$ for the topological interior. The mean curvature k_m of the (reduced) boundary of A is defined as in Section 3.1, where α represents the vapour phase and β the liquid phase.

For technical reason let us consider the modified energy

$$W(\rho) := \rho\psi(\rho) - l(\rho), \tag{33}$$

where l is the Maxwell line which is uniquely characterized by the property that there exists two points $\alpha, \beta \in [t_0, t_1]$ at which the tangent line on $\rho\psi(\rho)$ is equal to the difference quotient, see Fig. 3.

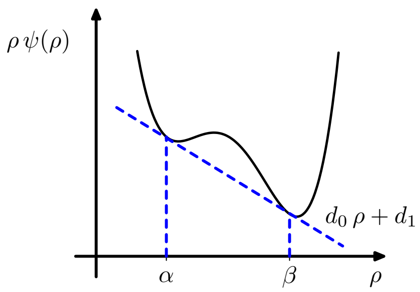

Figure 3: *The free energy*

Maxwell conditions:

$$(i) \qquad d_0 = (\alpha\psi(\alpha))' = (\beta\psi(\beta))' \tag{34}$$

$$(ii) \qquad \beta\psi(\beta) - \alpha\psi(\alpha) = d_0(\beta - \alpha) \tag{35}$$

Here, $(\,\cdot\,)'$ means the derivative with respect to ρ.

Maxwell line:

$$l(\rho) := d_0\rho + d_1 \tag{36}$$

Observe, as we subtract the Maxwell line, the two minima of W at α and β are zero. The corresponding total energy is denoted by

$$\mathcal{E}_\varepsilon(\rho) = \int_\Omega \frac{\varepsilon^2}{2}|\nabla\rho(x)|^2 + W(\rho(x))dx.$$

$\mathcal{E}_\varepsilon$ differs from the original energy $\mathcal{A}_\varepsilon$ only by the constant $d_0 m + d_1|\Omega|$. Therefore the minimization problem (P1) remains unchanged if we consider $\mathcal{E}_\varepsilon$ instead of $\mathcal{A}_\varepsilon$. This stands in contrast to the case of fixed pressure. There, we cannot modify the energy in the same manner, because the volume of Ω varies.

3.5 Main results

3.5.1 Asymptotic behaviour of ρ_ε as $\varepsilon \to 0$

One of the main aims of this study is to establish an explicit expansion of ρ_ε up to the first order in ε. More precisely, we will prove the following theorem.

Theorem 3.1
Let (A1) – (A4) be satisfied. Further, let $U \subset\subset \mathring{A}$ and $V \subset\subset \Omega\backslash\overline{A}$ be open sets. Then

$$\rho_{\varepsilon_k}(x) = \alpha - \frac{d_0 + \lambda_{\varepsilon_k}}{W''(\alpha)} + O(\varepsilon_k^2) \quad \textit{for} \;\; x \in U$$

and

$$\rho_{\varepsilon_k}(x) = \beta - \frac{d_0 + \lambda_{\varepsilon_k}}{W''(\beta)} + O(\varepsilon_k^2) \quad \textit{for} \;\; x \in V$$

as $k \to \infty$. In particular,

$$\rho_{\varepsilon_k}(x) = \rho^0_{\varepsilon_k}(x) + \rho^1_{\varepsilon_k}(x)\varepsilon_k + o(\varepsilon_k) \quad \textit{for} \;\; x \in U \cup V$$

as $k \to \infty$, where

$$\rho^0_{\varepsilon_k}(x) = \begin{cases} \alpha & \textit{if } x \in U, \\ \beta & \textit{if } x \in V, \end{cases} \qquad \rho^1_{\varepsilon_k}(x) = -\frac{c_0(n-1)k_m}{W''(\rho^0_{\varepsilon_k}(x))(\beta - \alpha)}.$$

Here, $c_0 := \int_\alpha^\beta \sqrt{2W(t)}dt$ and λ_{ε_k} is the Lagrange multiplier, cf. (40).

In Section 3.6 we will see that assumption (A4) and the existence of interior points of A and $\Omega\backslash\overline{A}$ are ensured. Furthermore, we will show that any global minimizer is constant if the average density $\hat{\rho} := m/|\Omega|$ lies not between α and β which justifies hypothesis (A3).

3.5.2 Equilibrium conditions

Due to the Gibb's equation the local parts of the Gibb's free energy g and the pressure p may be written as functions of the density ρ, i.e.

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

Using these representations for g and p we may express the equilibrium conditions in the following form.

Theorem 3.2
Let (A1) – (A4) be satisfied. Further, let $U \subset\subset \mathring{A}$ and $V \subset\subset \Omega\backslash\overline{A}$ be open sets.
If $\psi \in C^3(t_0, t_1)$ then the following conditions have to be fulfilled in equilibrium.

(i) Phase equilibrium condition:

$$g(\rho_{\varepsilon_k}(x_2)) = g(\rho_{\varepsilon_k}(x_1)) + O(\varepsilon_k^2) \quad \textit{for} \;\; x_1, x_2 \in U \cup V$$

as $k \to \infty$.

(ii) Mechanical equilibrium condition:

$$p(\rho_{\varepsilon_k}(x_2)) - p(\rho_{\varepsilon_k}(x_1)) = -c_0(n-1)k_m\varepsilon_k + o(\varepsilon_k) \quad \textit{for} \;\; x_1 \in U \textit{ and } x_2 \in V$$

as $k \to \infty$.

For variational problem (P2) we will verify that there exists only one phase in equilibrium. In accordance to condition (A3) we set $C_1 = m/\beta$ and $C_2 = m/\alpha$.

Theorem 3.3
Let $\varepsilon > 0$, $\mathcal{M} := \{G \in \mathbb{R}^n : G$ *is a bounded domain with Lipschitz continuous boundary and* $|G| \in [C_1, C_2]\}$ *and* $\mathcal{A}_\varepsilon$ *be defined as in variational problem (P2). Then*

$$\mathcal{A}_\varepsilon(\rho, \Omega) \geq d_0 m + \min\left\{\frac{(d_1 + p_0)}{\alpha}, \frac{(d_1 + p_0)}{\beta}\right\} m \tag{37}$$

for all $(\rho, \Omega) \in H^1(\Omega) \times \mathcal{M}$, *where* d_0 *and* d_1 *are chosen as in equation (36) and* p_0 *is the external pressure. In particular,*

(i) $\mathcal{A}_\varepsilon(\rho, \Omega) = d_0 m + \dfrac{(d_1 + p_0)}{\alpha}$ *if and only if* $\rho \equiv \alpha$ *and* $\Omega \in \mathcal{M}$ *with* $|\Omega| = \dfrac{m}{\alpha}$.

(ii) $\mathcal{A}_\varepsilon(\rho, \Omega) = d_0 m + \dfrac{(d_1 + p_0)}{\beta}$ *if and only if* $\rho \equiv \beta$ *and* $\Omega \in \mathcal{M}$ *with* $|\Omega| = \dfrac{m}{\beta}$.

3.6 Some preliminary results for the van der Waals–Cahn–Hilliard phase field model

In this section we summarize for the convenience of the reader some fundamental results of variational problem (P1) which we need for our further considerations. We start with stating some basic properties of minimizers ρ_ε, cf. [GM88].

For an arbitrary but fixed $\varepsilon > 0$ *there exists a global minimizer of variational problem (P1). Moreover, any local minimizer* ρ_ε *of variational problem (P1) satisfies the following properties:*

(i) ρ_ε *is uniformly bounded.*

(ii) $\rho_\varepsilon \in C^3(\Omega)$.

(iii) ρ_ε *is a solution of the Euler–Lagrange equation*

$$\varepsilon^2 \triangle \rho_\varepsilon - \big(\rho_\varepsilon \psi(\rho_\varepsilon)\big)' = \lambda_\varepsilon,$$

where λ_ε *denotes the Lagrange multiplier and* $(\,\cdot\,)'$ *stands for the derivative with respect to* ρ.

For $\varepsilon = 0$ the variational problem (P1) may be stated in the following form:
Minimize

$$\mathcal{A}_0(\rho) = \int_\Omega \rho(x)\psi(\rho(x))dx, \quad \rho \in L^1(\Omega), \tag{38}$$

subject to $\int_\Omega \rho(x)dx = m$.

Observe, that for $\varepsilon = 0$ any Lebesgue measurable function ρ_0 with $\rho_0(x) \in \{\alpha, \beta\}$ for a.e. $x \in \Omega$ and $\int_\Omega \rho_0 dx = m$ is a global minimizer. In particular, we do not get any restrictions on the shape of the interface as interfacial energy is neglected. The term $\frac{\varepsilon^2}{2}|\nabla\rho_\varepsilon|^2$ of the van der Waals–Cahn–Hilliard phase field model in contrast includes this energy. It penalizes changes of the density. Moreover, minimizers of (P1) try to minimize the interfacial area. This phenomenon and the following asymptotic properties are shown in [Mod87]:

Let (A1) – (A3) be satisfied and let ρ_ε, $\varepsilon > 0$, be a global minimizer of variational problem (P1). Then the following statements hold:

(i) There exists a sequence $\{\varepsilon_k\}_{k\in\mathbb{N}}$ with $\lim_{k\to\infty}\varepsilon_k = 0$ such that the corresponding sequence $\{\rho_{\varepsilon_k}\}_{k\in\mathbb{N}}$ of global minimizers ρ_{ε_k} converges in $L^1(\Omega)$ as $k\to\infty$.

(ii) If $\rho_{\varepsilon_j}\to\rho_0$ in $L^1(\Omega)$ as $j\to\infty$ and $\lim_{j\to\infty}\varepsilon_j = 0$ then

$$\rho_0(x) = \begin{cases}\alpha \\ \beta\end{cases} \qquad \text{for a.e. } x\in\Omega,$$

where $\alpha|A| + \beta|\Omega\backslash A| = m$ and $A = \{x\in\Omega : \rho_0(x) = \alpha\}$.

(iii) The set A is a solution of the following geometric variational problem:

$$P(A,\Omega) = \min\left\{P(F,\Omega) :\ F\subset\Omega,\ |F| = \frac{\beta|\Omega| - m}{\beta-\alpha}\right\},$$

where $P(A,\Omega)$ is the perimeter of A in Ω, see equation (43) for the definition of the perimeter.

(iv) If $\rho_{\varepsilon_j}\to\rho_0$ in $L^1(\Omega)$ as $j\to\infty$ and $\lim_{j\to\infty}\varepsilon_j = 0$ then the modified energy $\mathcal{E}_{\varepsilon_j}$ satisfies the relation

$$\mathcal{E}_{\varepsilon_j}(\rho_{\varepsilon_j}) = \int_\Omega \frac{{\varepsilon_j}^2}{2}|\nabla\rho_{\varepsilon_j}|^2 + W(\rho_{\varepsilon_j})dx = c_0 P(A,\Omega)\varepsilon_j + o(\varepsilon_j) \tag{39}$$

as $\varepsilon_j\to 0$, where $c_0 = \int_\alpha^\beta \sqrt{2W(t)}dt$.

Note, items (i) and (ii) imply assumption (A4).
The asymptotic behaviour of the Lagrange multiplier λ_ε was investigated by Luckhaus and Modica [LM89]:

Let assumptions (A1) – (A4) be satisfied. Then

$$\lambda_{\varepsilon_k} = -d_0 + \frac{c_0(n-1)k_m}{\beta-\alpha}\varepsilon_k + o(\varepsilon_k) \tag{40}$$

as $\varepsilon_k\to 0$, where d_0 is defined as in (34).

To prove the asymptotic expansion in Theorem 3.1 we also take advantage from a local energy result due to Hutchinson and Tonegawa [HT00]. They introduced for an open ball with radius r, $B_r(x_0) := \{x \in \mathbb{R}^n : ||x - x_0|| := \left(\sum_{k=1}^n |x_k - x_{0,k}|^2\right)^{1/2} < r\}$, the scaled energy

$$E_\varepsilon(r, x_0) = \frac{1}{r^{n-1}} \int_{B_r(x_0)} \frac{\varepsilon}{2} |\nabla \rho_\varepsilon(x)|^2 + \frac{1}{\varepsilon} W(\rho_\varepsilon(x)) dx,$$

and obtained modified to our situation the following local energy estimate:

Let assumptions (A1) – (A4) be satisfied. Further, let $B_r(x_0) \subset G$, $G \subset\subset \Omega$ be open and $r > s > 0$. Then there exists a number $\eta_1 > 0$ such that

$$E_{\varepsilon_k}(r, x_0) - E_{\varepsilon_k}(s, x_0) \geq -M_2 r \tag{41}$$

for $\varepsilon_k \leq \eta_1$, where $M_2 > 0$ is some constant depending only on G.

This energy estimate is based on an upper and lower bound for the density ρ_ε, cf. [HT00]:

Let assumptions (A1) – (A4) be satisfied. Moreover, let G be an open set with $G \subset\subset \Omega$. Then there exists a number $\eta_2 > 0$ such that

$$\alpha - M_1 \varepsilon_k \leq \rho_{\varepsilon_k}(x) \leq \beta + M_1 \varepsilon_k, \quad x \in G, \tag{42}$$

for all $\varepsilon_k \leq \eta_2$, where $M_1 > 0$ is some constant depending only on G

Before we proceed we like to recall the definitions of a BV–function and of a minimal perimeter with volume constraint.

For any open set $G \subset \mathbb{R}^n$, $n \geq 2$, and $f \in L^1(G)$ we set

$$\int_G |Df| = \sup\left\{ \int_G f(x) \, \mathrm{div} g(x) dx : g \in C_0^1(G), \ |g(x)| \leq 1 \ \text{for} \ x \in G \right\},$$

where $C_0^1(G)$ is the space of real continuous differentiable functions with compact support on G. If $\int_G |Df| < \infty$ then f is said to have *bounded variation* in G. The corresponding space of functions is denoted by

$$BV(G) = \left\{ f \in L^1(G) : \int_G |Df| < \infty \right\}.$$

Now let $L \subset \mathbb{R}^n$, $n \geq 2$, be any Borel set. Then the perimeter of L in G is defined by

$$P(L, G) := \int_G |D\chi_L|, \qquad \text{where} \quad \chi_L(x) = \begin{cases} 0 & \text{for } x \in \mathbb{R}^n \backslash L \\ 1 & \text{for } x \in L \end{cases}. \tag{43}$$

A Borel set $S \subset \Omega$ is said to *minimize perimeter in Ω with a volume constraint* if for every $G \subset\subset \Omega$, G open, the following two relations hold:

$$\int_G |D\chi_S| < \infty$$

$$\int_G |D\chi_S| \leq \int_G |D\chi_L| \qquad \forall L \subset \Omega \quad \text{with} \quad L \triangle S \subset\subset G, \ |L \cap G| = |S \cap G|.$$

Sets $S \subset \Omega$ which minimize perimeter in Ω with a volume constraint fulfill the following properties, cf. [GMT83], [Giu84] and [DeG55].

(i) If $|S \cap \Omega| > 0$ and $|\Omega \backslash S| > 0$, then there exist two non–empty balls $B_1, B_2 \subset\subset \Omega$ and a real $\delta > 0$ such that

$$\min\{\operatorname{dist}(B_1, \Omega \backslash S), \operatorname{dist}(B_2, S)\} \geq \delta. \tag{44}$$

(ii) $\partial^* S \cap \Omega$ is an analytic $(n-1)$–dimensional manifold and

$$\mathcal{H}_s((\partial S \backslash \partial^* S) \cap \Omega) = 0 \qquad \text{for every real } \; s > n - 8, \tag{45}$$

where ∂S and $\partial^* S$ is the topological and the reduced boundary of S respectively, see [Giu84] for more details.

Observe, the set $A = \{x \in \Omega : \rho_0(x) = \alpha\}$ minimizes perimeter in Ω with a volume constraint. Therefore, property (ii) implies that ∂A has minimal surface area. Thus we have an analogous situation to the sharp interface model. Property (i) ensures the existence of interior points of A and $\Omega \backslash A$.

The structure of a minimal surface depends on the vessel and on the enclosed volume. The determination of a minimal surface can be quite challenging even for very simple vessels. For instance, the modified isoperimetric problem for a box is still open, see [RR]. A conjecture is that the minimal surface has up to symmetry one of the three shapes shown in Figure 4. Which is the right choice depends on the shape of the box and on the value of the enclosed volume. Other possible candidates for minimal area are the surfaces in Figure 5.

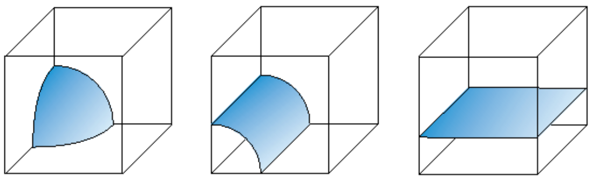

Figure 4: *Probable minimal surfaces for a box, taken from [RR].*

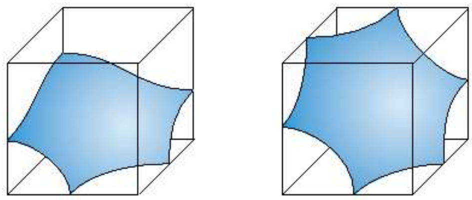

Figure 5: *Further possible candidates for minimal surfaces, taken from [RR].*

3.7 Auxiliary results and the proofs of Theorem 3.1, 3.2 and 3.3

At first we show that it sufficies to consider variational problem (P1) under the assumption (A3) because otherwise any global minimizer is constant.

Theorem 3.4
If the average density $\hat{\rho} \in (t_0, \alpha]$ or $\hat{\rho} \in [\beta, t_1)$ then any global minimizer of (P1) is constant, i.e. $\rho_\varepsilon(x) = \hat{\rho}$ for $x \in \Omega$.

Proof:
Without loss of generality we may assume that $\hat\rho \in (t_0, \alpha)$. Let us suppose there exists a non–constant global minimizer ρ_ε. Then the Lebesgue measure of the set $S = \{x \in \Omega : \rho_\varepsilon(x) \neq \hat\rho\}$ is greater than zero. We define the chopped function

$$\tilde\rho_\varepsilon(x) := \max\big\{c, \min\{\alpha, \rho_\varepsilon(x)\}\big\}, \quad x \in \Omega,$$

where $c \in (t_0, \alpha)$ is so chosen that $\int_\Omega \tilde\rho_\varepsilon(x)dx = m$.
Obviously, $\tilde\rho_\varepsilon \in H^1(\Omega)$ and

$$\int_\Omega W(\tilde\rho_\varepsilon)dx \leq \int_\Omega W(\rho_\varepsilon)dx, \qquad \int_\Omega |\nabla\tilde\rho_\varepsilon|^2 dx \leq \int_\Omega |\nabla\rho_\varepsilon|^2 dx.$$

W' is strictly monotone increasing on (t_0, α). Thus we have

$$W'(\rho) - W'(\hat\rho) < 0 \qquad \text{for } \rho \in (t_0, \hat\rho)$$

and

$$W'(\rho) - W'(\hat\rho) > 0 \qquad \text{for } \rho \in (\hat\rho, \alpha).$$

Integration of the latter expressions implies

$$W(\tilde\rho_\varepsilon) - W'(\hat\rho)\tilde\rho_\varepsilon > W(\hat\rho) - W'(\hat\rho)\hat\rho \qquad \text{for } \tilde\rho_\varepsilon \in (t_0, \hat\rho)$$

and

$$W(\tilde\rho_\varepsilon) - W'(\hat\rho)\tilde\rho_\varepsilon > W(\hat\rho) - W'(\hat\rho)\hat\rho \qquad \text{for } \tilde\rho_\varepsilon \in (\hat\rho, \alpha).$$

Since the Lebesgue measure of S is greater than zero we get

$$\int_\Omega W(\tilde\rho_\varepsilon)dx > \int_\Omega W(\hat\rho)dx$$

which is a contradiction to the assumption that ρ_ε is a non–constant global minimizer. ∎

Theorem 3.5
Let $\varepsilon = 0$ and ρ_0 be any global minimizer of (38).

(i) If $\hat\rho \in (\alpha, \beta)$, then $\rho_0(x) \in \{\alpha, \beta\}$ for a.e. $x \in \Omega$ with $\int_\Omega \rho_0(x)dx = m$.

(ii) If $\hat\rho \in (t_0, \alpha]$ or $\hat\rho \in [\beta, t_1)$, then $\rho_0(x) = \hat\rho$ for a.e. $x \in \Omega$.

Proof:
Assertion (i) follows immediately from the definition of the modified energy $\mathcal{E}_0$. Item (ii) is shown analogously to Theorem 3.4. ∎

Next we verify that the scaled energy $\frac{1}{\varepsilon}\mathcal{E}_\varepsilon$ of (P1) tends to zero on open relatively compact sets in A and $\Omega \backslash A$.

Theorem 3.6
Let (A1) – (A4) be satisfied. Further, let $U \subset\subset \mathring{A}$ and $V \subset\subset \Omega\backslash\overline{A}$ be open sets. Then

$$\int_{U\cup V} \frac{\varepsilon_k}{2}\,|\nabla\rho_{\varepsilon_k}(x)|^2 + \frac{1}{\varepsilon_k} W(\rho_{\varepsilon_k}(x))dx = o(1) \qquad \text{as} \quad k \to \infty.$$

Proof:
The upper energy estimates

$$c_0 P(A,\Omega\backslash\overline{U}) \leq \liminf_{k\to\infty} \int_{\Omega\backslash\overline{U}} \Big(\frac{\varepsilon_k}{2}|\nabla\rho_{\varepsilon_k}(x)|^2 + \frac{1}{\varepsilon_k}W(\rho_{\varepsilon_k}(x))\Big)dx \tag{46}$$

$$c_0 P(A,\Omega\backslash\overline{V}) \leq \liminf_{k\to\infty} \int_{\Omega\backslash\overline{V}} \Big(\frac{\varepsilon_k}{2}|\nabla\rho_{\varepsilon_k}(x)|^2 + \frac{1}{\varepsilon_k}W(\rho_{\varepsilon_k}(x))\Big)dx \tag{47}$$

can be established by the same arguments as Modica [Mod87] used to get relation (39). Observe, for open sets $U \subset\subset \mathring{A}$ and $V \subset\subset \Omega\backslash\overline{A}$ the following perimeters are equal:

$$P(A,\Omega) = P(A,\Omega\backslash\overline{U}) = P(A,\Omega\backslash\overline{V})$$

Therefore we obtain

$$\int_U \frac{\varepsilon_k}{2}|\nabla\rho_{\varepsilon_k}(x)|^2 + \frac{1}{\varepsilon_k}W(\rho_{\varepsilon_k}(x))dx = o(1) \qquad \text{as} \quad k\to\infty$$

as well as

$$\int_V \frac{\varepsilon_k}{2}|\nabla\rho_{\varepsilon_k}(x)|^2 + \frac{1}{\varepsilon_k}W(\rho_{\varepsilon_k}(x))dx = o(1) \qquad \text{as} \quad k\to\infty.$$

■

Theorem 3.6 and the local energy estimate (41) are the main tools to obtain uniform convergence results for sequences of global minimizers.

Theorem 3.7
Let (A1) – (A4) be fulfilled. Then $\{\rho_{\varepsilon_k}\}_{k\in\mathbb{N}}$ converges uniformly to α on open sets $U \subset\subset \mathring{A}$ and to β on open sets $V \subset\subset \Omega\backslash\overline{A}$.

Proof:
We only prove that $\{\rho_{\varepsilon_k}\}_{k\in\mathbb{N}}$ converges uniformly to α on open sets $U \subset\subset \mathring{A}$. The uniform convergence result on open sets $V \subset\subset \Omega\backslash\overline{A}$ can be achieved similarly.
We suppose this were not true. Then there exists a number $\delta > 0$ and points $x_j \in U$, $j\in\mathbb{N}$, such that

$$\left|\rho_{\varepsilon_{kj}}(x_j) - \alpha\right| > \delta, \quad j\in\mathbb{N},$$

for some subsequence $\{\varepsilon_{kj}\}_{j\in\mathbb{N}}$. By definition of A we also may assume that

$$\left|\rho_{\varepsilon_{kj}}(x_j) - \beta\right| > \delta, \quad j\in\mathbb{N}.$$

Now let us define $d = \operatorname{dist}(U,\Omega\backslash\overline{A}) > 0$. Then we obtain by means of inequality (41) for $\varepsilon_j < r < d$, $j\in\mathbb{N}$, and each ball $B_r(x_j)$, $j\in\mathbb{N}$, the estimate

$$\begin{aligned} E_{\varepsilon_{kj}}(r,x_j) &= \frac{1}{r^{n-1}}\int_{B_r(x_j)} \frac{\varepsilon_{kj}}{2}|\nabla\rho_{\varepsilon_{kj}}(x)|^2 + \frac{1}{\varepsilon_{kj}}W(\rho_{\varepsilon_{kj}}(x))dx \\ &\geq -M_1 r + \frac{1}{\varepsilon_{kj}^{n-1}}\int_{B_{\varepsilon_{kj}}(x_j)} \frac{\varepsilon_{kj}}{2}|\nabla\rho_{\varepsilon_{kj}}(x)|^2 + \frac{1}{\varepsilon_{kj}}W(\rho_{\varepsilon_{kj}}(x))dx \\ &\geq -M_1 r + \frac{1}{\varepsilon_{kj}^{n-1}}\int_{B_{\varepsilon_{kj}}(x_j)} \frac{1}{\varepsilon_{kj}}W(\rho_{\varepsilon_{kj}}(x))dx \end{aligned}$$

Consequently, we get for $r > 0$ sufficiently small

$$\lim_{j\to\infty} E_{\varepsilon_{kj}}(r, x_j) > -M_1 r + b_n C > b_n \frac{C}{2},$$

where $C = \min\{W(h) : h \in (t_0, \alpha - \delta] \cup [\alpha + \delta, \beta - \delta] \cup [\beta + \delta, t_1)\} > 0$ and b_n is the volume of the unit ball in $\mathbb{R}^n$. However, this is a contradiction to Theorem 3.6. ■

Next we show that global minimizers ρ_ε converge on open relatively compact sets in $\mathring{A}$ and $\Omega\backslash\overline{A}$ at least with order ε to α and to β respectively.

Theorem 3.8
Let (A1) – (A4) be satisfied and let $U \subset\subset \mathring{A}$ and $V \subset\subset \Omega\backslash\overline{A}$ be open sets. Then there exists a number $\eta_3 > 0$ such that

$$\alpha - M_3\varepsilon_k \le \rho_{\varepsilon_k}(x) \le \alpha + M_3\varepsilon_k, \quad x \in U,$$

and

$$\beta - M_3\varepsilon_k \le \rho_{\varepsilon_k}(x) \le \beta + M_3\varepsilon_k, \quad x \in V,$$

for all $\varepsilon_k \le \eta_3$, where $M_3 > 0$ is some constant depending only on U and V.

Proof:
In view of estimate (42) we only have to verify the inequalities

$$\rho_{\varepsilon_k}(x) \le \alpha + M_3\varepsilon_k \quad \text{for } x \in U \qquad \text{and} \qquad \rho_{\varepsilon_k}(x) \ge \beta - M_3\varepsilon_k \quad \text{for } x \in V \tag{48}$$

if $\varepsilon_k \le \eta_3$.
The structure of W assures that there exist a constant $C > 0$ and a number $\delta > 0$ such that

(i) $W'(h) \ge 0$ for $h \in [\alpha, \alpha + \delta]$ and $W'(h) \le 0$ for $h \in [\beta - \delta, \beta]$,

(ii) $W''(h) \ge C > 0$ for $h \in [\alpha - \delta, \alpha + \delta] \cup [\beta - \delta, \beta + \delta]$.

Further we define $4\,d = \min\{\mathrm{dist}(U, \Omega\backslash\overline{A}), \mathrm{dist}(V, \overline{A})\}$ as well as $\overline{B}_{r_1,r_2}(x_0) = \big\{x \in \mathbb{R}^n : r_1 \le ||x - x_0|| \le r_2\big\}$. The proof is divided into two steps.

Step 1: First of all we show that

$$\rho_{\varepsilon_k}(x) \le \alpha + M_3\varepsilon_k \quad \text{for } x \in U \tag{49}$$

if M_3 (depending on k_m) is chosen sufficiently large and $\varepsilon_k > 0$ is sufficiently small. This is done by contradiction. We suppose estimate (49) were not true. Then there exist a subsequence $\{\varepsilon_{kj}\}_{j\in\mathbb{N}}$ and points $x_j \in U$, $j \in \mathbb{N}$, such that

$$\rho_{\varepsilon_{kj}}(x_j) > \alpha + M_3\varepsilon_{kj}.$$

Further, as $\{\rho_{\varepsilon_k}\}_{k\in\mathbb{N}}$ converges uniformly to α on $\overline{U}_1$, $U_1 := U \cup \bigcup_{j=1}^{\infty} B_{3d}(x_j)$, there exists a number $j_0 \in \mathbb{N}$ such that

$$\max_{x\in\overline{U}_1} |\rho_{\varepsilon_{k_j}}(x) - \alpha| < \delta$$

for all $j \geq j_0$.
Now our plan is to construct functions g_j modified to $\rho_{\varepsilon_{k_j}}$ which have an interior maximum point in $\overline{B}_{3d}(x_j)$. For this reason we choose a sequence of smooth functions $\varphi_j \in C^\infty(B_{4d}(x_j))$, $j \geq j_0$, which fulfills the following conditions

$$\text{(i)} \quad \alpha + M_3 \frac{\varepsilon_{kj}}{2} \leq \varphi_j \leq \alpha + \delta \;\text{ on }\; \overline{B}_{3d}(x_j), \quad j \geq j_0, \tag{50}$$

$$\text{(ii)} \quad \varphi_j = \alpha + M_3 \frac{\varepsilon_{kj}}{2} \;\text{ on }\; \overline{B}_d(x_j) \quad\text{and}\quad \varphi_j = \alpha + \delta \;\text{ on }\; \overline{B}_{2d,3d}(x_j), \quad j \geq j_0. \tag{51}$$

In addition, we may assume that the sequence $\{\triangle\varphi_j\}$ is uniformly bounded on $\overline{B}_{3d}(x_j)$.
Now we define

$$g_j(x) = \rho_{\varepsilon_{k_j}}(x) - \varphi_j(x) \quad \text{for } x \in \overline{B}_{3d}(x_j), \quad j \geq j_0.$$

Then the following estimates are satisfied:

$$\text{(i)} \quad g_j(x) < \alpha + \delta - \alpha - \delta = 0 \quad \text{for} \quad x \in \partial B_{3d}(x_j) \tag{52}$$

$$\text{(ii)} \quad \max_{x\in\overline{B}_{3d}(x_j)} g_j(x) > \alpha + M_3\varepsilon_{kj} - \alpha - M_3\frac{\varepsilon_{kj}}{2} = M_3\frac{\varepsilon_{kj}}{2} \tag{53}$$

Item (i) and (ii) assure that the functions g_j, $j \geq j_0$, have an interior maximum point y_j in $\overline{B}_{3d}(x_j)$. Thus we deduce

$$\begin{aligned}
0 \;\geq\; & \varepsilon_{kj}\triangle g_j(y_j) = \varepsilon_{kj}\big(\triangle\rho_{\varepsilon_{k_j}}(y_j) - \triangle\varphi_j(y_j)\big) = \frac{W'(\rho_{\varepsilon_{k_j}}(y_j))}{\varepsilon_{kj}} + \frac{d_0 + \lambda_{\varepsilon_{k_j}}}{\varepsilon_{kj}} - \varepsilon_{kj}\triangle\varphi_j(y_j) \\
= \;& \frac{W'(t\rho_{\varepsilon_{k_j}}(y_j) + (1-t)\varphi_j(y_j))}{\varepsilon_{kj}}\Bigg|_{t=0}^{1} + \frac{W'(\varphi_j(y_j))}{\varepsilon_{kj}} + \frac{d_0 + \lambda_{\varepsilon_{k_j}}}{\varepsilon_{kj}} - \varepsilon_{kj}\triangle\varphi_j(y_j) \\
= \;& \frac{g_j(y_j)}{\varepsilon_{kj}} \int_0^1 W''(t\rho_{\varepsilon_{k_j}}(y_j) + (1-t)\varphi_j(y_j))dt + \frac{W'(\varphi_j(y_j))}{\varepsilon_{kj}} + \frac{d_0 + \lambda_{\varepsilon_{k_j}}}{\varepsilon_{kj}} - \varepsilon_{kj}\triangle\varphi_j(y_j) \\
\geq \;& \frac{g_j(y_j)}{\varepsilon_{kj}} \min_{h\in[\alpha-\delta,\alpha+\delta]} W''(h) + \frac{d_0 + \lambda_{\varepsilon_{k_j}}}{\varepsilon_{kj}} - \varepsilon_{kj}\triangle\varphi_j(y_j) \\
\geq \;& \frac{M_3}{2} \min_{h\in[\alpha-\delta,\alpha+\delta]} W''(h) + \frac{d_0 + \lambda_{\varepsilon_{k_j}}}{\varepsilon_{kj}} - \varepsilon_{kj}\triangle\varphi_j(y_j)
\end{aligned} \tag{54}$$

as $\alpha - \delta \leq t\rho_{\varepsilon_{k_j}}(y_j) + (1-t)\varphi_j(y_j) \leq \alpha + \delta$ for $t \in [0,1]$ and $\min_{h\in[\alpha-\delta,\alpha+\delta]} W''(h) \geq C > 0$. Since the sequence $\{\triangle\varphi_j\}$ is uniformly bounded we obtain

$$|\varepsilon_{kj}\triangle\varphi_j(y_j)| \leq \frac{M_3}{4}C$$

for $\varepsilon_{kj} > 0$ sufficiently small. The latter combined with (54) gives

$$0 \geq \frac{d_0 + \lambda_{\varepsilon_{kj}}}{\varepsilon_{kj}} + \frac{M_3}{4} C.$$

But this is in view of (40) for $M_3 > 0$ sufficiently large and $\varepsilon_{kj} > 0$ sufficiently small impossible.
Step 2: Now we suppose that

$$\min_{x \in \overline{V}} \rho_{\varepsilon_{kj}}(x) < \beta - M_3 \varepsilon_{kj}$$

for some sequence $\{\varepsilon_{kj}\}_{j \in \mathbb{N}}$ and argue similarly as in Step 1. We select points $\hat{x}_j \in \overline{V}$, $j \in \mathbb{N}$, with

$$\rho_{\varepsilon_{kj}}(\hat{x}_j) = \min_{x \in \overline{V}} \rho_{\varepsilon_{kj}}(x).$$

Moreover, as $\{\rho_{\varepsilon_k}\}_{k \in \mathbb{N}}$ converges uniformly to β on $\overline{V}_1$, $V_1 := V \cup \bigcup_{j=1}^{\infty} B_{3d}(\hat{x}_j)$, there exists some $\hat{j}_0 \in \mathbb{N}$ such that

$$\max_{x \in \overline{V}_1} |\rho_{\varepsilon_{kj}}(x) - \beta| < \delta$$

for all $j \geq \hat{j}_0$.
Next we take smooth functions $\hat{\varphi}_j \in C^\infty(B_{4d}(\hat{x}_j))$ which satisfy the following conditions:

(i) $\beta - \delta \leq \hat{\varphi}_j \leq \beta - M_3 \frac{\varepsilon_{kj}}{2}$ on $\overline{B}_{3d}(\hat{x}_j)$, $\quad j \geq \hat{j}_0$,

(ii) $\hat{\varphi}_j = \beta - M_3 \frac{\varepsilon_{kj}}{2}$ on $\overline{B}_d(\hat{x}_j)$ and $\hat{\varphi}_j = \beta - \delta$ on $\overline{B}_{2d,3d}(\hat{x}_j)$, $\quad j \geq \hat{j}_0$.

We also may assume that the sequence $\{\triangle \hat{\varphi}_j\}$ is uniformly bounded in $\overline{B}_{3d}(\hat{x}_j)$.
Consequently, we derive for

$$\hat{g}_j(x) := \rho_{\varepsilon_{kj}}(x) - \hat{\varphi}_j(x), \quad x \in \overline{B}_{3d}(\hat{x}_j), \quad j \geq \hat{j}_0,$$

the estimates

(i) $\hat{g}_j(x) > \beta - \delta - \beta + \delta = 0$ for $x \in \partial \overline{B}_{3d}(\hat{x}_j)$,

(ii) $\min_{x \in \overline{B}_{3d}(\hat{x}_j)} g_j(x) < \beta - M_3 \varepsilon_{kj} - \beta + M_3 \frac{\varepsilon_{kj}}{2} = -M_3 \frac{\varepsilon_{kj}}{2}$.

Thus $\hat{g}_j$ has an interior minimum point $\hat{y}_j$ in $\overline{B}_{3d}(\hat{x}_j)$, $j \geq j_0$. Therefore we have

$$\begin{aligned}
0 \ &\leq\ \varepsilon_{kj} \triangle \hat{g}_j(\hat{y}_j) = \varepsilon_{kj}\big(\triangle \rho_{\varepsilon_{kj}}(\hat{y}_j) - \triangle \hat{\varphi}_j(\hat{y}_j)\big) = \frac{W'(\rho_{\varepsilon_{kj}}(\hat{y}_j))}{\varepsilon_{kj}} + \frac{d_0 + \lambda_{\varepsilon_{kj}}}{\varepsilon_{kj}} - \varepsilon_{kj} \triangle \hat{\varphi}_j(\hat{y}_j) \\
&=\ \frac{\hat{g}_j(\hat{y}_j)}{\varepsilon_{kj}} \int_0^1 W''(t\rho_{\varepsilon_{kj}}(\hat{y}_j) + (1-t)\hat{\varphi}_j(\hat{y}_j))dt + \frac{W'(\hat{\varphi}_j(\hat{y}_j))}{\varepsilon_{kj}} + \frac{d_0 + \lambda_{\varepsilon_{kj}}}{\varepsilon_{kj}} - \varepsilon_{kj} \triangle \hat{\varphi}_j(\hat{y}_j) \\
&\leq\ \frac{\hat{g}_j(\hat{y}_j)}{\varepsilon_{kj}} \min_{h \in [\beta - \delta, \beta + \delta]} W''(h) + \frac{d_0 + \lambda_{\varepsilon_{kj}}}{\varepsilon_{kj}} - \varepsilon_{kj} \triangle \hat{\varphi}_j(\hat{y}_j) \\
&\leq\ \frac{-M_3}{2} \min_{h \in [\beta - \delta, \beta + \delta]} W''(h) + \frac{d_0 + \lambda_{\varepsilon_{kj}}}{\varepsilon_{kj}} - \varepsilon_{kj} \triangle \hat{\varphi}_j(\hat{y}_j)
\end{aligned}$$

since $\beta - \delta \le t\rho_{\varepsilon_{k_j}}(\hat{y}_j) + (1-t)\hat{\varphi}_j(\hat{y}_j) \le \beta + \delta$ for $t \in [0,1]$ and $\min_{h\in[\beta-\delta,\beta+\delta]} W''(h) \ge C > 0$. We end up with

$$0 \le \frac{d_0 + \lambda_{\varepsilon_{kj}}}{\varepsilon_{kj}} - \frac{M_3}{4}\hat{C}$$

for $\varepsilon_{kj} > 0$ sufficiently small which is a contradiction to (40) if $M_3 > 0$ is chosen large enough.
Combining Step 1 and Step 2 shows the claim. ■

Now we are in a position to derive the asymptotic expansion of ρ_ε as $\varepsilon \to 0$.

Proof of Theorem 3.1:
We choose $\delta > 0$ so small that

(i) W' is monotone increasing on the intervals $[\alpha-\delta, \alpha+\delta]$ and $[\beta-\delta, \beta+\delta]$.

(ii) $W''(h) \ge C > 0$ for $h \in [\alpha-\delta,\alpha+\delta] \cup [\beta-\delta,\beta+\delta]$, $C > 0$ some constant.

Furthermore, we set $\varepsilon_0 = \min\{|W'(\alpha-\delta/2)|, |W'(\alpha+\delta/2)|, |W'(\beta-\delta/2)|, |W'(\beta+\delta/2)|\}/(2|\lambda_0|)$, $\lambda_0 := c_0(n-1)k_m/(\beta-\alpha)$. Since $|d_0 + \lambda_{\varepsilon_k}| \le 2\lambda_0\varepsilon_k$ for k sufficiently large, there exist numbers $\alpha_{\varepsilon_k} \in [\alpha-\delta/2, \alpha+\delta/2]$ and $\beta_{\varepsilon_k} \in [\beta-\delta/2, \beta+\delta/2]$ such that

$$W'(\alpha_{\varepsilon_k}) = W'(\beta_{\varepsilon_k}) = -(d_0 + \lambda_{\varepsilon_k})$$

if $\varepsilon_k < \varepsilon_0$. Moreover, we have

$$W'(\alpha_{\varepsilon_k}) = W''(h_{1,\varepsilon_k})(\alpha_{\varepsilon_k} - \alpha), \quad h_{1,\varepsilon_k} \in [\alpha-\delta/2, \alpha+\delta/2]$$

and

$$W'(\beta_{\varepsilon_k}) = W''(h_{2,\varepsilon_k})(\beta_{\varepsilon_k} - \beta), \quad h_{2,\varepsilon_k} \in [\beta-\delta/2, \beta+\delta/2].$$

In consequence,

$$\max\{|\alpha_{\varepsilon_k} - \alpha|, |\beta_{\varepsilon_k} - \beta|\} \le \frac{2\lambda_0}{C}\varepsilon_k.$$

From Taylor's theorem we conclude

$$W'(\alpha_{\varepsilon_k}) = W''(\alpha)(\alpha_{\varepsilon_k} - \alpha) + O(\varepsilon_k^2) \quad \text{and} \quad W'(\beta_{\varepsilon_k}) = W''(\beta)(\beta_{\varepsilon_k} - \beta) + O(\varepsilon_k^2)$$

as $k \to \infty$. This implies

$$\alpha_{\varepsilon_k} = \alpha - \frac{d_0 + \lambda_{\varepsilon_k}}{W''(\alpha)} + O(\varepsilon_k^2) \quad \text{and} \quad \beta_{\varepsilon_k} = \beta - \frac{d_0 + \lambda_{\varepsilon_k}}{W''(\beta)} + O(\varepsilon_k^2).$$

Next we show that there exist some $\eta_4 > 0$ and some constant $M_4 > 0$ depending only on U and V such that

(i) $\alpha_{\varepsilon_k} - M_4\varepsilon_k^2 \le \rho_{\varepsilon_k} \le \alpha_{\varepsilon_k} + M_4\varepsilon_k^2, \quad x \in U,$

and

(ii) $\beta_{\varepsilon_k} - M_4\varepsilon_k^2 \leq \rho_{\varepsilon_k} \leq \beta_{\varepsilon_k} + M_4\varepsilon_k^2, \quad x \in V,$

for all $\varepsilon_k < \eta_4$.
This is done by contradiction. We suppose that there exists a sequence $\{\varepsilon_{k_j}\}_{k\in\mathbb{N}}$ and points $x_j \in U$, $j \in \mathbb{N}$, such that

$$\rho_{\varepsilon_{k_j}}(x_j) > \alpha_{\varepsilon_{k_j}} + M_4\varepsilon_{k_j}^2$$

for any $M_4 > 0$. Since $\{\rho_{\varepsilon_{k_j}}\}_{k\in\mathbb{N}}$ converges uniformly to α on $\overline{U}_1$, $U_1 := U \cup \bigcup_{j=1}^{\infty} B_{3d}(x_j)$ and $4d := \operatorname{dist}(U, \Omega\backslash A)$, we may assume that

$$\max_{x\in\overline{U}_1} |\rho_{\varepsilon_{k_j}}(x) - \alpha| < \frac{\delta}{2}$$

for j sufficiently large. Next we proceed similarly as in the proof of Theorem 3.8. To obtain the upper estimate of (i) we just have to replace α by α_{ε_k} and ε_{k_j} by $\varepsilon_{k_j}^2$ in (50), (51), (52) and (53). Thus we end up with the inequality

$$\begin{aligned} 0 \;\geq\; & \triangle g_j(y_j) = \triangle\rho_{\varepsilon_{k_j}}(y_j) - \triangle\varphi_j(y_j) = \frac{W'(\rho_{\varepsilon_{k_j}}(y_j))}{\varepsilon_{k_j}^2} + \frac{d_0 + \lambda_{\varepsilon_{k_j}}}{\varepsilon_{k_j}^2} - \triangle\varphi_j(y_j) \\ = \;& \frac{W'(\alpha_{\varepsilon_{k_j}})}{\varepsilon_{k_j}^2} + \frac{W''(h)}{\varepsilon_{k_j}^2}(\rho_{\varepsilon_{k_j}}(y_j) - \alpha_{\varepsilon_{k_j}}) + \frac{d_0 + \lambda_{\varepsilon_{k_j}}}{\varepsilon_{k_j}^2} - \triangle\varphi_j(y_j), \quad h \in [\alpha-\delta, \alpha+\delta], \\ \geq \;& \frac{M_4}{2} \min_{h\in[\alpha-\delta,\alpha+\delta]} W''(h) - \triangle\varphi_j(y_j) \end{aligned} \tag{55}$$

which cannot be true for $M_4 > 0$ sufficiently large.
The lower estimate and statement (ii) can be established analogously. ■

Now we attain the equilibrium conditions of Theorem 3.2 by straightforward calculation.

Proof of Theorem 3.2:
To (i): We expand g by Taylor's theorem such that we obtain in combination with Theorem 3.1 the following form:

$$g(\rho_{\varepsilon_k}(x)) = g(\rho_{\varepsilon_k}^0(x)) - g'(\rho_{\varepsilon_k}^0(x))\frac{d_0 + \lambda_{\varepsilon_k}}{W''(\rho_{\varepsilon_k}^0(x))} + O(\varepsilon_k^2)$$

Since $g(\rho) = W'(\rho) + d_0$ we have $g(\alpha) = g(\beta) = d_0$ and $g'(\rho) = W''(\rho)$. Hence we yield

$$g(\rho_{\varepsilon_k}(x)) = -\lambda_{\varepsilon_k} + O(\varepsilon_k^2) \quad \text{for } \; x \in U \cup V$$

and the phase equilibrium condition is established.

To (i): From the Maxwell conditions we deduce

$$\alpha\psi(\alpha) = d_0\alpha + d_1 = g(\alpha)\alpha + d_1 \quad \text{and} \quad \beta\psi(\beta) = d_0\beta + d_1 = g(\beta)\beta + d_1.$$

The latter combined with the relation

$$p(\rho_{\varepsilon_k}) = \rho_{\varepsilon_k}^2\psi'(\rho_{\varepsilon_k}) = \rho_{\varepsilon_k}(g(\rho_{\varepsilon_k}) - \psi(\rho_{\varepsilon_k}))$$

gives

$$p(\rho_{\varepsilon_k}^0(x)) = \rho_{\varepsilon_k}^0(x)g(\rho_{\varepsilon_k}^0(x)) - \rho_{\varepsilon_k}^0(x)\psi(\rho_{\varepsilon_k}^0(x)) = -d_1 \quad \text{for} \quad x \in U \cup V.$$

In consequence, we get by means of the relation $p'(\rho) = \rho g'(\rho)$ the mechanical equilibrium condition

$$\begin{aligned}
p(\rho_{\varepsilon_k}(x_2)) - p(\rho_{\varepsilon_k}(x_1)) &= p'(\rho_{\varepsilon_k}^0(x_2))(\rho_{\varepsilon_k}(x_2) - \rho_{\varepsilon_k}^0(x_2)) - \\
&\qquad p'(\rho_{\varepsilon_k}^0(x_1))(\rho_{\varepsilon_k}(x_1) - \rho_{\varepsilon_k}^0(x_1)) + O(\varepsilon_k^2) \\
&= g'(\rho_{\varepsilon_k}^0(x_2))\rho_{\varepsilon_k}^0(x_2)(\rho_{\varepsilon_k}(x_2) - \rho_{\varepsilon_k}^0(x_2)) - \\
&\qquad g'(\rho_{\varepsilon_k}^0(x_1))\rho_{\varepsilon_k}^0(x_1)(\rho_{\varepsilon_k}(x_1) - \rho_{\varepsilon_k}^0(x_1)) + O(\varepsilon_k^2) \\
&= -c_0(n-1)k_m\varepsilon_k + o(\varepsilon_k)
\end{aligned}$$

for $x_1 \in U$ and $x_2 \in V$ as $\varepsilon_k \to 0$. Hence both equilibrium conditions are verified. ∎

Finally we will show that for pressure control only one phase remains in equilibrium.

Proof of Theorem 3.3:
Let $\varepsilon > 0$ be arbitrary but fixed. Since $W \geq 0$ by definition we obtain the lower bound

$$\begin{aligned}
\mathcal{A}_\varepsilon(\rho, \Omega) &= \int_\Omega \Big(\frac{\varepsilon^2}{2}|\nabla\rho(x)|^2 + W(\rho(x))\Big)dx + d_0 m + (d_1 + p_0)|\Omega| \\
&\geq d_0 m + (d_1 + p_0)|\Omega| \geq d_0 m + \min\Big\{\frac{(d_1 + p_0)}{\alpha}, \frac{(d_1 + p_0)}{\beta}\Big\}m.
\end{aligned}$$

Furthermore, for an arbitrary $\Omega \in \mathcal{M}$ we have

$$\int_\Omega \Big(\frac{\varepsilon^2}{2}|\nabla\rho(x)|^2 + W(\rho(x))\Big)dx = 0$$

if and only if $\rho \equiv \alpha$ or $\rho \equiv \beta$ because $\rho \in C^3(\Omega)$. This implies

(i) for $d_1 + p_0 \geq 0$:

$$\mathcal{A}_\varepsilon(\rho, \Omega) = d_0 m + (d_1 + p_0)\frac{m}{\beta} \qquad \text{if and only if} \quad \rho \equiv \beta \text{ and } |\Omega| = \frac{m}{\beta}.$$

(ii) for $d_1 + p_0 \leq 0$:

$$\mathcal{A}_\varepsilon(\rho, \Omega) = d_0 m + (d_1 + p_0)\frac{m}{\alpha} \qquad \text{if and only if} \qquad \rho \equiv \alpha \text{ and } |\Omega| = \frac{m}{\alpha}.$$

■

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