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Sharp limit of the viscous Cahn-Hilliard equation and thermodynamic consistency

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Diffuse and sharp interface models represent two alternatives to describe phase transitions with an interface between two coexisting phases. The two model classes can be independently formulated. Thus there arises the problem whether the sharp limit of the diffuse model fits into the setting of a corresponding sharp interface model. We call a diffuse model admissible if its sharp limit produces interfacial jump conditions that are consistent with the balance equations and the 2nd law of thermodynamics for sharp interfaces. We use special cases of the viscous Cahn-Hilliard equation to show that there are admissible as well as non-admissible diffuse interface models.

1 Introduction

We consider two coexisting phases in a body that are represented by two regions with high and low density. The two region are separated by a moving phase boundary. In order to describe the evolution of that body two alternative models are available. The models are called diffuse interface model and sharp interface model, respectively.

A diffuse interface model describes the phase boundary as an interfacial layer. Here the density smoothly changes from a high to a low value but with a steep gradient [4, 7]. On the other hand, the sharp interface model describes the interfacial layer by the evolution of a hypersurface [1, 2].

Both alternatives can be established independently of each other. However, the physical basis of a sharp interface model consists of simpler assumptions which are more directly related to experiments than the corresponding assumptions that are needed to establish a diffuse interface model. For this reason we consider the sharp model as a reference for a diffuse model in the same physical context.

In this context it is important to know whether the diffuse model embodies the same physics as the sharp model. In order to solve this problem we suggest the following strategy. Let us assume that we have two thermodynamically consistent models of diffuse and sharp interface type, respectively. At first we study the properties of the diffuse model for small values of the interfacial thickness. In order to carry out the sharp limit of the diffuse model, we use the method of formal matched asymptotic analysis, which is a well established tool for the understanding of diffuse models [4, 6, 7, 8]. If a sharp limit exists, we will obtain sharp interface equations as a limiting case of the diffuse model. In a second step we compare the limiting equations of the diffuse model with the corresponding equations of the sharp model. If we find coincidence we call the diffuse model admissible. If there is no coincidence the diffuse model is called non-admissible and has to be rejected.

In this paper we illustrate the described situation by means of the viscous Cahn-Hilliard model

[3, 4, 5]. For the same variables that appear in the viscous Cahn-Hilliard model we establish a corresponding sharp interface model.

Comparing the limiting equations of the diffuse model with the equations of the sharp model leads to an interesting observation. Both models are equipped with local non-negative entropy productions. This property is preserved in the sharp limit of the diffuse model, i.e. the sharp limit of the diffuse dissipation function is non-negative as well. In a next step we use that limit function to calculate the interfacial dissipation function according to the rules of the sharp model. We observe that we do not necessarily obtain a local non-negative interfacial entropy production. In more detail, the two main propositions of this paper read:

1. The sharp limit of the classical Cahn-Hilliard equation without viscosity leads to a negative interfacial entropy production.

2. The sharp limit of the viscous Cahn-Hilliard equation contains a parameter that can be adjusted so that a non-negative interfacial dissipation function results.

This unexpected behavior is a consequence of the fact that the Cahn-Hilliard model without viscosity has a local entropy production that is much smaller in the transition layer than in the bulk regions.

The paper is organized as follows:

In Chapters 2 and 3 we represent our main results by a detailed summary of the paper. In Chapter 2 we introduce the two kinds of models and in Chapter 3 we carefully describe the main propositions.

The Chapter 3 starts with the sharp limit of the viscous Cahn-Hilliard model and a subsequent comparison of the limiting equations with the sharp interface model from Chapter 2. In particular the interfacial entropy production resulting from the sharp limit of the viscous Cahn-Hilliard model is identified by a comparison with the interfacial entropy production of the sharp model.

The Chapters 4 through 7 contain motivations and proofs.

In Chapters 4 and 5 we show thermodynamic consistency of the diffuse and the sharp model, respectively.

Finally Chapters 6 and 7 contain a detailed description of the applied matched asymptotic analysis.

2 Description of diffuse and sharp interface models

We consider a moving interface between two adjacent phases at constant temperature T. Two kinds of models are available. The *diffuse interface* setting considers the interface as a thin region. Here the thermodynamic state suffer a smooth but steep transition between the states characterizing the adjacent bulk domains. The *sharp interface* setting considers the interface as a hypersurface without thickness. Across the interface the thermodynamic state may discontinuously change.

2.1 Diffuse interface setting

We study in one space dimension the evolution of a single concentration $u : [0, \infty) \times \Omega \to \mathbb{R}$, which is described by the viscous Cahn-Hilliard equation,

$$\partial_t u = -\partial_x f \quad \text{with} \quad f = -M\partial_x \left(\mu + \gamma\varepsilon^2\partial_t u\right) \quad \text{and} \quad \mu = F'(u) - \beta\varepsilon^2\partial_{xx}u \,, \tag{1}$$

on $\Omega = [0, 1]$ and with the initial and boundary values

$$u(0, x) = u_0(x), \qquad \partial_x u(t, 0) = \partial_x u(t, 1) = 0, \qquad f(t, 0) = f(t, 1) = 0 \,. \tag{2}$$

The mobility $M > 0$ is a constant. The function $F : [0, 1] \to \mathbb{R}$ is assumed to be a double well function allowing the modeling of a phase transition. The quantity ε is proportional to the thickness of the interfacial region. We are particularly interested in the limit $\varepsilon \to 0$, where $\beta > 0$ and $\gamma \geq 0$ are of order $\mathcal{O}(1)$. In this case there exist a class of initial conditions where a phase transition may appear, and is represented by a single interface between two coexisting phases. These are characterized by low and high values of the concentration u.

The evolution equation (1) generates an inequality for the free energy function $\psi = F(u) + \beta\varepsilon^2|\partial_x u|^2/2$. The inequality reads

$$\partial_t\psi + \partial_x(f(\mu + \gamma\varepsilon^2\partial_t u) - \beta\varepsilon^2\partial_x u\partial_t u) = -T\xi \qquad \text{with} \qquad T\xi = \frac{1}{M}f^2 + \gamma\varepsilon^2(\partial_t u)^2 \geq 0 \,. \tag{3}$$

The quantity ξ is the non-negative entropy production. Many authors call ξ dissipation function.

2.2 Sharp interface setting

Bulk equations. The evolution of two coexisting phases can also be described within a sharp interface setting. Here we consider the case where the space interval $\Omega = [0, 1]$ decomposes into two regions $\Omega^-(t) = [0, x_{\mathrm{I}}(t))$ and $\Omega^+(t) = (x_{\mathrm{I}}(t), 1]$ which are separated by the point x_{I}. The time dependent function $\hat{x}_{\mathrm{I}} : [0, \infty) \to \Omega$ determines the motion of x_{I}. For later use we define $\chi^\pm = \lim_{x\in\Omega^\pm\to x_{\mathrm{I}}} \chi(x)$ denoting limiting values of a generic function χ which lives in Ω^+ and Ω^-, respectively. The double bracket $[\![\chi]\!] = \chi^+ - \chi^-$ denotes the difference of χ at the interface.

We study the evolution equations

$$\partial_t u = -\partial_x f \quad \text{with} \quad f = -M\partial_x\mu \quad \text{and} \quad \mu = F'(u) \qquad \text{for} \quad x \in \Omega^\pm, \tag{4}$$

with a positive constant $M > 0$. It is understood that we may have different functions F in Ω^+ and Ω^-. However, for simplicity this fact is not indicated here. Moreover, we use the same function as defined in the diffuse setting.

The initial boundary value problem in the sharp interface setting considers an initial density and boundary values at the external boundaries

$$u(0, x) = u_0(x), \qquad f(t, 0) = f(t, 1) = 0. \tag{5}$$

Obviously further boundary values at the interface $x_{\rm I}$ are needed. These boundary values rely on various jump conditions that will be formulated in a subsequent paragraph.

In each of the two bulk regions we have a free energy function $\psi = F(u)$. Corresponding to (4), the free energy inequalities in the two bulk regions read

$$\partial_t \psi + \partial_x (f\mu) = -T\xi \qquad \text{and} \qquad T\xi = \frac{1}{M} f^2 \geq 0 \quad \text{for} \quad x \in \Omega^{\pm}. \tag{6}$$

Remark. The described sharp interface model is a simplified version of a model for a two-constituent body with two partial mass densities ρ_1 and ρ_2 and two velocities v_1 and v_2. The simplification concerns the total mass density $\rho = \rho_1 + \rho_2$ and the barycentric velocity $v = (\rho_1 v_1 + \rho_2 v_2)/\rho$. We assume $\rho = 1$ and $v = 0$. Thus the concentration $u = \rho_1/\rho$ is the only mass variable. The two assumptions imply special representations of the mass fluxes $\dot{m}_1 = \rho_1(v_1 - \dot{x}_{\rm I})$ and $\dot{m}_2 = \rho_2(v_2 - \dot{x}_{\rm I})$ across the interface, namely

$$\dot{m}_1^{\pm} = f^{\pm} - u^{\pm}\dot{x}_I \,, \qquad \dot{m}_2^{\pm} = -f^{\pm} - (1-u^{\pm})\dot{x}_I \qquad \text{and} \qquad \dot{m}^{\pm} = \dot{m}_1^{\pm} + \dot{m}_2^{\pm} = -\dot{x}_I \,. \tag{7}$$

Moreover a body with two constituents needs for its description two chemical potentials, whereas only a single chemical potential has appeared up to now. This fact is likewise due to the simplifying assumption that we only consider a single mass variable, namely u in the bulk and $u_{\rm I}$ on the interface. However, even in this case two chemical potentials play a role in the theory. These are introduced here according to the definitions

$$\mu_1 = \psi + (1-u)\mu, \qquad \mu_2 = \psi - u\mu \quad \text{in the bulk,} \tag{8}$$

and

$$\mu_{\rm I,1} = \psi_{\rm I} + (1-u_{\rm I})\mu_{\rm I}, \qquad \mu_{\rm I,2} = \psi_{\rm I} - u_{\rm I}\mu_{\rm I} \quad \text{on the interface.} \tag{9}$$

The quantity $\psi_{\rm I}$ is the interfacial free energy. If it is given by a function $\psi_{\rm I} = \hat{\psi}_{\rm I}(u_{\rm I})$ we have $\mu_{\rm I} = \partial_{u_{\rm I}}\psi_{\rm I}$.

Interface equations. In this study we consider an interface $I(t) = \{\hat{x}_{\rm I}(t)\}$ between Ω^+ and Ω^- that is equipped with mass and energy. The interfacial balance of mass determines the evolution of the interfacial concentration variable $u_{\rm I}$ according to

$$\partial_t u_{\rm I} + [\![\dot{m}u + f]\!] = 0 \,. \tag{10}$$

The corresponding interfacial free energy balance reads

$$\partial_t \psi_{\rm I} + [\![\dot{m}\psi + f\mu]\!] = -T\xi_{\rm I} \,. \tag{11}$$

The right hand side of (11) represents the interfacial dissipation function $\xi_{\rm I}$. In the isothermal case it is given by

$$T\xi_{\rm I} = -[\![\dot{m}_1(\mu_1 - \mu_{\rm I,1}) + \dot{m}_2(\mu_2 - \mu_{\rm I,2})]\!] \geq 0 \,. \tag{12}$$

We proceed with the general case. The three equations (10), (11) and (12) form the basis to obtain the necessary jump conditions for the determination of the four unknowns at the interface.

These are the two interface values of the bulk concentration, $u^{\pm}$, the interfacial concentration u_{I} and the motion $\hat{x}_{\mathrm{I}}$ of the interface.

The jump condition (10) is a generalized Stefan condition, which will be supplemented now by three thermodynamically consistent kinetic relations. These can be chosen so that the inequality (12) is identically satisfied.

To this end we note that the total mass flux $\dot{m}$ turns out to be continuous, implying that (12) can also be written as

$$T\xi_{\mathrm{I}} = -\dot{m}_1^+(\mu^+ - \mu_{\mathrm{I}}) + \dot{m}_1^-(\mu^- - \mu_{\mathrm{I}}) - \dot{m}[\![\mu_2]\!] \geq 0 \,. \tag{13}$$

Allowing cross effects between the different sides of the interface and the two components we choose as kinetic relations

$$\begin{pmatrix} \mu^+ - \mu_{\mathrm{I}} \\ -(\mu^- - \mu_{\mathrm{I}}) \\ [\![\mu_2]\!] \end{pmatrix} = - \begin{pmatrix} \tilde{L}_{11} & \tilde{L}_{12} & \tilde{L}_{13} \\ \tilde{L}_{21} & \tilde{L}_{22} & \tilde{L}_{23} \\ \tilde{L}_{31} & \tilde{L}_{32} & \tilde{L}_{33} \end{pmatrix} \begin{pmatrix} \dot{m}_1^+ \\ \dot{m}_1^- \\ \dot{m} \end{pmatrix} , \tag{14}$$

where the matrix $\tilde{L}$ of kinetic coefficients are assumed to be positive definite.

For the determination of the four unknowns u_{I}, u^+, u^- and $\dot{x}_{\mathrm{I}}$ at the interface, we thus have obtained four equations, viz. (10) and (14).

The special case where the mass flux $\dot{m}_1$ is continuous also becomes important. Here the interfacial mass balance (10) implies a time independent interfacial mass density u_{I}, and the dissipation function (12) reduces to

$$T\xi_{\mathrm{I}} = -\dot{m}_1[\![\mu_1]\!] - \dot{m}_2[\![\mu_2]\!] \geq 0 \,. \tag{15}$$

A simple possibility to satisfy (15) is given by the two kinetic relations

$$\begin{pmatrix} [\![\mu_1]\!] \\ [\![\mu_2]\!] \end{pmatrix} = - \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \dot{m}_1 \\ \dot{m}_2 \end{pmatrix} , \tag{16}$$

with a positive definite matrix L of kinetic coefficients.

For a more detailed description of sharp interface models we refer the interested reader to the textbook [1] and to [2].

3 The sharp limit of the viscous Cahn-Hilliard model

In order to describe a phase transition between two coexisting phases we have introduced two model variants. A diffuse interface model represented by the viscous Cahn-Hilliard equation and a sharp interface setting with equations in the bulk phases and jump conditions at the interface. Our main objective is a comparison of the two settings.

In this section we present the main results of this study. The details of the necessary calculations are found in the subsequent chapters.

3.1 Formal asymptotic expansions

In the sharp limit of a diffuse model the interface between two bulk phases is defined by a hypersurface where the solution of the diffuse model assumes a given value: $I^\varepsilon(t) = \{x \in (0,1) \,:\, u^\varepsilon(t,x) = u_*\}$.

The sharp limit relies on formal series in the small parameter ε. In the bulk phases we write

$$\chi^\varepsilon(t,x) = \chi^{(0)}(t,x) + \varepsilon\chi^{(1)}(t,x) + \varepsilon^2\chi^{(2)}(t,x) + \mathcal{O}(\varepsilon^3), \tag{17}$$

and call this the outer expansion of a generic function χ^ε. In the ε-neighborhood of the interface we introduce an inner coordinate z according to

$$x = x_{\mathrm{I}}^\varepsilon(t) + \varepsilon z\ , \tag{18}$$

and define $\tilde{\chi}^\varepsilon(t,z) = \chi^\varepsilon(t, x_{\mathrm{I}}^\varepsilon(t) + \varepsilon z)$. The formal series

$$\tilde{\chi}^\varepsilon(t,z) = \tilde{\chi}^{(0)}(t,z) + \varepsilon\tilde{\chi}^{(1)}(t,z) + \varepsilon^2\tilde{\chi}^{(2)}(t,z) + \mathcal{O}(\varepsilon^3) \tag{19}$$

is called the inner expansion. The resulting jump conditions at the interface are derived by means of the inner expansion.

3.2 Relations between the diffuse model and the sharp model

We define requirements so that a diffuse model represent an admissible approximation of a sharp model.

The diffuse model (1)-(3) is an admissible approximation of the sharp model (4)-(16) up to order $\mathcal{O}(\varepsilon^k)$ if it has for every initial density u_0 a solution u^ε with the following properties:

1 The expansions (17) and (19) exist.

2 The outer expansions (17) satisfy the bulk equations (4) and (6) of the sharp model up to $\mathcal{O}(\varepsilon^k)$.

3 The expansions (17) and (19) imply representations of the interfacial density u_{I}, the interfacial dissipation function ξ_{I} and the kinetic coefficients L that satisfy the jump conditions (10) - (16) of the sharp model up to $\mathcal{O}(\varepsilon^k)$.

3.3 The order $\mathcal{O}(1)$ equations

In the bulk phases the sharp limit of the viscous Cahn-Hilliard model yields in the leading order $\mathcal{O}(1)$

$$\partial_t u^{(0)} = -\partial_x f^{(0)} \qquad \text{with} \quad f^{(0)} = -M\partial_x\mu^{(0)} \quad \text{for} \quad x \in \Omega^\pm\ , \tag{20}$$

where $\mu^{(0)} = F'(u^{(0)})$ is the corresponding chemical potential.

The resulting free energy balance in the bulk phases is given by

$$\partial_t\psi^{(0)} + \partial_x(f^{(0)}\mu^{(0)}) = -T\xi^{(0)} \qquad \text{with} \qquad T\xi^{(0)} = \frac{1}{M}(f^{(0)})^2 \geq 0 \quad \text{for} \quad x \in \Omega^\pm. \tag{21}$$

In the same order we obtain the following conditions at the interface:

$$\partial_t u_{\mathrm{I}}^{(0)} = 0, \qquad [\![\dot{m}_{1,2}^{(0)}]\!] = 0, \qquad [\![\mu_{1,2}^{(0)}]\!] = 0 \,. \tag{22}$$

These results are used to exploit the interfacial free energy balance (11) and (12) of the sharp model.

$$\partial_t \psi_{\mathrm{I}}^{(0)} = 0, \qquad -T\xi_{\mathrm{I}}^{(0)} = [\![\dot{m}_1^{(0)}\mu_1^{(0)} + \dot{m}_2^{(0)}\mu_2^{(0)}]\!] = 0 \,. \tag{23}$$

Thus in the leading order, the sharp limit of the diffuse model agrees with the sharp interface model. The diffuse model is admissible of order $\mathcal{O}(1)$. However, we find a sharp interface that is in local equilibrium. Note that viscosity does not appear in the leading order $\mathcal{O}(1)$.

Remarks. 1. Representations of the chemical potentials $\mu_{1,2}^{(0),\pm}$ and of the mass fluxes $\dot{m}_{1,2}^{(0),\pm}$ in terms of solutions of the viscous Cahn-Hilliard model are given by (103)-(107).

2. The equations $(22)_{2,3}$ represent two algebraic equations for the interface values $u^{(0),\pm}$. Its graphic solution is called *Maxwell construction*. The equations $(22)_2$ can be written in the form of a Stefan condition, $[\![f^{(0)}]\!] = \dot{x}_{\mathrm{I}}^{(0)}[\![u^{(0)}]\!]$, which serves to determine the interface speed.

3.4 The order $\mathcal{O}(\varepsilon)$ equations

In the bulk phases the sharp limit of the viscous Cahn-Hilliard model yields in the order $\mathcal{O}(\varepsilon)$

$$\partial_t u^{(1)} = -\partial_x f^{(1)} \qquad \text{with} \quad f^{(1)} = -M\partial_x \mu^{(1)} \quad \text{for} \quad x \in \Omega^{\pm} \,, \tag{24}$$

where $\mu^{(1)} = F''(u^{(0)})u^{(1)}$ is the $\mathcal{O}(\varepsilon)$ contribution of the chemical potential.

The resulting free energy balance in the bulk phases in order $\mathcal{O}(\varepsilon)$ reads

$$\partial_t \psi^{(1)} + \partial_x (f\mu)^{(1)} = -T\xi^{(1)} \qquad \text{with} \qquad T\xi^{(1)} = \frac{1}{M}(f^2)^{(1)} \geq 0 \quad \text{for} \quad x \in \Omega^{\pm}. \tag{25}$$

At the interface we obtain in the order $\mathcal{O}(\varepsilon)$ a constant interfacial density and continuous mass fluxes:

$$\partial_t u_{\mathrm{I}}^{(1)} = 0, \qquad [\![\dot{m}_{1,2}^{(1)}]\!] = 0 \,. \tag{26}$$

However, the chemical potentials are not continuous anymore but now are given by kinetic relations:

$$\begin{pmatrix} [\![\mu_1^{(1)}]\!] \\ [\![\mu_2^{(1)}]\!] \end{pmatrix} = -\begin{pmatrix} K_{11} & K_{12} \\ K_{21} & K_{22} \end{pmatrix} \begin{pmatrix} \dot{m}_1^{(0)} \\ \dot{m}_2^{(0)} \end{pmatrix} \,. \tag{27}$$

The matrix K of kinetic in coefficients in (27) is symmetric and has the representation

$$K = \begin{pmatrix} -2A + B + \gamma C & -A + B + \gamma C \\ -A + B + \gamma C & B + \gamma C \end{pmatrix} \,. \tag{28}$$

As in the leading order we use these results to exploit the interfacial free energy balance (11) and (12) of the sharp model. There follows

$$\partial_t \psi_{\mathrm{I}}^{(1)} = 0, \qquad -T\xi_{\mathrm{I}}^{(1)} = \dot{m}_1^{(0)}[\![\mu_1^{(1)}]\!] + \dot{m}_2^{(0)}[\![\mu_2^{(1)}]\!] \,, \tag{29}$$

and with (27) we obtain

$$T\xi_{\mathrm{I}}^{(1)} = K_{11}(\dot{m}_1^{(0)})^2 + (K_{12}+K_{21})\dot{m}_1^{(0)}\dot{m}_2^{(0)} + K_{22}(\dot{m}_2^{(0)})^2 \,. \tag{30}$$

Thus there is only one property missing so that the diffuse model is also an admissible approximation in the order $\mathcal{O}(\varepsilon)$ of the sharp model. This property is the non-negativity of the interfacial entropy production $\xi_{\mathrm{I}}^{(1)}$, which will be discussed in the next sections.

Remarks. 1. The quantities A, B and C in the definition of the matrix K are abbreviations, whose definitions in terms of solutions of the viscous Cahn-Hilliard model are given by (128) and (129). The chemical potentials $\mu_{1,2}^{(1),\pm}$ and mass fluxes $\dot{m}_1^{(1),\pm}$ are defined by (125)-(127) and (118), respectively. The influence of the viscosity of the Cahn-Hilliard model is indicated here by the coefficient γ, see (1).

2. Interfacial density $u_I^{(1)}$ and interfacial dissipation $\xi_I^{(1)}$ function can be calculated from the solution of the viscous Cahn-Hilliard problem according to the equations (116) and (155), respectively.

3. Finally note the remarkable symmetry of the matrix K. It reflects the often postulated Onsager symmetry of kinetic coefficients. Apparently that symmetry is embodied in the viscous Cahn-Hilliard model.

3.5 Entropy production in the sharp limit of the viscous Cahn-Hilliard equation.

The question if the sharp limit of the viscous Cahn-Hilliard equation is an admissible approximation of the sharp model is intimately related to the sign of the interfacial entropy production. In this section we start the corresponding discussion.

Recall that we have $\xi_{\mathrm{I}}^{(0)} = 0$ in the leading order. Thus the non-negativity of the interfacial entropy production must be guaranteed by $\xi_{\mathrm{I}}^{(1)}$. Obviously, $\xi_{\mathrm{I}}^{(1)}$ is non-negative for every mass flux $\dot{m}_{1,2}^{(0)}$ iff the matrix K is positive semi-definite. Before we test that property some preliminary remarks are in order.

Usually the inner expansions of the diffuse model encode the properties of the resulting sharp interface. However, up to now the inner entropy production $\tilde{\xi}^{\varepsilon}$ does not occur. Rather we used the representation of the interfacial entropy production of the sharp model, namely the version (15), and calculated the occurrent mass fluxes and chemical potentials by means of the corresponding limit functions of the diffuse model. In this section we proceed that way. A calculation of the interfacial entropy production by means of $\tilde{\xi}^{\varepsilon}$ will be the subject of the next section.

To simplify the discussion on the definiteness of the matrix K we consider the widely used double well function

$$F(u) = \frac{1}{2}u^2(u-1)^2 \tag{31}$$

and set the Cahn-Hilliard coefficient $\beta = 1$ and the mobility $M = 1$.

The exploitation of the jump conditions $(22)_{4,5}$ leads to

$$u^{(0),-} = 0 \qquad \text{and} \qquad u^{(0),+} = 1 \,. \tag{32}$$

According to the inner equation (97) of the inner concentration, $\tilde{u}^{(0)}$ is given by a simple traveling wave with shift parameter α:

$$\tilde{u}^{(0)} = \frac{1}{2} + \frac{1}{2}\tanh\left(\frac{1}{2}\big(z+\alpha\big)\right). \tag{33}$$

By means of (32), (33) and (116) the interfacial concentration comes out as $u_{\mathrm{I}}^{(1)} = \alpha$. Recall that α is determined by the level set value u_* of the concentration u. Obviously u_* can be arbitrarily chosen within the transition region.

Next we use the definitions (128) and (129) to calculate the quantities A, B and C in the definition of the matrix K. We obtain

$$A = \alpha\,, \qquad B = \alpha - 1 \qquad \text{and} \qquad C = \frac{1}{6}\,. \tag{34}$$

The matrix K then assumes the explicit form

$$K = \begin{pmatrix} -\alpha - 1 + \gamma/6 & -1 + \gamma/6 \\ -1 + \gamma/6 & \alpha - 1 + \gamma/6 \end{pmatrix}. \tag{35}$$

Now it is easy to test if the matrix K is positive semi-definite. At first we consider the classical Cahn-Hilliard model, i.e. $\gamma = 0$. In this case the eigenvalues $\lambda_{1,2}$ of K are

$$\lambda_{1,2} = -1 \pm \sqrt{1+\alpha^2}. \tag{36}$$

We observe that one eigenvalue is negative and we conclude that the Cahn-Hilliard model without viscosity is not an admissible approximation of a sharp model in the order $\mathcal{O}(\varepsilon)$.

The case with viscosity, i.e. $\gamma \neq 0$, yields

$$\lambda_{1,2} = -\Big(1 - \frac{\gamma}{6}\Big) \pm \sqrt{\Big(1 - \frac{\gamma}{6}\Big)^2 + \alpha^2}. \tag{37}$$

For $\alpha \neq 0$ even here there is a negative eigenvalue. However, for $\alpha = 0$ and $\gamma \geq 6$ the eigenvalues are $\{0, \gamma/3 - 2\}$. Thus for $\gamma \geq 6$ there are no negative eigenvalues. Recall, the condition $\alpha = 0$ uniquely determines the level set value u_* and implies a vanishing interfacial concentration, i.e. $u_{\mathrm{I}}^{(1)} = 0$.

We conclude that the sharp limit of the viscous Cahn-Hilliard model generates a non-negative interfacial entropy production capable and is thus an admissible approximation of order $\mathcal{O}(\varepsilon)$ of a sharp interface model.

3.6 Relation between the inner entropy production of the diffuse model and the interfacial entropy production of the sharp model

We proceed with a discussion of the peculiar result but from a different point of view. Here we start from the inner entropy production $\tilde{\xi}^{\varepsilon}$ and study its relation to the interfacial entropy production $\xi_{\mathrm{I}}^{\varepsilon}$ that was calculated in the last section.

The inner version of the representation $(3)_2$ reads

$$T\tilde{\xi}^{\varepsilon} = \frac{1}{M}\big(\tilde{f}^{\varepsilon}\big)^2 + \gamma\big(\varepsilon\partial_t\tilde{u}^{\varepsilon} - \dot{x}_I^{\varepsilon}\partial_z\tilde{u}^{\varepsilon}\big)^2 \geq 0\,. \tag{38}$$

Obviously, the limit $\varepsilon \to 0$ will not change the sign of the leading term. We obtain

$$T\tilde{\xi}^{(0)} = \frac{1}{M}\big(\tilde{f}^{(0)}\big)^2 + \gamma\big(\dot{x}_I^{(0)}\partial_z\tilde{u}^{(0)}\big)^2 \geq 0\,. \tag{39}$$

Next we relate the non-negative entropy production $\tilde{\xi}^{(0)}$ to the interfacial entropy production (15) of the sharp model. Recall that its approximation $\xi_{\mathrm{I}}^{(1)}$, see (29), was obtained as follows. We calculated mass fluxes and chemical potentials from the diffuse model in the corresponding orders and inserted the results into (15) to obtain (29). In Section 7 we show that the same result follows from the relation (155), viz.

$$\xi_{\mathrm{I}}^{(1)} = \int_{-\infty}^{0} \tilde{\xi}^{(0)} - \xi^{(0),-}\,dz + \int_{0}^{+\infty} \tilde{\xi}^{(0)} - \xi^{(0),+}\,dz\,. \tag{40}$$

We observe that the sign of $\tilde{\xi}^{(0)}$ does not determine the sign of $\xi_{\mathrm{I}}^{(1)}$.

Next we use a graphic interpretation of the relation (40) to rederive its sign. To this end we use a further result of the asymptotics, namely (133),

$$-\dot{x}_I^{(0)}\tilde{u}^{(0)} + \tilde{f}^{(0)} = c_0\,, \tag{41}$$

which is the basis for the Stefan condition. The constant c_0 is given by $c_0 = \dot{m}_1^{(0),\pm}$.

Elimination of the flux in (39) yields

$$T\tilde{\xi}^{(0)} = \frac{1}{M}\big(\dot{x}_I^{(0)}\tilde{u}^{(0)} + c_0\big)^2 + \gamma\big(\dot{x}_I^{(0)}\partial_z\tilde{u}^{(0)}\big)^2 \geq 0\,. \tag{42}$$

We exploit this representation by means of the explicit density $\tilde{u}^{(0)}$ from the last section, (33). In this case it is also easy to determine the interface values of the bulk dissipation $\xi^{(0),\pm} = \lim_{z\to\pm\infty}\tilde{\xi}^{(0)}$. There results an explicit representation of $\tilde{\xi}^{(0)}$ depending on the parameter $c_0/\dot{x}_I^{(0)}$.

At we consider again the classical Cahn-Hilliard case with $\gamma = 0$. A short calculation shows that there are two different regimes depending on the value of $c_0/\dot{x}_I^{(0)}$. In the first regime $\tilde{\xi}^{(0)}$ is non-monotone and its global minimum is small than the dissipation $\xi^{(0),\pm}$ of the bulk phases at the interface. In the second regime $\tilde{\xi}^{(0)}$ is monotone. The two cases are depicted in Figure 1.

Obviously the interfacial entropy production must be non-negative for any choice of the parameter $c_0/\dot{x}_I^{(0)}$. This violated in the non-monotone case that represent in the left Figure. At first glance one might try to shift the parameter α to generate a positive value of $\xi_{\mathrm{I}}^{(1)}$. However, this shift will lead to a conflict for the monotone case in Figure 1 right.

The viscous Cahn-Hilliard equation, i.e. $\gamma \neq 0$, is more complicated, because $\xi_I^{(1)}$ additionally depends on the gradient $\tilde{u}^{(0)}$. The Figure 2 again shows two possible variants. Also here it is possible to choose $c_0/\dot{x}_I^{(0)}$ so that the entropy production becomes negative. However, the proof the last section shows that for $\alpha = 0$ and $\gamma > 6$ every choice of $c_0/\dot{x}_I^{(0)}$ leads to a non-negative entropy production.

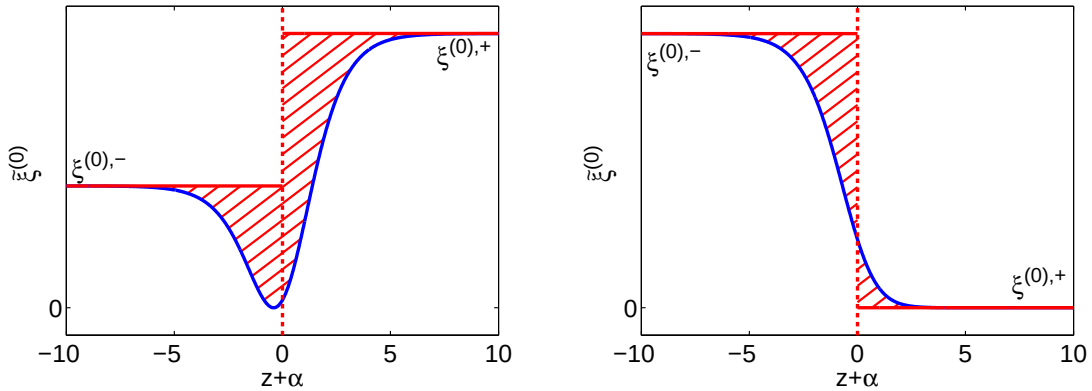

Figure 1: Blue: $\xi^{(0),\pm}$, Shaded areas indicate $\xi_{\mathrm{I}}^{(1)}$, Left: $\gamma = 0$ and $c_0/\dot{x}_I^{(0)} = -0.4$ Right: $\gamma = 0$ and $c_0/\dot{x}_I^{(0)} = -1$

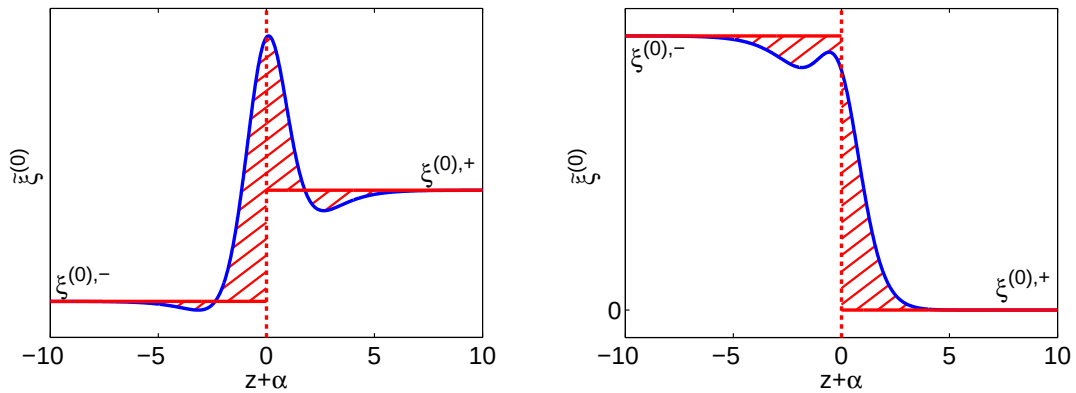

Figure 2: Blue: $\xi^{(0),\pm}$, Shaded areas indicate $\xi_{\mathrm{I}}^{(1)}$, Left: $\gamma = 10$ and $c_0/\dot{x}_I^{(0)} = -0.4$ Right: $\gamma = 10$ and $c_0/\dot{x}_I^{(0)} = -1$

4 Thermodynamics of the diffuse interface setting

In this chapter we start the motivations and proofs of the propositions of the previous chapters. The proof of thermodynamic consistency of the viscous Cahn-Hilliard model starts from a more general model where variations of temperature are allowed.

Basic variables. We consider a body $\Omega \subset \mathbb{R}$ whose thermodynamic state at time $t \geq 0$ is described in every point $x \in \Omega$ by two variables. These are the concentration $u : [0, \infty) \times \Omega \to \mathbb{R}$ and the (internal) energy density $e : [0, \infty) \times \Omega \to \mathbb{R}_+$.

Conservation laws. The descriptions of the phenomena relies on the conservation laws for concentration and energy

$$\partial_t u + \partial_x f = 0, \qquad \text{and} \qquad \partial_t e + \partial_x q = 0\,. \tag{43}$$

The functions $f : [0,\infty) \times \Omega \to \mathbb{R}$ and $q : [0,\infty) \times \Omega \to \mathbb{R}$ are the diffusion flux and the heat flux, respectively.

These quantities are related to the variables by thermodynamically consistent constitutive functions. In general the constitutive quantities may depend on e and u and on their derivatives. Next we derive explicit constitutive function that are compatible with the 2nd law of thermodynamics.

The 2nd law of thermodynamics. The following four axioms embody a simplified version of the 2nd law of thermodynamics. The Axioms I and II contain universal statements, whereas Axioms III and IV describe the properties of the material at hand.

I There exist an entropy density/entropy flux pair (η, φ) that satisfies an equation of balance

$$\partial_t \eta + \partial_x \varphi = \xi. \tag{44}$$

II The entropy flux has to be determined so that the entropy production ξ is equipped with the following properties:

(i) ξ is non-negative for every solution of the system of balance equations (43)$_{1,2}$,

(ii) ξ is represented by a sum of binary products *flux* $\times$ *driving force*:

$$\xi = \sum_{A=1}^{N} F_A D_A \geq 0. \tag{45}$$

(iii) ξ is zero in equilibrium.

III Our constitutive model relies on an entropy density that is given by a concave constitutive function of the general form

$$\eta = h(e, u, u_x) \qquad \text{with} \quad u_x = \partial_x u\,. \tag{46}$$

IV (Absolute) temperature and the chemical potential are defined by

$$\frac{1}{T} = \frac{\partial h}{\partial e} \qquad \text{and} \qquad \frac{\mu}{T} = -\left(\frac{\partial h}{\partial u} - \partial_x \frac{\partial h}{\partial u_x}\right). \tag{47}$$

Exploitation of the 2nd law of thermodynamics. In this section we present a possible constitutive model that is compatible with the four axioms. At first we calculate the dissipation function. To this end we insert the entropy function (46) into (44), carry out the time derivative and substitute the time derivatives of e and u by the corresponding equations of balance. After rearranging of terms we obtain

$$\xi = \partial_x \left(\varphi - \frac{q}{T} + \frac{\mu f}{T} + \frac{\partial h}{\partial u_x}\partial_t u\right) + q\partial_x\left(\frac{1}{T}\right) - f\partial_x\left(\frac{\mu}{T}\right)\,. \tag{48}$$

If we were to proceed in the usual way we would end up with the classical Cahn-Hilliard model without viscosity. In order to introduce viscosity we consider the identity

$$\frac{1}{T}(\partial_t u)^2 + \partial_x\Big(\frac{f\partial_t u}{T}\Big) - f\partial_x\Big(\frac{\partial_t u}{T}\Big) = 0\,, \tag{49}$$

which follows by multiplying the concentration balance (43)$_1$ with $\partial_t u/T$. Next we multiply the identity by a constant γ and add the expression to the dissipation function, which then reads

$$\xi = \partial_x \left(\varphi - \frac{q}{T} + \frac{(\mu + \gamma \partial_t u) f}{T} + \frac{\partial h}{\partial u_x} \partial_t u \right) + q \partial_x \left(\frac{1}{T} \right) - f \partial_x \left(\frac{\mu + \gamma \partial_t u}{T} \right) + \frac{\gamma}{T} (\partial_t u)^2 \,. \tag{50}$$

Now we choose the entropy flux as

$$\varphi = \frac{q}{T} - \frac{(\mu + \gamma \partial_t u) f}{T} - \frac{\partial h}{\partial u_x} \partial_t u \,. \tag{51}$$

This choice implies the entropy production

$$\xi = q \partial_x \left(\frac{1}{T} \right) - f \partial_x \left(\frac{\mu + \gamma \partial_t u}{T} \right) + \frac{\gamma}{T} (\partial_t u)^2 \,. \tag{52}$$

Thus there is entropy production due to (i) heat conduction, (ii) diffusion and (iii) viscosity. The non-negativity of ξ is guaranteed by $\gamma \geq 0$ and the simple constitutive laws

$$q = a \partial_x \left(\frac{1}{T} \right) \quad \text{and} \quad f = -M \partial_x \left(\frac{\mu + \gamma \partial_t u}{T} \right) \qquad \text{with} \quad a > 0, \quad M > 0 \,. \tag{53}$$

Balance equation of the free energy. For applications the energy density e is usually replaced by the temperature T as a variable. That substitution is accompanied by a Legendre transform of the entropy density. To this end we introduce the free energy density $\psi = e - Th$ as a function of (T, u, u_x). In terms of ψ, the chemical potential and the entropy flux can be rewritten as

$$\mu = \frac{\partial \psi}{\partial u} - T \partial_x \left(\frac{1}{T} \frac{\partial \psi}{\partial u_x} \right) \quad \text{and} \quad \varphi = \frac{q}{T} - f \frac{\mu + \gamma \partial_t u}{T} + \frac{1}{T} \frac{\partial \psi}{\partial u_x} \partial_t u \,. \tag{54}$$

In the isothermal case, i.e. $T = \text{const.}$, the entropy balance can easily be rewritten as a balance for the free energy. It results from a combination of the balance equations for energy and entropy and the relations (54). The balance equation for the free energy comes out as

$$\partial_t \psi + \partial_x \left(f(\mu + \gamma \partial_t u) - \frac{\partial \psi}{\partial u_x} \partial_t u \right) = -T \xi \,. \tag{55}$$

The viscous Cahn-Hilliard equation. We proceed with the isothermal case where our problem is reduced to solve a single PDE for the concentration. The PDE follows from the diffusion flux (53)$_2$ and the balance law (43)$_1$. We obtain

$$\partial_t u = M \partial_{xx} (\mu + \gamma \partial_t u) \quad \text{with} \quad \mu = \frac{\partial \psi}{\partial u} - \partial_x \left(\frac{\partial \psi}{\partial u_x} \right) \,. \tag{56}$$

The free energy density is chosen to be of van der Waals type, viz.

$$\psi = F(u) + \frac{\beta}{2} |\partial_x u|^2 \,, \tag{57}$$

with the positive constant β and a double well function $F : [0,1] \to \mathbb{R}$. In this case (56) becomes the viscous Cahn-Hilliard equation

$$\partial_t u = -\partial_x f \quad \text{with} \quad f = -M \partial_{xx} (\mu + \gamma \partial_t u) \quad \text{and} \quad \mu = F'(u) - \beta \partial_{xx} u \,. \tag{58}$$

5 Thermodynamics of the sharp interface setting

A further approach to describe the evolution of two coexisting phases is a sharp interface setting. Note, this approach is independent of a diffuse interface model.

Basic variables. We decompose the body $\Omega = [0,1]$ into two bulk regions $\Omega^+(t)$ and $\Omega^-(t)$, which are separated by the interface, i.e. by the point x_{I} in the 1D case. The time dependent function $\hat{x}_{\mathrm{I}} : [0,\infty) \to \Omega$ determines the motion of x_{I}.

In the two bulk regions $\Omega^\pm$ the thermodynamic state is described by the concentrations $u : [0,\infty) \times \Omega^\pm \to \mathbb{R}$ and the (internal) energy density $e : [0,\infty) \times \Omega^\pm \to \mathbb{R}_+$. The objective of the sharp interface setting is the determination of the basic variables in the two bulk regions and of the position of the *interface* $\hat{x}_{\mathrm{I}}(t)$.

Conservation laws. In the bulk regions $\Omega^\pm$ we have the conservation laws for concentration and energy as before, viz.

$$\partial_t u + \partial_x f = 0, \qquad \text{and} \qquad \partial_t e + \partial_x q = 0 \; . \tag{59}$$

Across the interface the corresponding conservation laws read

$$\partial_t u_{\mathrm{I}} + [\![\dot{m}_1]\!] = 0 \qquad \text{and} \qquad \partial_t e_{\mathrm{I}} + [\![e\dot{m} + q]\!] = 0 \; . \tag{60}$$

There are two mass fluxes at the interface, namely

$$\dot{m}_1^\pm = f^\pm - u^\pm \dot{x}_I \; , \qquad \dot{m}_2^\pm = -f^\pm - (1-u^\pm)\dot{x}_I \qquad \text{and} \qquad \dot{m}^\pm = \dot{m}_1^\pm + \dot{m}_2^\pm = -\dot{x}_I \; . \tag{61}$$

Furthermore the interface is equipped with surface densities $u_{\mathrm{I}} : [0,\infty) \to \mathbb{R}$ and $e_{\mathrm{I}} : [0,\infty) \to \mathbb{R}^+$.

In the sharp interface setting we need constitutive laws for the fluxes f and q in the bulk regions and for the mass fluxes $\dot{m}_1^\pm$ and $\dot{m}$ at the interface. Next we derive explicit constitutive function that are compatible with the 2nd law of thermodynamics.

The 2nd law of thermodynamics for the bulk. In the sharp interface setting, exclusively the constitutive axiom III is changed. The other axioms of the 2nd law of thermodynamics remain the same as in the diffuse setting. We have now

Axiom III: For our model body the entropy density is given by a concave constitutive function of the general form

$$\eta = h(e,u) \; . \tag{62}$$

Note that the space derivative of u does not appear here in the sharp setting.

Exploitation. The resulting constitutive equations can be read off from the corresponding equations of the diffuse setting. The entropy flux is now chosen by

$$\varphi = \frac{q - \mu f}{T} \; , \tag{63}$$

and the entropy production is represented by only two dissipative mechanisms:

$$\xi = q\partial_x\left(\frac{1}{T}\right) - f\partial_x\left(\frac{\mu}{T}\right) \; . \tag{64}$$

Consequently, the constitutive laws for the fluxes of heat and diffusion are

$$q = a\partial_x\left(\frac{1}{T}\right) \quad \text{and} \quad f = -M\partial_x\left(\frac{\mu}{T}\right) \qquad \text{with} \quad a > 0, \quad M > 0\,. \tag{65}$$

The 2nd law of thermodynamics for the interface. In an analogous manner to the bulk we give the corresponding axioms, that constitute the 2nd law of thermodynamics for the interface.

I There exist an entropy density/entropy flux pair $(\eta_{\rm I}, \varphi_{\rm I})$ satisfying an equation of balance

$$\partial_t \eta_{\rm I} + [\![\eta \dot{m} + \varphi]\!] = \xi_{\rm I}. \tag{66}$$

Note, that there is no (tangential) entropy flux $\varphi_{\rm I}$ in the 1D case.

II The interfacial entropy production $\xi_{\rm I}$ is equipped with the following properties:

(i) $\xi_{\rm I}$ is non-negative for every solution of the system of balance equations $(60)_{1,2}$,

(ii) $\xi_{\rm I}$ is represented by a sum of binary products *flux* $\times$ *driving force*:

$$\xi_{\rm I} = [\![\sum_{A=1}^{N} F_A D_A]\!] \geq 0. \tag{67}$$

(iii) $\xi_{\rm I}$ is zero in equilibrium.

III Our constitutive model relies on an entropy density that is given by a concave constitutive function of the general form

$$\eta_{\rm I} = h_{\rm I}(e_{\rm I}, u_{\rm I})\,. \tag{68}$$

IV Interfacial temperature and interfacial chemical potential are defined by

$$\frac{1}{T_{\rm I}} = \frac{\partial h_{\rm I}}{\partial e_{\rm I}} \qquad \text{and} \qquad \frac{\mu_{\rm I}}{T_{\rm I}} = -\frac{\partial h_{\rm I}}{\partial u_{\rm I}}\,. \tag{69}$$

Axioms I and II are universal statements about the properties of entropy density, entropy flux and entropy production. The Axiom III assumes that the entropy is a constitutive quantity that must be given by a material dependent constitutive function. For the case at hand that constitutive function is used in Axiom IV to give definitions of temperature and the chemical potential at the interface.

Exploitation of the interfacial 2nd law of thermodynamics. We calculate now the interfacial entropy production $\xi_{\rm I}$. To this end we start with (66) and insert here the function (68) and the entropy flux (63) for the bulk. The time derivatives are eliminated by the balance laws (60), and after some rearrangements we obtain the structure of the interfacial entropy as it is stated by Axiom II:

$$\xi_{\rm I} = [\![(e\dot{m} + q)\big(\frac{1}{T} - \frac{1}{T_{\rm I}}\big)]\!] - [\![\dot{m}_1\big(\frac{\mu_1}{T} - \frac{\mu_{\rm I,1}}{T_{\rm I}}\big)]\!] - [\![\dot{m}_2\big(\frac{\mu_2}{T} - \frac{\mu_{\rm I,2}}{T_{\rm I}}\big)]\!]\,. \tag{70}$$

Balance equation of the interfacial free energy. We introduce the free energy density $\psi_{\rm I} = e_{\rm I} - T_{\rm I} h_{\rm I}$ as a function of $(T_{\rm I}, u_{\rm I})$. Now we consider again the isothermal case, i.e. $T^+ = T^- =$

$T_{\rm I}$, and substitute in (66) the interfacial entropy by $\psi_{\rm I}$. The time derivative of $e_{\rm I}$ will be eliminated by $(60)_2$. After some rearrangement of terms we obtain the balance equation of the interfacial free energy,

$$\partial_t \psi_{\rm I} + [\![\psi \dot{m} + \mu f]\!] = -T\xi_{\rm I} \,. \tag{71}$$

There is usefull alternative to represent the jump bracket in (71) by

$$[\![\psi \dot{m} + \mu f]\!] = [\![\dot{m}_1 \mu_1 + \dot{m}_2 \mu_2]\!] \,. \tag{72}$$

The identity (72) relies on (7) and (8).

6 Formal asymptotic analysis of the isothermal viscous Cahn-Hilliard model

Objectives. The viscous Cahn-Hilliard model (58) contains two constitutive constants β and γ. We are interested here in the case where these constants are small. This is indicated by the substitutions $\beta \to \varepsilon^2\beta$ and $\gamma \to \varepsilon^2\gamma$ with β and γ now of order $\mathcal{O}(1)$. Thus we consider

$$\partial_t u = -\partial_x f \quad \text{with} \quad f = -M\partial_x \big(\mu + \gamma\varepsilon^2\partial_t u\big) \quad \text{and} \quad \mu = F'(u) - \beta\varepsilon^2\partial_{xx}u \,. \tag{73}$$

This equation is equipped with a free energy inequality, viz.

$$\partial_t\Big(F(u) + \frac{\beta\varepsilon^2}{2}|\partial_x u|^2\Big) + \partial_x\big(f(\mu + \gamma\varepsilon^2\partial_t u) - \beta\varepsilon^2\partial_x u\,\partial_t u\big) = -T\xi \,, \tag{74}$$

where the dissipation function is given by

$$T\xi = \frac{1}{M}f^2 + \gamma(\partial_t u)^2 \geq 0 \,. \tag{75}$$

The objective of this chapter is a study of the sharp limit $\varepsilon \to 0$ of the viscous Cahn-Hilliard equation (73) and of free energy inequality (74), respectively.

In particular we give a detailed comparison of the sharp limit of the viscous Cahn-Hilliard equation with the sharp interface model of the previous section.

The rules of formal asymptotic analysis. We assume that an initial and boundary value problem for the viscous Cahn-Hilliard model (1) has a solution $u^\varepsilon(t,x)$ with the following properties:

1 u^ε develops a transition layer with smooth but steep gradient between two adjacent bulk phases.

2 We choose a value u_* lying in the transition layer, and assume the existence of an interface that is here defined by

$$I^\varepsilon(t) = \{x \in (0,1) \,:\, u^\varepsilon(t,x) = u_*\} \,. \tag{76}$$

3 The interface I^ε at the position $x_{\rm I}^\varepsilon \in C^1([0,\infty),\mathbb{R})$ generates two regions $\Omega^\pm$ with $\Omega^- = [0, x_I^\varepsilon]$ and $\Omega^+ = [x_{\rm I}^\varepsilon, 1]$.

4 Away from I^ε, i.e. in the bulk phases, we assume the existence of an *outer expansion*

$$u^\varepsilon(t,x) = u^{(0)}(t,x) + \varepsilon u^{(1)}(t,x) + \mathcal{O}(\varepsilon^2) \; . \tag{77}$$

5 In the ε-neighborhood of I^ε we introduce a inner coordinate z according to

$$x = x_{\mathrm{I}}^\varepsilon + \varepsilon z \tag{78}$$

and define the inner variable by

$$\tilde{u}^\varepsilon(t,z) = u^\varepsilon(t, x_{\mathrm{I}}^\varepsilon(t) + \varepsilon z) \; . \tag{79}$$

6 The definition (79) implies the following transformation of derivatives:

$$\partial_x u^\varepsilon = \frac{1}{\varepsilon}\partial_z \tilde{u}^\varepsilon \quad \text{and} \quad \partial_t u^\varepsilon = \partial_t \tilde{u}^\varepsilon - \frac{1}{\varepsilon}\dot{x}_{\mathrm{I}}\partial_z \tilde{u}^\varepsilon \; . \tag{80}$$

7 Near to I^ε we assume the existence of an *inner expansion*

$$\tilde{u}^\varepsilon(t,z) = \tilde{u}^{(0)}(t,z) + \varepsilon \tilde{u}^{(1)}(t,z) + \varepsilon^2 \tilde{u}^{(2)}(t,z) + \mathcal{O}(\varepsilon^3) \; . \tag{81}$$

8 Correspondingly we assume the existence of an expansion of the interface position

$$x_{\mathrm{I}}^\varepsilon(t) = x_{\mathrm{I}}^{(0)}(t) + \varepsilon x_{\mathrm{I}}^{(1)}(t) + \mathcal{O}(\varepsilon^2) \; . \tag{82}$$

9 Matching conditions between inner and outer quantities are based on (79). We insert here the expansions (77), (81) and (82) and consider the limit $\varepsilon \to 0$, $z \to \infty$ with $\varepsilon z^n \to 0$ ($n \in \mathbb{N}_0$) to obtain the asymptotic correspondences

$$\tilde{u}^{(0)}(t,z) \overset{z\to\pm\infty}{\to} u^{(0),\pm}(t, x_{\mathrm{I}}^{(0)}) \; , \tag{83}$$

$$\partial_z \tilde{u}^{(0)}(t,z) \overset{z\to\pm\infty}{\to} 0 \; , \tag{84}$$

$$\partial_{zz} \tilde{u}^{(0)}(t,z) \overset{z\to\pm\infty}{\to} 0 \; , \tag{85}$$

$$\tilde{u}^{(1)}(t,z) - \partial_x u^{(0),\pm}(t, x_{\mathrm{I}}^{(0)})(z + x_{\mathrm{I}}^{(1)}) \overset{z\to\pm\infty}{\to} u^{(1),\pm}(t, x_{\mathrm{I}}^{(0)}) \; , \tag{86}$$

$$\partial_z \tilde{u}^{(1)}(t,z) \overset{z\to\pm\infty}{\to} \partial_x u^{(0),\pm}(t, x_{\mathrm{I}}^{(0)}) \; , \tag{87}$$

$$\partial_{zz} \tilde{u}^{(1)}(t,z) \overset{z\to\pm\infty}{\to} 0 \; , \tag{88}$$

$$\partial_z \tilde{u}^{(2)}(t,z) - \partial_{xx} u^{(0),\pm}(t, x_{\mathrm{I}}^{(0)})(z + x_{\mathrm{I}}^{(1)}) \overset{z\to\pm\infty}{\to} \partial_x u^{(1),\pm}(t, x_{\mathrm{I}}^{(0)}) \; , \tag{89}$$

$$\partial_{zz} \tilde{u}^{(2)}(t,z) \overset{z\to\pm\infty}{\to} \partial_{xx} u^{(0),\pm}(t, x_{\mathrm{I}}^{(0)}) \; , \tag{90}$$

$$\partial_{zzz} \tilde{u}^{(2)}(t,z) \overset{z\to\pm\infty}{\to} 0 \; , \tag{91}$$

$$\partial_t \tilde{u}^{(0)}(t,z) - \partial_x u^{(0),\pm}(t, x_{\mathrm{I}}^{(0)})\dot{x}_{\mathrm{I}}^{(0)} \overset{z\to\pm\infty}{\to} \partial_t u^{(0),\pm}(t, x_{\mathrm{I}}^{(0)}) \; . \tag{92}$$

In order to obtain these matching conditions we follow the scheme that is described in [7, 4]. It starts by inserting the inner and outer expansions into (79) and $(80)_2$, respectively.

$$\begin{aligned}
&\tilde{u}^{(0)}(t,z) + \varepsilon\tilde{u}^{(1)}(t,z) + \varepsilon^2\tilde{u}^{(2)}(t,z) + \mathcal{O}(\varepsilon^3) \\
= \;& u^{(0)}(t,x_{\mathrm{I}}^{(0)}) + \varepsilon\left(u^{(1)}(t,x_{\mathrm{I}}^{(0)}) + \partial_x u^{(0)}(t,x_{\mathrm{I}}^{(0)})(x_{\mathrm{I}}^{(1)}+z)\right) \\
&+\varepsilon^2\left(u^{(2)}(t,x_{\mathrm{I}}^{(0)}) + \partial_x u^{(1)}(t,x_{\mathrm{I}}^{(0)})(x_{\mathrm{I}}^{(1)}+z)\right) \\
&+\frac{\varepsilon^2}{2}\left(\partial_{xx}u^{(0)}(t,x_{\mathrm{I}}^{(0)})(x_{\mathrm{I}}^{(1)}+z)^2 + 2\partial_x u^{(0)}(t,x_{\mathrm{I}}^{(0)})x_{\mathrm{I}}^{(2)}\right) + \mathcal{O}(\varepsilon^3)
\end{aligned} \tag{93}$$

The matching conditons (83)–(92) follow by comparing terms of power ε^n.

The bulk equations according to the outer setting.

We insert the outer expansion (77) in the viscous Cahn-Hilliard equation (73) and obtain in orders $\mathcal{O}(1)$ and $\mathcal{O}(\varepsilon)$, respectively,

$$\partial_t u^{(0)} = -\partial_x f^{(0)}\,, \qquad \partial_t u^{(1)} = -\partial_x f^{(1)} \quad \text{for} \quad x \in \Omega^{\pm}\,. \tag{94}$$

The fluxes are

$$f^{(0)} = -M\partial_x\mu^{(0)}\,, \qquad f^{(1)} = -M\partial_x\mu^{(1)}\,, \tag{95}$$

with $\mu^{(0)} = F'(u^{(0)})$ and $\mu^{(1)} = F''(u^{(0)})u^{(1)}$. The initial boundary value problem for (94) needs equations that describe the jump of the variables across the interface between Ω^+ and Ω^-. Furthermore we need equations describing the motion of the interface. These equations will be derived next.

Equations of the inner setting.

The jump conditions and the interface motion are encoded by the viscous Cahn-Hilliard equation (1) in the inner setting. It results from a transformation of the derivatives in (1) by means of the rules (80):

$$\partial_t\tilde{u}^{\varepsilon} - \frac{\dot{x}_{\mathrm{I}}^{\varepsilon}}{\varepsilon}\partial_z\tilde{u}^{\varepsilon} + \frac{1}{\varepsilon}\partial_z\tilde{f}^{\varepsilon} = 0\,. \tag{96}$$

Here we introduce the inner expansion (81) and obtain in the leading order $\mathcal{O}(\varepsilon^{-2})$

$$\partial_z(\tilde{\mu}^{(0)} - \beta\partial_{zz}\tilde{u}^{(0)}) = 0 \quad \text{with} \quad \tilde{\mu}^{(0)} = F'(\tilde{u}^{(0)})\,. \tag{97}$$

In the next order, viz. $\mathcal{O}(\varepsilon^{-1})$, we have

$$-\dot{x}_I^{(0)}\partial_z\tilde{u}^{(0)} + \partial_z\tilde{f}^{(0)} = 0 \tag{98}$$

with the zeroth order flux

$$\tilde{f}^{(0)} = -M\partial_z\left(\tilde{\mu}^{(1)} - \beta\partial_{zz}\tilde{u}^{(1)} - \gamma\dot{x}_I^{(0)}\partial_z\tilde{u}^{(0)}\right) \quad \text{and} \quad \tilde{\mu}^{(1)} = F''(\tilde{u}^{(0)})\tilde{u}^{(1)}\,. \tag{99}$$

Finally we identify the equations of order $\mathcal{O}(1)$. These read

$$\partial_t \tilde{u}^{(0)} - (\dot{x}_I \partial_z \tilde{u})^{(1)} + \partial_z \tilde{f}^{(1)} = 0 \tag{100}$$

with the first order flux

$$\tilde{f}^{(1)} = -M\partial_z \left(\tilde{\mu}^{(2)} - \beta \partial_{zz} \tilde{u}^{(2)} + \gamma \partial_t \tilde{u}^{(0)} - \gamma \big(\dot{x}_I^{(1)} \partial_z \tilde{u}^{(0)} + \dot{x}_I^{(0)} \partial_z \tilde{u}^{(1)} \big) \right) \tag{101}$$

and the second order chemical potential

$$\tilde{\mu}^{(2)} = \frac{1}{2} F'''(\tilde{u}^{(0)})(\tilde{u}^{(1)})^2 + F''(\tilde{u}^{(0)})\tilde{u}^{(2)} \ . \tag{102}$$

The interface conditions of the leading order problem (94)$_1$.

The $\mathcal{O}(\varepsilon^{-2})$ equation (97) of the inner setting yields the discontinuities of $u^{(0)}$ at the interface between Ω^+ and Ω^-:

$$[\![\mu_1^{(0)}]\!] = 0 \quad \text{with} \quad \mu_1^{(0),\pm} = -F(u^{(0),\pm}) - (1 - u^{(0),\pm})F'(u^{(0),\pm}) \tag{103}$$

$$[\![\mu_2^{(0)}]\!] = 0 \quad \text{with} \quad \mu_2^{(0),\pm} = F(u^{(0),\pm}) - u^{(0),\pm}F'(u^{(0),\pm}) \ . \tag{104}$$

Thus the difference $\mu = \mu_1 - \mu_2$ is also continuous:

$$[\![\mu^{(0)}]\!] = 0 \quad \text{with} \quad \mu^{(0),\pm} = F'(u^{(0),\pm}) \tag{105}$$

From the $\mathcal{O}(\varepsilon^{-1})$ equation (98) we obtain

$$[\![\dot{m}_1^{(0)}]\!] = 0 \quad \text{with} \quad \dot{m}_1^{(0),\pm} = f^{(0),\pm} - \dot{x}_I^{(0)} u^{(0),\pm} \ . \tag{106}$$

The jump conditions (105) and (104) represent two algebraic equations for the limiting values $u^{(0),\pm}$. Their explicit determination relies on the observation that according to (105) the slopes of the free energy density at $u^{(0),\pm}$ must be equal, whereas (104) is a statement on the secant of the two points, which must have the same slope as the tangents. These rules are known as Maxwells common tangent construction.

The equations (106) imply the classical Stefan condition. It states the continuity of the mass flux $\dot{m}_1$ in the leading order. As a consequence of (106) we also have the continuity of the mass flux $\dot{m}_2$ in the same order:

$$[\![\dot{m}_2^{(0)}]\!] = 0 \quad \text{with} \quad \dot{m}_2^{(0),\pm} = -f^{(0),\pm} - \dot{x}_I^{(0)}(1 - u^{(0),\pm}). \tag{107}$$

Derivation of the interface conditions of the leading order problem (94)$_1$. The integration of (97) leads to

$$\tilde{\mu}^{(0)} - \beta \partial_{zz} \tilde{u}^{(0)} = c \quad \text{with} \quad c = \mu^{(0),\pm}. \tag{108}$$

The equality (108)$_2$ is a consequence of the matching conditions (83) and (85). Thus $\mu^{(0)}$ is continuous as it is stated by (105).

Next we multiply (97) by $\tilde{u}^{(0)}$ to generate a further integral, which follows from the identity $\partial_x(F(u^\varepsilon) - u^\varepsilon F'(u^\varepsilon)) = -u^\varepsilon \partial_x F'(u^\varepsilon)$. The integral reads

$$-\tilde{\mu}_2^{(0)} - \beta\big(\tilde{u}^{(0)}\partial_{zz}\tilde{u}^{(0)}\big) + \frac{\beta}{2}\big(\partial_z \tilde{u}^{(0)}\big)^2 = d \quad \text{with} \quad d = \mu_2^{(0),\pm}. \tag{109}$$

The integration constant $(109)_2$ follows from the matching conditions (83)–(85). Thus the continuity of $\mu_2^{(0)}$ has been established.

The proof of the Stefan condition (106) relies on (98). Its integration leads to

$$-\dot{x}_I^{(0)}\tilde{u}^{(0)} + \tilde{f}^{(0)} = -\dot{x}_I^{(0)} u^{(0),\pm} + f^{(0),\pm}. \tag{110}$$

As before we have determined the integration constant by the matching conditions (83)–(85).

A comparison of $-\dot{x}_I^{(0)} u^{(0),\pm} + f^{(0),\pm}$ with the sharp interface definition $(7)_1$ of the mass flux identifies the corresponding mass flux of the sharp limit procedure:

$$\dot{m}_1^{(0)} = -\dot{x}_I^{(0)} u^{(0),\pm} + f^{(0),\pm}. \tag{111}$$

We conclude that the diffuse model implies a continuous mass flux $\dot{m}_1^{(0)}$ in the sharp limit. Thus we may write

$$[\![\dot{m}_1^{(0)}]\!] = 0. \tag{112}$$

Now recall the interface balance (10) for the concentration u_{I}. Up to know there is no sharp limit expression for u_{I}. However, if we introduce the sharp limit result (112) in (10), we may establish consistency of the two models by the statement: $u_{\mathrm{I}}^{(0)}$ is constant in time. Next we will show, the interface concentration $u_{\mathrm{I}}^{(0)}$ even assumes the value zero.

To this end we consider the total mass in the sharp interface model. Here the total mass consists of the two masses of the bulk phases and of the interfacial mass. We have

$$M = \int_0^{x_{\mathrm{I}}} u\,dx + \int_{x_{\mathrm{I}}}^1 u\,dx + u_{\mathrm{I}}\,. \tag{113}$$

In the diffuse interface setting we decompose the total mass $M = \int_0^1 u\,dx$ into the corresponding contributions and hereafter we expand:

$$\begin{aligned} M &= \int_0^{x_{\mathrm{I}}^\varepsilon - \varepsilon} u^\varepsilon\,dx + \varepsilon \int_{-1}^{+1} \tilde{u}^\varepsilon\,dz + \int_{x_{\mathrm{I}}^\varepsilon + \varepsilon}^1 u^\varepsilon\,dx \\ &= \int_0^{x_{\mathrm{I}}^{(0)}} u^{(0)}\,dx + \int_{x_{\mathrm{I}}^{(0)}}^1 u^{(0)}\,dx + \varepsilon \int_{-1}^{+1} \tilde{u}^{(0)}\,dz \\ &\quad + \varepsilon \left(u^{(0),-}(x_{\mathrm{I}}^{(1)} - 1) + \int_0^{x_{\mathrm{I}}^{(0)}} u^{(1)}\,dx - u^{(0),+}(x_{\mathrm{I}}^{(1)} + 1) + \int_{x_{\mathrm{I}}^{(0)}}^1 u^{(1)}\,dx \right) + \mathcal{O}(\varepsilon^2)\,. \end{aligned} \tag{114}$$

In the leading order we obtain

$$M = \int_0^{x_{\mathrm{I}}^{(0)}} u^{(0)}\,dx + \int_{x_{\mathrm{I}}^{(0)}}^1 u^{(0)}\,dx\,. \tag{115}$$

As before we compare the sharp interface result (113) with the diffuse interface result (115). We conclude that the total mass is already used up in the bulk phases. Thus it follows $u_{\mathrm{I}}^{(0)} = 0$.

The interface conditions of the first order problem (94)$_2$, Part 1: Interfacial mass balance.

In the first order the interface becomes equipped with an interfacial concentration $u_{\mathrm{I}}^{(1)}$, which is defined by

$$u_{\mathrm{I}}^{(1)} = \int_{-\infty}^{0} (\tilde{u}^{(0)} - u^{(0),-})\, dz + \int_{0}^{+\infty} (\tilde{u}^{(0)} - u^{(0),+})\, dz \,. \tag{116}$$

The time derivative of $u_{\mathrm{I}}^{(1)}$ is related to the mass flux $\dot{m}_1^{(1)}$ by

$$\partial_t u_{\mathrm{I}}^{(1)} + [\![\dot{m}_1^{(1)}]\!] = 0 \tag{117}$$

with

$$\dot{m}_1^{(1),\pm} = f^{(1),\pm} - \dot{x}_{\mathrm{I}}^{(0)} u^{(1),\pm} - \dot{x}_{\mathrm{I}}^{(1)} u^{(0),\pm} + (\partial_x f^{(0)} - \dot{x}_{\mathrm{I}}^{(0)} \partial_x u^{(0)})^{\pm} x_{\mathrm{I}}^{(1)} \,. \tag{118}$$

The representation (116) shows that $u_{\mathrm{I}}^{(1)}$ does not depend on time. This is a consequence of the fact that $u^{(0),\pm}$ is determined by the Maxwells common tangent construction. Thus the integration constant c in (108) is independent of time. Then also $\tilde{u}^{(0)}$ is time independent. We conclude from (117) that $\dot{m}_1^{(1)}$ is continuous:

$$[\![\dot{m}_1^{(1)}]\!] = 0 \,. \tag{119}$$

Derivation of the interface conditions of the first order problem (94)$_2$, Part 1: Interfacial mass balance. In preparation we rewrite the bulk equation (94)$_1$ at the $\pm$ sides of the interface. To this end we use the identities

$$\partial_t u^{(0),\pm}(t, x_{\mathrm{I}}^{(0)}) = \dot{u}^{(0),\pm}(t, x_{\mathrm{I}}^{(0)}(t)) - \dot{x}_{\mathrm{I}}^{(0)} (\partial_x u^{(0)})^{\pm}(t, x_{\mathrm{I}}^{(0)}) \tag{120}$$

and obtain (94)$_1$ in the form

$$\dot{u}^{(0),\pm} - \dot{x}_{\mathrm{I}}^{(0)} (\partial_x u^{(0)})^{\pm} + (\partial_x f^{(0)})^{\pm} = 0. \tag{121}$$

This equation is now subtracted from the order $\mathcal{O}(1)$ equation (100) of the inner setting. After some rearrangements we have

$$\partial_t(\tilde{u}^{(0)} - u^{(0),\pm}) + \partial_z \left(-(\dot{x}_I \partial_z \tilde{u})^{(1)} + \tilde{f}^{(1)} - (-\dot{x}_{\mathrm{I}}^{(0)} \partial_x u^{(0)} + \partial_x f^{(0)})^{\pm} (z + x_{\mathrm{I}}^{(1)}) \right) = 0. \tag{122}$$

Next we integrate (122) along the z coordinate, namely from $-\infty$ to 0 on the $-$ side and from 0 to $+\infty$ on the $+$ side of the interface. Then we add the resulting equations. Here we apply the matching conditions (83)–(91) to the term under the z derivative of (122). Finally we use (116) and (118) as definitions for $u_{\mathrm{I}}^{(1)}$ and $\dot{m}_1^{(1),\pm}$, respectively. In this way we deduce from (122) the interfacial mass balance

$$\partial_t u_{\mathrm{I}}^{(1)} + [\![\dot{m}_1^{(1)}]\!] = 0. \tag{123}$$

This fits well to the equation (60)$_1$ of the sharp interface setting.

The interface conditions of the first order problem (94)$_2$, Part 2: Kinetic relations.

The first order problem (94)$_2$ needs two further interface conditions. These are called *kinetic relations*, because they relate the mass fluxes to the jump of the chemical potentials. The kinetic relations read

$$[\![\mu^{(1)}]\!] = A\dot{m}^{(0)}, \qquad [\![\mu_2^{(1)}]\!] = A\dot{m}_1^{(0)} - (B+\gamma C)\dot{m}^{(0)}. \tag{124}$$

Here the first order contributions to the chemical potentials are represented by

$$\mu^{(1),\pm} = F''(u^{(0),\pm})u^{(1),\pm} + \left(\partial_x F'(u^{(0)})\right)^{\pm} x_{\mathrm{I}}^{(1)} , \tag{125}$$

$$\mu_1^{(1),\pm} = (1-u^{(0),\pm})F''(u^{(0),\pm})u^{(1),\pm} + \left(\partial_x(F(u^{(0)}) + (1-u^{(0)})F'(u^{(0)}))\right)^{\pm} x_{\mathrm{I}}^{(1)} , \tag{126}$$

$$\mu_2^{(1),\pm} = -u^{(0),\pm}F''(u^{(0),\pm})u^{(1),\pm} + \left(\partial_x(F(u^{(0)}) - u^{(0)}F'(u^{(0)}))\right)^{\pm} x_{\mathrm{I}}^{(1)} . \tag{127}$$

The kinetic coefficients A, B and C are given by

$$A = \frac{1}{M}u_{\mathrm{I}}^{(1)} , \qquad C = \int_{-\infty}^{+\infty} (\partial_z \tilde{u}^{(0)})^2 \, dz . \tag{128}$$

and

$$B = \frac{1}{M}\int_{-\infty}^{0} (\tilde{u}^{(0)})^2 - (u^{(0),-})^2 \, dz + \frac{1}{M}\int_{0}^{+\infty} (\tilde{u}^{(0)})^2 - (u^{(0),+})^2 \, dz . \tag{129}$$

A simple rearrangement of terms shows that the kinetic relations (124) can be rewritten in the following symmetric form:

$$[\![\mu_1^{(1)}]\!] = -K_{11}\dot{m}_1^{(0)} - K_{12}\dot{m}_2^{(0)} \tag{130}$$

$$[\![\mu_2^{(1)}]\!] = -K_{21}\dot{m}_1^{(0)} - K_{22}\dot{m}_2^{(0)} \tag{131}$$

with the matrix

$$K = \begin{pmatrix} -2A+B+\gamma C & -A+B+\gamma C \\ -A+B+\gamma C & B+\gamma C \end{pmatrix} , \tag{132}$$

which apparently is symmetric.

Derivation of the interface conditions of the first order problem (94)$_2$, Part 2: Kinetic relations. The proof of (124)$_1$ starts from (110), which we write as

$$-\dot{x}_I^{(0)}(\tilde{u}^{(0)} - u^{(0),\pm}) + \tilde{f}^{(0)} - f^{(0),\pm} = 0. \tag{133}$$

Here we insert the flux $\tilde{f}^{(0)}$ according to (99) and $f^{(0)} = -M\partial_x\mu^{(0)}$ from (94)$_1$ to obtain

$$-\dot{x}_I^{(0)}(\tilde{u}^{(0)} - u^{(0),\pm}) - M\partial_z\left(\tilde{\mu}^{(1)} - \partial_x\mu^{(0),\pm}(z + x_{\mathrm{I}}^{(1)}) - \beta\partial_{zz}\tilde{u}^{(1)} - \gamma\dot{x}_I^{(0)}\partial_z\tilde{u}^{(0)}\right) = 0. \tag{134}$$

As before we integrate this equation along the z coordinate and apply again the matching conditions (83)–(91) to the various terms under the z derivative. The result is the proposition (124)$_1$.

The proof of (124)$_2$ also starts from (110), but now we write

$$-\dot{x}_I^{(0)}\partial_z\tilde{u}^{(0)} + \partial_z\tilde{f}^{(0)} = 0\ . \tag{135}$$

Multiplication of this equation by $\tilde{u}^{(0)}$ yields

$$-\big(-\dot{x}_I^{(0)}\tilde{u}^{(0)} + \tilde{f}^{(0)}\big)\partial_z\tilde{u}^{(0)} + \partial_z\Big(-\dot{x}_I\big(\tilde{u}^{(0)}\big)^2 + \tilde{u}^{(0)}\tilde{f}^{(0)}\Big) = 0. \tag{136}$$

By (110) and (111) we have $\dot{m}_1^{(0)} = -\dot{x}_I^{(0)}\tilde{u}^{(0)} + \tilde{f}^{(0)}$ and furthermore $\dot{m}^{(0)} = -\dot{x}_I$. Recall that $\dot{m}_1^{(0)}$ and $\dot{m}^{(0)}$ are independent of z. Thus we can easily integrate (136) and obtain with an appropriately chosen integration constant

$$-\dot{m}_1^{(0)}(\tilde{u}^{(0)} - u^{(0),\pm}) + \dot{m}^{(0)}\big((\tilde{u}^{(0)})^2 - (u^{(0),\pm})^2\big) + (\tilde{u}^{(0)}\tilde{f}^{(0)} - u^{(0),\pm}f^{(0),\pm}) = 0\ . \tag{137}$$

Herein the flux $\tilde{f}^{(0)}$ is inserted according to (99). The flux $f^{(0)} = -M\partial_x\mu^{(0)}$ results from (94)$_1$. In both fluxes we replace the space derivatives of $F'(u)$ by derivatives of $F(u) - uF'(u)$. That substitution relies on the identity $\partial_x(F(u^\varepsilon) - u^\varepsilon F'(u^\varepsilon)) = -u^\varepsilon\partial_x F'(u^\varepsilon)$ implying

$$u^{(0)}\partial_x\mu^{(0)} = \partial_x\mu_2^{(0)} \qquad \text{and} \qquad \tilde{u}^{(1)}\partial_z\tilde{\mu}^{(0)} + \tilde{u}^{(0)}\partial_z\tilde{\mu}^{(1)} = \partial_z\tilde{\mu}_2^{(1)}\ . \tag{138}$$

Thus (137) becomes

$$\begin{aligned}-\dot{m}_1^{(0)}\big(\tilde{u}^{(0)} - u^{(0),\pm}\big) + \dot{m}^{(0)}\big((\tilde{u}^{(0)})^2 - (u^{(0),\pm})^2\big) + M\big(\partial_z\tilde{\mu}_2^{(1)} - \partial_x\mu_2^{(0),\pm}\big)&\\ +M\beta\tilde{u}^{(0)}\partial_{zzz}\tilde{u}^{(1)} + M\tilde{u}^{(1)}\partial_z\tilde{\mu}^{(0)} + \gamma M\dot{x}_I^{(0)}\tilde{u}^{(0)}\partial_{zz}\tilde{u}^{(0)} &= 0\end{aligned} \tag{139}$$

Finally we use (97)$_1$, viz. $\partial_z(\tilde{\mu}^{(0)} - \partial_{zz}\tilde{u}^{(0)}) = 0$, to obtain

$$\begin{aligned}&-\dot{m}_1^{(0)}\big(\tilde{u}^{(0)} - u^{(0),\pm}\big) + \dot{m}^{(0)}\big((\tilde{u}^{(0)})^2 - (u^{(0),\pm})^2\big) + M\big(\partial_z\tilde{\mu}_2^{(1)} - \partial_x\mu_2^{(0),\pm}\big)\\ &+\beta M\partial_z\big(\tilde{u}^{(0)}\partial_{zz}\tilde{u}^{(1)} + \tilde{u}^{(1)}\partial_{zz}\tilde{u}^{(0)} - \partial_z\tilde{u}^{(0)}\partial_z\tilde{u}^{(1)}\big)\\ &+\gamma M\dot{x}_I^{(0)}\partial_z\big(\tilde{u}^{(0)}\partial_z\tilde{u}^{(0)}\big) - \gamma M\dot{x}_I^{(0)}\big(\partial_z\tilde{u}^{(0)}\big)^2 = 0\ .\end{aligned} \tag{140}$$

Integration of this equation along the z coordinate and identification of the various abbreviations yields the proposition (124)$_2$.

7 Formal asymptotic analysis of the interfacial free energy inequality

In this section we derive the interfacial free energy inequality in an analogous manner as we have derived the jump conditions for the concentration. We start from the free energy inequality (74) of the diffuse model and insert here the outer and the inner expansions of the concentration u. After this we compare the resulting equations with the corresponding equations of the sharp model. That comparison allows to identify the interfacial dissipation function of the diffuse model.

The free energy inequality in the outer setting.

We insert the outer expansion (77) in the free energy inequality (74) of the viscous Cahn-Hilliard equation and in the dissipation function (75). In the leading order we obtain the balance law

$$\partial_t \psi^{(0)} + \partial_x (f^{(0)} \mu^{(0)}) = -T\xi^{(0)} \tag{141}$$

with the dissipation function

$$T\xi^{(0)} = \frac{1}{M}(f^{(0)})^2 \geq 0 \,. \tag{142}$$

The free energy inequality in the inner setting.

At first we transform the free energy balance (74) by means of the rules (80) to obtain

$$\begin{aligned} &\frac{\partial}{\partial t}\Big(\tilde{F}^\varepsilon + \frac{\beta}{2}(\partial_z \tilde{u}^\varepsilon)^2\Big) - \frac{\dot{x}_{\mathrm{I}}^\varepsilon}{\varepsilon}\frac{\partial}{\partial z}\Big(\tilde{F}^\varepsilon + \frac{\beta}{2}(\partial_z \tilde{u}^\varepsilon)^2\Big) \\ &+\frac{1}{\varepsilon}\frac{\partial}{\partial z}\Big(\tilde{f}^\varepsilon\big(\tilde{\mu}^\varepsilon + \varepsilon\gamma(\varepsilon\partial_t \tilde{u}^\varepsilon - \dot{x}_{\mathrm{I}}^\varepsilon \partial_z \tilde{u}^\varepsilon)\big) - \beta\partial_z \tilde{u}^\varepsilon\big(\varepsilon\partial_t \tilde{u}^\varepsilon - \dot{x}_{\mathrm{I}}^\varepsilon \partial_z \tilde{u}^\varepsilon\big)\Big) \quad = \quad -T\tilde{\xi}^\varepsilon \end{aligned} \tag{143}$$

The transformed dissipation function (75) reads in inner variables:

$$T\tilde{\xi}^\varepsilon = \frac{1}{M}\big(\tilde{f}^\varepsilon\big)^2 + \gamma\big(\varepsilon\partial_t \tilde{u}^\varepsilon - \dot{x}_{\mathrm{I}}^\varepsilon \partial_z \tilde{u}^\varepsilon\big)^2 \,. \tag{144}$$

In (143) we introduce the inner expansion (81). Due to (97) and (98) we conclude that the orders $\mathcal{O}(\varepsilon^{-2})$ and $\mathcal{O}(\varepsilon^{-1})$ are identically satisfied. The next order $\mathcal{O}(1)$ yields

$$\begin{aligned} &\partial_t\Big(\tilde{F}^{(0)} + \frac{\beta}{2}(\partial_z \tilde{u}^{(0)})^2\Big) - \partial_z\left[\dot{x}_I^\varepsilon \tilde{F}^\varepsilon\right]^{(1)} + \partial_z\left[\tilde{f}^\varepsilon \tilde{\mu}^\varepsilon\right]^{(1)} \\ &+\frac{\beta}{2}\partial_z\left[\dot{x}_{\mathrm{I}}^\varepsilon(\partial_z \tilde{u}^\varepsilon)^2\right]^{(1)} - \beta\partial_z\big(\partial_t \tilde{u}^{(0)}\partial_z \tilde{u}^{(0)}\big) - \gamma\partial_z\big(\dot{x}_{\mathrm{I}}^{(0)}\tilde{f}^{(0)}\partial_z \tilde{u}^{(0)}\big) \quad = \quad -T\tilde{\xi}^{(0)} \end{aligned} \tag{145}$$

where the dissipation function is given by

$$T\tilde{\xi}^{(0)} = \frac{1}{M}\big(\tilde{f}^{(0)}\big)^2 + \gamma(\dot{x}_{\mathrm{I}}^{(0)}\partial_z \tilde{u}^{(0)})^2 \,. \tag{146}$$

In (145) we have used the abbreviations

$$\left[\dot{x}_{\mathrm{I}}^\varepsilon \tilde{F}^\varepsilon\right]^{(1)} = \dot{x}_{\mathrm{I}}^{(0)}\tilde{F}^{(1)} + \dot{x}_{\mathrm{I}}^{(1)}\tilde{F}^{(0)} \tag{147}$$

$$\left[\tilde{f}^\varepsilon \tilde{\mu}^\varepsilon\right]^{(1)} = \tilde{f}^{(1)}\big(\tilde{\mu}^{(0)} - \beta\partial_{zz}\tilde{u}^{(0)}\big) + \tilde{f}^{(0)}\big(\tilde{\mu}^{(1)} - \beta\partial_{zz}\tilde{u}^{(1)}\big) \tag{148}$$

$$\left[\dot{x}_{\mathrm{I}}^\varepsilon(\partial_z \tilde{u}^\varepsilon)^2\right]^{(1)} = \dot{x}_{\mathrm{I}}^{(1)}(\partial_z \tilde{u}^{(0)})^2 + 2\dot{x}_{\mathrm{I}}^{(0)}\partial_z \tilde{u}^{(0)}\partial_z \tilde{u}^{(1)} \,. \tag{149}$$

The interfacial free energy inequality of the leading order.

The leading orders, i.e. $\mathcal{O}(\varepsilon^{-2})$ and $\mathcal{O}(\varepsilon^{-1})$, of the diffuse free energy inequality in inner variables do not give any new information, because the leading oders of the inequality are identically satisfied. This is a consequence of previous results. In fact, the continuity of the mass fluxes (106) and (107) and the chemical potentials (104) and (104) yields in the leading order

$$[\![\dot{m}_1^{(0)}\mu_1^{(0)} + \dot{m}_2^{(0)}\mu_2^{(0)}]\!] = 0 \,. \tag{150}$$

A comparison of (150) with the free energy inequality (11) and (12) of the sharp model leads to two conclusions: (i) there is no dissipation in the leading order and (ii) the interfacial free energy is time independent. We write

$$\xi_{\mathrm{I}}^{(0)} = 0 \qquad \text{and} \qquad \partial_t \psi_{\mathrm{I}}^{(0)} = 0 \,. \tag{151}$$

The total free energy Ψ of the system is an additive quantity. Therefore it can be represented by

$$\Psi = \int_0^{x_{\mathrm{I}}} \psi \, dx + \int_{x_{\mathrm{I}}}^1 \psi \, dx + \psi_{\mathrm{I}} \,. \tag{152}$$

Starting from here we can show $\psi_{\mathrm{I}}^{(0)} = 0$. This follows in an analogous manner to the reasoning of $u_{\mathrm{I}}^{(0)} = 0$ via the equation (112). In this context recall that $\psi_{\mathrm{I}}^{(0)}$ satisfies a conservation law.

The interfacial free energy balance inequality of the order $\mathcal{O}(\varepsilon)$.

Here we have the following results. In order $\mathcal{O}(\varepsilon)$ the interfacial free energy is represented by

$$\psi_{\mathrm{I}}^{(1)} = \int_{-\infty}^0 \Big(\tilde{F}^{(0)} - F^{(0),-} + \frac{\beta}{2}(\partial_z \tilde{u}^{(0)})^2\Big)\, dz + \int_0^{+\infty} \Big(\tilde{F}^{(0)} - F^{(0),+} + \frac{\beta}{2}(\partial_z \tilde{u}^{(0)})^2\Big)\, dz \,, \tag{153}$$

and satisfies the equation of balance

$$\partial_t \psi_{\mathrm{I}}^{(1)} + [\![(\psi \dot{m})^{(1)}]\!] + [\![(f\mu)^{(1)}]\!] = -T\xi_{\mathrm{I}}^{(1)} \,, \tag{154}$$

with the dissipation function

$$\xi_{\mathrm{I}}^{(1)} = \int_{-\infty}^0 \tilde{\xi}^{(0)} - \xi^{(0),-} \, dz + \int_0^{+\infty} \tilde{\xi}^{(0)} - \xi^{(0),+} \, dz \,. \tag{155}$$

An equivalent representation of $\xi_{\mathrm{I}}^{(1)}$ is given by

$$T\xi_{\mathrm{I}}^{(1)} = [\![\mu_1^{(1)}\dot{m}_1^{(0)} + \mu_2^{(1)}\dot{m}_2^{(0)}]\!] \,. \tag{156}$$

Finally we use the kinetic relations (130) and (131) of the sharp limit of the diffuse model to obtain from (156) the representation

$$T\xi_{\mathrm{I}}^{(1)} = K_{11}(\dot{m}_1^{(0)})^2 + (K_{12} + K_{21})(\dot{m}_1^{(0)}\dot{m}_2^{(0)}) + K_{22}(\dot{m}_2^{(0)})^2 \,. \tag{157}$$

Derivation of interfacial free energy balance inequality of the order $\mathcal{O}(\varepsilon)$. From the inner equation (145) we subtract the corresponding bulk equations (141) at the interface. The result can be written as

$$\begin{aligned}
&\partial_t\Big(\tilde{F}^{(0)} - F^{(0),\pm} + \frac{\beta}{2}(\partial_z\tilde{u}^{(0)})^2\Big) \\
-\partial_z\left[\dot{x}_I^\varepsilon\tilde{F}^\varepsilon\right]^{(1)} &+ \partial_x(\dot{x}_I^{(0)}F^{(0),\pm}) + \partial_z\left[\tilde{f}^\varepsilon\tilde{\mu}^\varepsilon\right]^{(1)} - \partial_r\big(f^{(0),\pm}\mu^{(0),\pm}\big) \\
+\frac{\beta}{2}\partial_z\left[\dot{x}_I^\varepsilon(\partial_z\tilde{c}^\varepsilon)^2\right]^{(1)} &- \beta\partial_z(\partial_t\tilde{c}^{(0)}\partial_z\tilde{c}^{(0)}) - \gamma\partial_z(\dot{x}_I^{(0)}\tilde{f}^{(0)}\partial_z\tilde{c}^{(0)}) \quad = \quad -T(\tilde{\xi}^{(0)} - \xi^{(0),\pm})\,.
\end{aligned} \tag{158}$$

As before we integrate this equation along the z coordinate and apply again the matching conditions (83)–(91) to the various terms under the z derivative. By a subsequent comparison of the integrated equation (158) with the corresponding sharp model inequality (11) and (12) we identify the propositions (153)–(155). Note that the interfacial chemical potentials $\mu_{\mathrm{I},1}$ and $\mu_{\mathrm{I},2}$ drop out in (12), because the appearing mass fluxes are continuous.

Next we show that the interfacial dissipation function is given by (156). We start from (146) and use the relations (98), $(138)_2$ and (97) to obtain after a straightforward calculation the identity

$$\begin{aligned}
T\tilde{\xi}^{(0)} \quad = \quad & -\dot{m}_1^{(0)}\partial_z\tilde{\mu}_1^{(1)} - \dot{m}_2^{(0)}\partial_z\tilde{\mu}_2^{(1)} \\
& +\beta\dot{x}_I^{(0)}\partial_z\Big(\tilde{u}^{(0)}\partial_{zz}\tilde{u}^{(1)} + \tilde{u}^{(1)}\partial_{zz}\tilde{u}^{(0)} - \partial_z\tilde{u}^{(0)}\partial_z\tilde{u}^{(1)}\Big) + \beta\dot{m}_1^{(0)}\partial_{zzz}\tilde{u}^{(1)} \\
& +\gamma\dot{x}_I^{(0)}\dot{m}_1^{(0)}\partial_{zz}\tilde{u}^{(0)} + \gamma(\dot{x}_I^{(0)})^2\partial_z(\tilde{u}^{(0)}\partial_z\tilde{u}^{(0)})
\end{aligned} \tag{159}$$

In an analogous manner we obtain the bulk dissipation function

$$T\xi^{(0)} = -\dot{m}_1^{(0)}\partial_x\mu_1^{(0)} - \dot{m}_2^{(0)}\partial_x\mu_2^{(0)}\,. \tag{160}$$

Now we subtract from (159) the equation (160). After this we integrate along the inner coordinate z and apply again the matching conditions (83)–(91). Finally we compare the result with the sharp model result (12) and end up with the proposition (156).

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References

[1] I. Müller, Thermodynamics, Interaction of Mechanics and Mathematics Series, Pitman Advanced Publishing Program, Boston, 1985.

[2] W. Dreyer, Jump Conditions at phase boundaries for ordered and disordered phases, WIAS Preprint No. 869, 2003.

[3] J. W. Cahn and J. E. Hilliard, Free energy of a nonuniform system. I. Interfacial energy, Journal of Chemical Physics **28**, 1958, 258–267.

[4] R. L. Pego, Front Migration in the Nonlinear Cahn-Hilliard Equation, Proceedings the Royal Society A **422** (1863), 1989, 261–278.

[5] A. Novick-Cohen, On the viscous Cahn-Hilliard equation, Material Instabilities in Continuum and Related Mathematical Problems, Oxford University Press, 1988, 329–342.

[6] L.C. Evans and M. Portilheiro, Irreversibilty and hysteresis for a forward-backward diffusion equation, Mathematical Models and Methodes in Applied Sciences **14** (11), 2004, 1599–1620.

[7] G. Caginalp and P. C. Fife, Dynamics of Layerd Interfaces Arising from Phase Boundaries, SIAM Journal on Applied Mathematics **48** (3), 1988, 506–518.

[8] W. Dreyer, J. Giesselmann, C. Kraus and C. Rohde, Asymptotic analysis for Korteweg models, Interfaces Free Boundary **14**, 2012, 105–143.