A Revised Model For Diffusion Induced Segregation Processes

T. Blesgen

Max-Planck-Institute for Mathematics in the Sciences,
Inselstraße 22-26, 04103 Leipzig, Germany

EMail: blesgen@mis.mpg.de, Phone:+49(341) 9959-804

Abstract:
A mathematical model for chalcopyrite disease within sphalerite is developed. As one main result, by analysing the system enthalpy, correct expressions for the reaction terms in a sytem undergoing phase transitions are worked out. For the resulting equations, the thermodynamical validity is shown and the existence of a unique solution is proved.

1 Introduction

In the present work we are concerned with diffusion-induced segregation (DIS) phenomena. This class is characterised by segregation processes that can only take place after a sufficient amount of a diffusor has penetrated the crystal. We will exemplary study the so-called chalcopyrite disease within sphalerite, which is a well-known and extensively-discussed problem arising in geology and a particular example of DIS, but the techniques developed here apply as well for other DIS phenomena.

In [3], a first model for chalcopyrite disease has been developed, [3] also provides references to the mineralogical experiments and illuminates the physical background. But as a deeper thermodynamical analysis in this article reveals, the reaction terms chosen in this first model are only approximately true and will in general depend on the phase parameter (the function χ introduced later on). The principles worked out are quite general and will apply whenever reactions and phase transitions take place simultaneously. The presentation is completed by showing existence and uniqueness of the solutions.

2 Derivation of the revised model

Let us consider the following reaction diffusion equations

$$\partial_t c_i = \operatorname{div}(J_i) + r_i = \left(\sum_l \frac{\partial}{\partial x_l} J_{i,l} \right) + r_i, \; i = 1, \ldots, 4. \tag{1}$$

In (1), $c_i = c_i(x,t)$ denotes the relative number of species i, $i = 1, \ldots, 4$ per available lattice point at time t and space point $x \in \Omega$, Ω a (time-independent) domain in $\mathbb{R}^D$, $1 \leq D \leq 3$. By $T_0 > 0$ we denote a stop time and by $\Omega_{T_0} := \Omega \times (0, T_0)$ a cylinder in space-time.

We introduce the notations

$$c_1 \approx \mathrm{Fe}^{3+},\; c_2 \approx \mathrm{Fe}^{2+},\; c_3 \approx \mathrm{Cu}^{+},\; c_4 \approx \mathrm{Zn}^{2+},\; c_5 \approx \text{vacancies}.$$

c_1 satisfies $c_1 = \frac{N_{\mathrm{Fe}}^{3+}}{N_{\mathrm{Me}}}$, where $N_{\mathrm{Fe}^{3+}}$ is the number of Fe^{3+} atoms and N_{Me} is the number of metal ion sites. Similar relationships hold for c_2, c_3 and c_4. It is an essential property of this formulation that there is no equation for c_5, but the vacancy concentration is obtained implicitly by the conservation of mass

$$c_5 = 1 - \sum_{i=1}^{4} c_i.$$

In (1), r_i denote the reaction terms and J_i the fluxes of metal ions of species i. The reaction terms model the jumps of the electrons. A first ansatz is $r = (r_1, -r_1, 0, 0)$ and (see (22) below for explanation)

$$r_1 = k(c_2^2 - \kappa c_1 c_e),$$

where $k > 0$ and $k\kappa > 0$ are the reaction rates and c_e denotes the electron concentration. If we assume that all sulphur places are occupied by S^{2-}, by the condition of electric neutrality we can compute

$$\begin{aligned} c_e &= 2 - 3c_1 - 2c_2 - c_3 - 2c_4 \\ &= 2 - 2(c_1 + c_2 + c_3 + c_4) - c_1 + c_3 \\ &= 2c_5 - c_1 + c_3. \end{aligned} \tag{2}$$

In the presence of phase transitions the reaction rates may not be chosen to be constants, as we shall see below.

Onsager's postulate, [11], [12] states that each thermodynamic flux is linearly related to every thermodynamic force. Since in our case the thermodynamic forces are the negative chemical potential gradients, we obtain the phenomenological equations, see [10], p.137,

$$J_i = \sum_{j=1}^{4} L_{ij} \nabla \mu_j, \quad 1 \le i \le 4, \tag{3}$$

with a constant mobility matrix L. The Onsager reciprocity law, [11], [12], [10] states that L has to be symmetric which we assume in the following. To simplify the existence theory we will further assume in the sequel that L is positive definite. By

$$\mu_j = \frac{\partial f}{\partial c_j}$$

we denote the chemical potential.

In this work the temperature T is held constant reflecting the situation of the mineralogical experiments. Let f denote the Helmholtz free energy density of the system, which is the convex hull of the free energy density of f_1, f_2 with f_1 for chalcopyrite, f_2 for sphalerite. Hence, the two different phases or lattice orders are characterised by two different free energies, and f is the convex hull of f_1 and f_2.

For order-disorder phase transitions, we make the first ansatz

$$f_l = f_l(c) = k_B T \sum_{i=1}^{5} \beta_i^l c_i \ln c_i + \sum_{i=1}^{3} E_i c_i + \left(\sum_{i=1}^{4} \alpha_i c_i \right)^2, \quad l = 1, 2. \tag{4}$$

The elastic coefficients α_i do not change for both phases, only the β_i^l differ. The convex terms $c_i \ln c_i$ are motivated by considerations from statistical mechanics on the system entropy by counting the different configurations. The term $\sum_{i=1}^{3} E_i c_i$ refers to the system enthalpy and is a consequence of the presence of the Fe-reaction. It will be discussed in the subsequent section.

The expression $(\sum_{i=1}^{4} \alpha_i c_i)^2$ is a consequence of Hooke's law. The constants α_i correspond to the ion radii and measure the volume response when replacing Zn^{2+} by other metal ions. In (4), the β_i^1, β_i^2 are positive constants and k_B is the Boltzmann constant.

Eq. (4) is a very reasonable term for a numerical computation, since (4) implies infinite slope of Df_l if one component c_j approaches 0 or 1. This guarantees, see [13],

$$c_j \in (0, 1) \quad \text{in } \Omega,\ t > 0 \tag{5}$$

and c_j has physical meaning. As there is no maximum principle for systems of equations, without the logarithmic terms in (4), Condition (5) may be violated even if $c_j \in (0, 1)$ holds for $t = 0$.

At this stage, a control mechanism for the segregation process is introduced. The following principle is well known. Let $\chi = \chi(x, t) \in [0, 1]$ be a function that measures the volume fraction of the chalcopyrite phase; e.g. $\chi(x_0, t_0) = 0$ means that for $t = t_0$ in $x_0 \in \Omega$ only the sphalerite phase is present, $\chi(x_0, t_0) = \frac{1}{2}$ that the system is in x_0 in an intermediate state with no dominant phase.

Let $\gamma > 0$ be a small constant, denoting the square of the thickness of the interface between sphalerite and chalcopyrite phase. We define the density of the mixing entropy s_M by

$$s_M(\chi) = W(\chi) + \frac{\gamma}{2} |\nabla \chi|^2, \tag{6}$$

with the double-well potential

$$W(\chi) := \chi \ln \chi + (1-\chi)\ln(1-\chi). \tag{7}$$

Since $f := \text{conv}(f_1, f_2)$, we will consider f as the convex combination of f_1 and f_2. Because s_M is subtracted from the entropy density s, the thermodynamic relation $f = e - Ts$ thus implies

$$f(c,\chi) := \chi f_1(c) + (1-\chi) f_2(c) + T s_M(\chi). \tag{8}$$

The phase parameter χ is governed by the modified Allen-Cahn equation

$$\tau \partial_t \chi = -\partial_\chi \left(\frac{f}{T} \right) = \gamma \triangle \chi - \omega(c,\chi), \tag{9}$$

where $\gamma \triangle \chi$ comes from the first variation of $-\int_\Omega \frac{\gamma}{2} |\nabla \chi|^2$ w.r.t. χ and τ is a scaling parameter to adjust the different time scales between mass diffusion and growing of the chalcopyrite phase. The driving force ω in (9) is given by

$$\omega(c,\chi) := \ln \left(\frac{\chi}{1-\chi} \right) + m(c). \tag{10}$$

The value $m(c)$ accounts for the growing of chalcopyrite in copper rich regions and is gained implicitly by $\tau \partial_t \chi = -\partial_\chi (f/T)$. Since so far the final formula for f has not been derived, we will postpone the discussion of this term and of the mechanism responsible for the growing of chalcopyrite in copper rich regions. The final definition of ω is given in (29).

3 An enthalpy principle for a purely reactive system

We want to incorporate the electron jumps by including reaction terms in the model. The reactions are represented in the free energy by enthalpic terms. To understand the nature of these enthalpic terms, we consider a purely reactive system without diffusion and derive general properties of reactive systems.

Let the domain Ω comprise of substances A, B, C and D subject to the reactions

$$\begin{aligned} A + B &\overset{r_+}{\rightarrow} C + D, \\ A + B &\overset{r_-}{\leftarrow} C + D. \end{aligned}$$

Let $\tilde{c}_1$, $\tilde{c}_2$, $\tilde{c}_3$ and $\tilde{c}_4$ denote the concentration of substances A, B, C and D where we assume

$$\sum_{i=1}^{4} \tilde{c}_i = 1. \tag{11}$$

In the language of partial differential equations, these reactions can be written as, see [8],

$$\begin{aligned} \partial_t \tilde{c}_1 &= \partial_t \tilde{c}_2 = -r_+ \tilde{c}_1 \tilde{c}_2 + r_- \tilde{c}_3 \tilde{c}_4, \\ \partial_t \tilde{c}_3 &= \partial_t \tilde{c}_4 = +r_+ \tilde{c}_1 \tilde{c}_2 - r_- \tilde{c}_3 \tilde{c}_4. \end{aligned} \tag{12}$$

From statistical mechanics we infer

$$\begin{aligned} r_+ &= \exp\Big(\frac{\tilde{E}_1 + \tilde{E}_2 - \tilde{E}_S}{k_B T}\Big), \\ r_- &= \exp\Big(\frac{\tilde{E}_3 + \tilde{E}_4 - \tilde{E}_S}{k_B T}\Big), \end{aligned} \tag{13}$$

where $\tilde{E}_1 + \tilde{E}_2$ is the energy level before the reaction $A + B \to C + D$, $\tilde{E}_3 + \tilde{E}_4$ the energy level after the reaction. $\tilde{E}_S$ is the activation energy or sattle point energy that has to be exceeded to start the reaction.

For the free energy we make the ansatz

$$\tilde{F}(\tilde{c}) = \int_\Omega k_B T \sum_{i=1}^{4} \tilde{c}_i \Big(\ln \tilde{c}_i + \frac{\tilde{E}_i}{k_B T} \Big). \tag{14}$$

Now we will show the following properties of $\tilde{F}$:

$$\partial_t \tilde{F}(\tilde{c}(t)) = 0 \quad \text{iff} \quad \partial_t \tilde{c}_i = 0,\ 1 \leq i \leq 4, \tag{15}$$

$$\partial_t \tilde{F}(\tilde{c}(t)) \leq 0, \tag{16}$$

$$\tilde{F}(\tilde{c}(t)) \text{ is critical} \quad \text{iff} \quad \partial_t \tilde{c}(t) = 0. \tag{17}$$

In order to show (15), (16), after setting

$$R := -r_+ \tilde{c}_1 \tilde{c}_2 + r_- \tilde{c}_3 \tilde{c}_4 = \partial_t \tilde{c}_1 = \partial_t \tilde{c}_2 = -\partial_t \tilde{c}_3 = -\partial_t \tilde{c}_4,$$

elementary computations yield

$$\begin{aligned} \partial_t \tilde{F}(\tilde{c}) &= \int_\Omega k_B T\, R \Big[\ln \Big(\frac{\tilde{c}_1 \tilde{c}_2}{\tilde{c}_3 \tilde{c}_4} \Big) + \frac{\tilde{E}_1 + \tilde{E}_2 - \tilde{E}_S}{k_B T} - \frac{\tilde{E}_3 + \tilde{E}_4 - \tilde{E}_S}{k_B T} \Big] \\ &= \int_\Omega k_B T\, R \ln \Big[\Big(\frac{\tilde{c}_1 \tilde{c}_2}{\tilde{c}_3 \tilde{c}_4} \Big) \Big(\frac{r_+}{r_-} \Big) \Big]. \end{aligned} \tag{18}$$

We observe

$$\ln\left(\frac{\tilde{c}_1\tilde{c}_2\, r_+}{\tilde{c}_3\tilde{c}_4\, r_-}\right) = 0 \qquad \text{iff} \qquad \tilde{c}_1\tilde{c}_2\, r_+ = \tilde{c}_3\tilde{c}_4\, r_-$$

and together with (18) we find (15). Eq. (18) directly implies the free energy inequality (16). To see this, let us consider the two mutual exclusive cases:

$$\text{(A)} \qquad R \geq 0 \qquad \Longleftrightarrow \qquad \tilde{c}_3\tilde{c}_4 r_- \geq \tilde{c}_1\tilde{c}_2 r_+ \qquad \Longleftrightarrow \qquad \ln\left(\frac{\tilde{c}_1\tilde{c}_2\, r_+}{\tilde{c}_3\tilde{c}_4\, r_-}\right) \leq 0,$$

$$\text{(B)} \qquad R < 0 \qquad \Longleftrightarrow \qquad \tilde{c}_3\tilde{c}_4 r_- < \tilde{c}_1\tilde{c}_2 r_+ \qquad \Longleftrightarrow \qquad \ln\left(\frac{\tilde{c}_1\tilde{c}_2\, r_+}{\tilde{c}_3\tilde{c}_4\, r_-}\right) > 0.$$

This discussion reveals the natural structure of the problem,

$$((\ln(\tilde{c}_1\tilde{c}_2\, r_+) - \ln(\tilde{c}_3\tilde{c}_4\, r_-))(\tilde{c}_3\tilde{c}_4\, r_- - \tilde{c}_1\tilde{c}_2\, r_+) \leq 0, \tag{19}$$

from which we unconditionally infer $\partial_t \tilde{F}(\tilde{c}(t)) \leq 0$. We see that the canonical structure of the problem goes along with the ansatz of the free energy.

A critical point $\tilde{c}$ of $\tilde{F}$ is characterised by

$$\ln \tilde{c}_l + \frac{\tilde{E}_l}{k_B T} + 1 = 0 \qquad \text{for} \quad 1 \leq l \leq 4. \tag{20}$$

This implies $\partial_t \tilde{c}_i = 0,\ 1 \leq i \leq 4$ because from (20) it follows with (13)

$$\begin{aligned} \ln(\tilde{c}_1\tilde{c}_2 r_+) &= -2, \\ \ln(\tilde{c}_3\tilde{c}_4 r_-) &= -2 \end{aligned}$$

and when subtracting the last two identities we find

$$\ln\left(\frac{\tilde{c}_1\tilde{c}_2\, r_+}{\tilde{c}_3\tilde{c}_4\, r_-}\right) = 0.$$

This implies at once $\partial_t \tilde{c}_i = 0,\ 1 \leq i \leq 4$. The other implication in (17) is shown similarly.

4 Derivation of the complete model

Eq. (19) reveals the underlying structure of reaction-diffusion equations which allows to discuss the reaction terms and give a complete description of the model. The swift jumps of the electrons are integrated into the model by two reactions

$$\begin{aligned} Fe^{2+} &\xrightarrow{k} Fe^{3+} + e^-, \\ Fe^{2+} &\xleftarrow{\kappa k} Fe^{3+} + e^-. \end{aligned} \tag{21}$$

Here, e^- is a free lattice electron and k, κk are reaction rates. A formula for c_e has already been found with (2).

The standard approach to model Reactions (21) analogous to Eq. (12) is

$$r_1 = k(c_2^2 - \kappa c_1 c_e) \tag{22}$$

The principles leading to (22) are carefully explained in [8]. But as we will show, (22) is wrong in our case as the rates will depend on χ! With the knowledge of (19) we can obtain a consistent formulation of r that generalises (22). In this generalisation, the rates will depend on χ.

To perfectly adjust the model, we first remind that the oxidation of Fe is caused by swift shifts of the electrons and occurs thus much faster than any other process, i.e. faster than diffusion. Hence, it is reasonable to assume that this oxidation is instantaneous. Thus we will replace the equation for c_1 by a stationary elliptic equation.

Secondly, due to electric neutrality, we postulate

$$c_5 = \frac{1}{2} c_1. \tag{23}$$

This condition was found experimentally in [2] long before a mathematical model had been developed. Eq. (23) is the key to finding a consistent formulation for the reaction term. There is one difficulty here because (23) tells us that the movement of the vacancies is on the same fast time scale as the movement of the free electrons. We will bypass this problem by demanding $\partial_t c_5 = 0$ in the derivation of the reaction term in (27). All crystallographic measurements verify Relation (23), but the quick electron jumps are beyond the resolution horizon of todays methods.

As main consequence of (2) and (23) we find

$$c_e = c_3. \tag{24}$$

To end up with the reaction terms having the structure of (19), the logarithms have to have the same factors. Hence we assume

$$\beta_1^l + \frac{\beta_5^l}{2} = \beta_2^l = \beta_3^l = \beta_4^l =: b^l, \; l = 1, 2.$$

The final form of the free energy (4) is thus

$$f_l(c) = k_B T b^l \sum_{i=1}^{4} c_i \ln c_i + \sum_{i=1}^{3} c_i E_i + \Big(\sum_{i=1}^{4} \alpha_i c_i\Big)^2, \quad l = 1, 2. \tag{25}$$

Combined, (8) and (25) define the free energy.

$$\begin{aligned} F(c,\chi) &= \int_\Omega f(c,\chi) = \int_\Omega \Big[k_B T b_\chi \Big(\sum_{i=1}^{4} c_i \ln c_i\Big) + \sum_{i=1}^{3} c_i E_i + \Big(\sum_{i=1}^{4} \alpha_i c_i\Big)^2 \\ &\qquad + \frac{\gamma T}{2}|\nabla\chi|^2 + TW(\chi)\Big]. \end{aligned} \tag{26}$$

Here we introduced the abbreviation $b_\chi := \chi b^1 + (1-\chi) b^2$. The rates fulfil

$$r_+ = k\kappa \;=\; \exp\Big(\frac{E_1 + E_3 - E_S}{k_B T}\Big), \quad r_- = k = \exp\Big(\frac{2E_2 - E_S}{k_B T}\Big).$$

We can give a quick motivation for the correct reaction term by considering again a purely reactive system, this time with phase changes. If we consider the oxidation process alone (without diffusion!) we have

$$\partial_t c_4 = \partial_t c_5 = 0 \tag{27}$$

and from $\partial_t c_1 = \partial_t c_3$ and $\sum_{i=1}^{5} c_i = 1$ we infer $\partial_t c_2 = -2\partial_t c_1$. With these constraints we compute $\partial_t F(c(t),\chi(t))$ for the free energy (26), where we can drop $(\sum_{i=1}^{4} \alpha_i c_i)^2$ (the estimation of this term is possible as in Section 5). We find

$$\begin{aligned} \partial_t F(c(t),\chi(t)) &= \int_\Omega \Big[k_B T\, b_\chi \partial_t c_1 \ln\Big(\frac{c_1 c_3}{c_2^2}\Big) \\ &\qquad + \frac{E_1 + E_3 - E_S}{k_B T} - \frac{2E_2 - E_S}{k_B T} - (\partial_t \chi)^2\Big] \\ &= \int_\Omega \Big[k_B T\, b_\chi \partial_t c_1 \ln\Big(\frac{c_1 c_3 (r_+)^{1/b_\chi}}{c_2^2 (r_-)^{1/b_\chi}}\Big) - (\partial_t\chi)^2\Big]. \end{aligned}$$

The consistent form of the reaction term that replaces (22) is hence

$$r_1 = r_3 = -\frac{1}{2} r_2 = (k)^{1/b_\chi}\Big(c_2^2 - \kappa^{1/b_\chi} c_1 c_3\Big), \qquad r_4 = 0. \tag{28}$$

b^1 and b^2 should be in the magnitude of 1 and for $b^1 = b^2$ there would be no χ dependence. For $b^1 = b^2 = 1$ we fall back to standard formulas of r.

It remains to discuss the control mechanism for the chalcopyrite phase. (26) together with $\tau\partial_t\chi = -\partial_\chi(f/T) = \gamma\triangle\chi - \omega(c,\chi)$ gives rise to setting

$$\omega(c,\chi) = W'(\chi) + k_B(b^2 - b^1)\Big(\sum_{i=1}^{4} c_i \ln c_i + \overline{\alpha}\Big). \tag{29}$$

Here, $\overline{\alpha} > 0$ is a temperature-dependent constant. Additive constants occur in (26) because one can only measure the change δF of F when varying a quantity q, commonly temperature or volume, within some interval (q_0, q_1), finding the expression $\int_{q_0}^{q_1} \delta F$ for F. Frequently, we will set $\overline{\alpha} := \ln 3$.

To understand the principle of the control mechanism, we first freeze c_1, c_2 and c_4 and consider for constants $\alpha > 0, \beta > 0$, see Fig. 1,

$$\begin{aligned} \omega(c_3,\chi) &= W'(\chi) + m(c_3), \\ m(c_3) &= \beta c_3 \ln c_3 + \alpha. \end{aligned}$$

The mechanism thus obtained is similar to the one commonly used in phase field models, where c_3 plays the role of temperature. From convexity of $m(c_3)$ and from the magnitude of α and β, we get the existence of x_1, $x_2 \in (0,1)$, $x_1 < x_2$ with $m(c_3) > 0$ for $c_3 \in (0,x_1) \cup (x_2,1)$ and $m(c_3) < 0$ for $c_3 \in (x_1,x_2)$. Consequently for $c_3 < x_1$, the sphalerite phase is preferred, whereas for $x_1 < c_3 < x_2$, chalcopyrite can form. In practice, the branch $c_3 > x_2$ is never reached, and the chalcopyrite phase once it has formed does not destabilise at a later time.

Expression (29) is symmetric w.r.t. the variables $c_1,\dots,c_4$ and so the mechanism just explained also applies for the other variables. Yet there is unsymmetry which comes from the initial values for c. If we consider Fig. 1 again, this time imagining it as a function of c_1, then due to $c_1(t=0)$ one will stay in the part $(0,x_1)$. Hence, the reason why c_3 is mainly responsable for controling the chalcopyrite disease is caused by the size of initial values $c(t=0)$. Now, the derivation of the model is complete.

Find for $t \geq 0$ the vector (c_1,c_2,c_3,c_4), χ such that in $\Omega \subset \mathbb{R}^D$ for $t > 0$

$$0 = \operatorname{div}\left(\sum_{j=1}^{4} L_{1j}\nabla\mu_j\right) + k^{1/b_\chi}(c_2^2 - (\kappa)^{1/b_\chi} c_1 c_3),$$

$$
\begin{aligned}
\partial_t c_i &= \operatorname{div}\left(\sum_{j=1}^{4} L_{ij}\nabla\mu_j\right) + r_i(c,\chi),\ i=2,3,4,\\
\mu_i &= \frac{\partial f}{\partial c_i}(c,\chi),\ 1\le i\le 4,\\
\tau\partial_t\chi &= \gamma\triangle\chi - \omega(c,\chi)
\end{aligned}
$$

and for $t=0$, $x\in\Omega$

$$
\begin{aligned}
c_i(x,0) &= c_{0i}(x),\ i=2,3,4\\
\chi(x,0) &= \chi_0(x)
\end{aligned}
$$

and for $t>0$, $x\in\partial\Omega$

$$
\begin{aligned}
c_i &= g_i,\ 1\le i\le 4,\\
\mu_i &= h_i,\ 1\le i\le 4
\end{aligned}
\tag{30}
$$

with given Dirichlet data $g=(g_1,\dots,g_4)$ *and* $h=(h_1,\dots,h_4)$ *defined on* $\partial\Omega$.

5 The free energy inequality

We will show the thermodynamical correctness of System (30) under isothermal conditions, where the approximating elliptic equation is replaced by the original time-dependent formulation. It is suitable to reformulate (30).

$$
\partial_t c + \operatorname{div}(J) = r, \tag{31}
$$

$$
\tau\partial_t\chi = -\frac{\partial f}{\partial\chi}, \tag{32}
$$

where

$$
J = -L\nabla\mu
$$

and r is defined by (28). An application of the chain rule yields

$$
\frac{d}{dt}f(c,\chi) = \sum_{j=1}^{4}\frac{\partial f}{\partial c_j}\partial_t c_j + \frac{\partial f}{\partial\chi}\partial_t\chi. \tag{33}
$$

From (33) we learn that we have to test the equation for c_i with $\frac{\partial f}{\partial c_i}=\mu_i$, $1\le i\le 4$ and Eq. (32) with $\frac{\partial f}{\partial\chi}$. After integrating over Ω, one integration by parts we obtain

$$\frac{d}{dt}\int_\Omega f(c,\chi) - \int_\Omega \Big(\sum_{j=1}^4 \mu_j r_j + \sum_{j=1}^4 \nabla\mu_j \cdot J_j + \frac{\partial f}{\partial \chi}\partial_t \chi\Big) + \int_{\partial\Omega} \sum_{j=1}^4 \mu_j J_j \cdot \vec{\nu} = 0. \quad (34)$$

This is the constitutive equality for the Helmholtz free energy density f.

To recast (34) as an inequality, we have as the matrix L is positive definite

$$\sum_{j=1}^4 \nabla\mu_j \cdot J_j = -L\nabla\mu : \nabla\mu \leq 0. \quad (35)$$

Additionally, by (32), we have $\frac{\partial f}{\partial \chi}\partial_t\chi = -\tau(\partial_t\chi)^2 \leq 0$. It remains to show

$$\int_\Omega \sum_{j=1}^4 \mu_j r_j \leq 0. \quad (36)$$

We exploit the particular form of r and f and Structure (19). Let $Q(c) := \sum_{i=1}^4 \alpha_i c_i$. Since $r_1 = r_3 = -\frac{1}{2}r_2$, $r_4 = 0$ we have

$$\begin{aligned}
\int_\Omega \sum_{j=1}^4 \mu_j r_j &= \int_\Omega (\mu_1 - 2\mu_2 + \mu_3) r_1 \\
&= \int_\Omega \Big[k_B T\, b_\chi \Big(\ln\Big(\frac{c_1 c_3}{c_2^2}\Big) + \frac{E_1 + E_3 - E_S}{k_B T\, b_\chi} - \frac{2E_2 - E_S}{k_B T\, b_\chi}\Big) \\
&\qquad + 2(\alpha_1 - 2\alpha_2 + \alpha_3) Q(c)\Big] r_1 \\
&= \int_\Omega \Big[k_B T\, b_\chi \ln\Big(\frac{c_1 c_3 (r_+)^{1/b_\chi}}{c_2^2 (r_-)^{1/b_\chi}}\Big) + 2(\alpha_1 - \alpha_2 + \alpha_3) Q(c)\Big] r_1.
\end{aligned}$$

The first term can be estimated analogous to (19):

$$\int_\Omega k_B T b_\chi \ln\Big(\frac{c_1 c_3 (r_+)^{1/b_\chi}}{c_2^2 (r_-)^{1/b_\chi}}\Big) r_1 \leq 0 \quad (37)$$

but to estimate $\int_\Omega 2(\alpha_1 - 2\alpha_2 + \alpha_3) Q(c) r_1$ additional considerations are necessary. The logarithmic form (26) of the free energy guarantees $c_i > 0$ in

Ω_{T_0} for $t > 0$ if this is true for $t = 0$. In Section 6 a rigorous proof of this statement will be given. Hence we obtain $Q(c) > 0$ in Ω_{T_0}. Let

$$\sigma_1 := \sup_{x\in\overline{\Omega}} c_1(x,0), \quad \sigma_2 := \inf_{x\in\overline{\Omega}} c_{02}(x), \quad \sigma_3 := \sup_{x\in\overline{\Omega}} c_{03}(x), \tag{38}$$

where σ_1, σ_2, σ_3 are positive constants. By the parabolic maximum principle, [13], as for fixed c_2, c_3, χ the mapping $c_1 \mapsto r_1(c,\chi)$ decreases as c_1 increases, and (now for fixed c_1, c_3, χ) $c_2 \mapsto r_1(c,\chi)$ increases and finally $c_3 \mapsto r_1(c,\chi)$ decreases, we have $\sigma_1 = \sup_{\overline{\Omega_{T_0}}} c_1$, $\sigma_2 = \inf_{\overline{\Omega_{T_0}}} c_2$ and $\sigma_3 = \sup_{\overline{\Omega_{T_0}}} c_3$.

Now a sufficient condition for $r_1 > 0$ in Ω_{T_0} is

$$\kappa^{1/b_\chi} < \frac{\sigma_2^2}{\sigma_1\sigma_3}. \tag{39}$$

We remark that in the crystallographic measurements, the ratio constant κ never exceeded a value of 0.07 (otherwise the matrix becomes unstable). For an estimate of the volume term we require

$$\alpha_1 - 2\alpha_2 + \alpha_3 < 0. \tag{40}$$

This is a condition on the ion radii of Fe^{3+}, Fe^{2+} and Cu^+ and fulfiled in nature, see Table 1.

Together with $r_1 > 0$ and the above estimate this shows $\int_\Omega 2(\alpha_1 - 2\alpha_2 + \alpha_3)Q(c)r_1 < 0$. Hence, (36) is proved and we have shown the *constitutive free energy inequality*

$$\frac{d}{dt}\int_\Omega f(c(t),\chi(t)) + \int_{\partial\Omega}\sum_{j=1}^{4}\mu_j J_j\cdot\vec{\nu} \le 0. \tag{41}$$

In a thermodynamically closed system the fluxes on $\partial\Omega$ disappear. Hence we impose as condition on the Dirichlet data

$$h_i = 0,\ 1 \le i \le 4.$$

Instead we could impose the Neumann boundary conditions $\partial_\nu\mu_j = 0$, $1 \le j \le 4$ on $\partial\Omega$.

6 Existence of weak solutions for polynomial free energy

The rest of the article is devoted to the proof of global existence and uniqueness of a solution to the sharp interface model (30) with classical Dirichlet boundary conditions, i.e. $g = h = 0$, and with the elliptic equation in (30) replaced by the original parabolic equation. The proof of existence is done in three steps. An additional (and artificial) surface energy term $\int_\Omega \frac{\lambda}{2}|\nabla c|^2$ is added to the free energy functional leading to a diffuse interface model. This term is necessary to guarantee the existence of a minimiser (Lemma 1). The first part is contained in sections 7-13 and discusses the case of polynomial free energies for this diffuse interface model. Then we generalise to logarithmic free energies and finally the limit $\lambda \searrow 0$ is carried out. Some of the techniques used in the following sections were developed for the Cahn-Hilliard model, we mainly refer to [5], [6], [1] and in particular [7].

7 Preliminaries

In what follows, $f = f(c, \chi)$ denotes the free energy density without the surface energy terms $\frac{\gamma}{2}|\nabla\chi|^2 + \frac{\lambda}{2}|\nabla c|^2$. C will denote generic constants that can change from estimate to estimate. With the additional surface term the model is
Find for $t \geq 0$ the vector (c, μ, χ) such that in $\Omega_{T_0} := \Omega \times (0, T_0)$

$$\begin{aligned} \partial_t c &= \operatorname{div}(L\nabla\mu) + r(c, \chi), \\ \mu(c, \chi) &= \frac{\partial f}{\partial c}(c, \chi) - \lambda\triangle c, \\ \tau\partial_t\chi &= \gamma\triangle\chi - \omega(c, \chi) \end{aligned}$$

and for $t = 0$ in Ω

$$c(\cdot, 0) = c_0(\cdot), \quad \chi(\cdot, 0) = \chi_0(\cdot)$$

and for $t > 0$ in $\partial\Omega$

$$c_i = \mu_i = 0, \ 1 \leq i \leq 4. \tag{42}$$

$T_0 > 0$ denotes the stop time, $\omega = \partial_\chi f$, and $r(c, \chi)$ is given by (28).

Now, let us collect general properties of the model and some necessary tools that will be needed in the sequel. As a consequence of the assumed relation (23) the concentration vector c lies in the simplex

$$c \in \Sigma := \Big\{ d = (d_1, \dots, d_4) \in \mathbb{R}^4 \;\Big|\; \frac{3}{2} d_1 + d_2 + d_3 + d_4 = 1 \Big\}. \qquad (43)$$

We do not propose $0 \le c_i \le 1$ in Ω because for the polynomial free energies considered here this is simply not true. This is one of the reasons why logarithmic free energies are introduced later on. Let

$$\begin{aligned} X_1 &:= \Big\{ c \in H_0^{1,2}(\Omega; \mathbb{R}^4) \;\Big\|\; c \in \Sigma \text{ almost everywhere} \Big\}, \\ X_2 &:= H^{1,2}(\Omega; \mathbb{R}). \end{aligned}$$

Since we have (classical) Dirichlet boundary conditions for the equations of conservation of mass, we consider the space of test functions

$$Y := H_0^{1,2}(\Omega; \mathbb{R}^4)$$

and its dual

$$\mathcal{D} := (H_0^{1,2}(\Omega; \mathbb{R}^4))' = H^{-1,2}(\Omega; \mathbb{R}^4).$$

Let us now consider the mapping $\mathcal{L}(\mu) : Y \to \mathcal{D}$ corresponding to $\mu \mapsto -\mathrm{div}(L \nabla \mu)$ with Dirichlet boundary conditions, defined by

$$\mathcal{L}(\mu)(\zeta) := \int_\Omega L \nabla \mu : \nabla \zeta.$$

To simplify the argumentation later we will need the inverse $\mathcal{G}$ of $\mathcal{L}$. The existence of $\mathcal{G}$ is derived from the Poincaré inequality and the Lax-Milgram theorem, since L is positive definite. From this we find that $\mathcal{G}$ is positive definite, self-adjoint, injective and compact. Hence we have

$$(L \nabla \mathcal{G} v, \nabla \zeta)_{L^2} = (\zeta, v) \quad \text{for all } \zeta \in Y \text{ and } v \in \mathcal{D}.$$

We define for $v_1, v_2 \in \mathcal{D}$ the L scalar product by

$$(v_1, v_2)_L := (L \nabla \mathcal{G} v_1, \nabla \mathcal{G} v_2)_{L^2}$$

with the corresponding norm

$$\|v\|_L := \sqrt{(v, v)_L}.$$

Functions $v \in Y$ canonically define an element in Y and consequently, $(\cdot,\cdot)_L$ and $\|\cdot\|_L$ are as well defined for elements in Y.

With the help of Young's inequality we find for $\delta > 0$ and all $d \in Y$

$$\begin{aligned} \|d\|_{L^2} &= (L\nabla\mathcal{G}d, \nabla d)_{L^2} \\ &\leq \|L^{\frac{1}{2}}\nabla\mathcal{G}d\|_{L^2}\|L^{\frac{1}{2}}\nabla d\|_{L^2} \\ &\leq \frac{C_L}{\delta}\|d\|_L^2 + \delta\|\nabla d\|_{L^2}^2, \end{aligned} \tag{44}$$

where C_L is a positive constant depending on L.

The Green's function $\mathcal{G}$ allows to rewrite the conservation of mass equations as

$$\mathcal{G}(\partial_t c - r(c,\chi)) = \mu := \Big(\frac{\partial f}{\partial c_j}\Big)_{1\leq j\leq 4}. \tag{45}$$

8 The weak formulation of the problem

We call a triple $(c,\mu,\chi) \in L^2(0,T_0;\, H_0^{1,2}(\Omega;\mathbb{R}^4)) \times L^2(0,T_0;\, H_0^{1,2}(\Omega;\mathbb{R}^4)) \times L^2(0,T_0;\, H^{1,2}(\Omega;\mathbb{R}))$ with $r(c,\chi), \omega(c,\chi) \in L^1(\Omega_{T_0})$ a *weak solution* of (42) if

$$-\int\limits_{\Omega_{T_0}} \partial_t\xi\cdot(c-c_0) + \int\limits_{\Omega_{T_0}} L\nabla\mu : \nabla\xi - \int\limits_{\Omega_{T_0}} r(c,\chi)\xi = 0 \tag{46}$$

for all $\xi \in L^2(0,T_0;\, H_0^1(\Omega;\mathbb{R}^4))$ with $\partial_t\xi \in L^2(\Omega_{T_0})$, $\xi(T_0) = 0$, and

$$\int\limits_{\Omega_{T_0}} \mu\cdot\eta = \int\limits_{\Omega_{T_0}} \Big(\frac{\partial f}{\partial c}(c)\cdot\eta + \lambda\nabla c\cdot\nabla\eta\Big) \tag{47}$$

for all $\eta \in L^2(0,T_0;\, H_0^1(\Omega;\mathbb{R}^4)) \cap L^\infty(\Omega_{T_0};\mathbb{R}^4)$, and

$$-\int\limits_{\Omega_{T_0}} \tau\partial_t\zeta(\chi-\chi_0) + \int\limits_{\Omega_{T_0}} \gamma\nabla\chi\cdot\nabla\zeta - \int\limits_{\Omega_{T_0}} \omega(c,\chi)\zeta = 0 \tag{48}$$

for all $\zeta \in L^2(0,T_0;\, H^1(\Omega;\mathbb{R}))$ with $\partial_t\zeta \in L^2(\Omega_{T_0})$, $\zeta(T_0) = 0$.

9 A semi-implicit time discretisation

We fix an $M \in \mathbb{N}$ and set $h := \frac{T_0}{M}$. For $m \geq 1$ and given $(c^{m-1}, \mu^{m-1}, \chi^{m-1}) \in H_0^{1,2}(\Omega; \mathbb{R}^4) \times H_0^{1,2}(\Omega, \mathbb{R}^4) \times H^{1,2}(\Omega; \mathbb{R})$,

$$
\begin{aligned}
\frac{c^m - c^{m-1}}{h} &= \operatorname{div}(L\nabla\mu^m) + r(c^{m-1}, \chi^{m-1}), \\
\mu^m &= \frac{\partial f}{\partial c}(c^m, \chi^m) - \lambda \triangle c^m, \\
\tau \frac{\chi^m - \chi^{m-1}}{h} &= \gamma \triangle \chi^m + \omega(c^m, \chi^m)
\end{aligned}
\tag{49}
$$

defines the implicit time discretisation of System (42) except for the reaction term r that has been treated explicitly. Therefore, we call the resulting scheme semi-implicit. In (49), $\omega(c, \chi) = \partial_\chi f(c, \chi)$ and for the subsequent sections, let $r^{m-1} := r(c^{m-1}, \chi^{m-1})$.

10 Structural Assumptions

In order to be able to establish the existence of weak solutions in the sense of Section 8, the following assumptions are made:
(A1) $\Omega \subset \mathbb{R}^D$ is a bounded domain with Lipschitz boundary.
(A2) The free energy density f can be written as

$$f(c, \chi) = f^1(c, \chi) + f^2(c, \chi) \quad \text{for all } c \in \mathbb{R}^4,\ \chi \in \mathbb{R}$$

with $f^1, f^2 \in C^1(\mathbb{R}^4 \times \mathbb{R}; \mathbb{R})$ and $f^1(\cdot, \chi)$ convex for every $\chi \in \mathbb{R}$, $f^1(c, \cdot)$ convex for every $c \in \mathbb{R}^4$. Furthermore,
(A2.1) $f^1 \geq 0$.
(A2.2) There exists a constant $C_1 > 0$ such that

$$
\begin{aligned}
|\partial_c f^2(c, \chi)| &\leq C_1(|c| + 1) \quad \text{for all } c \in \Sigma, \chi \in \mathbb{R}, \\
|\partial_\chi f^2(c, \chi)| &\leq C_1(|\chi| + 1) \quad \text{for all } c \in \Sigma, \chi \in \mathbb{R}.
\end{aligned}
$$

(A2.3) For all $\delta > 0$ there exists a constant $C_\delta > 0$ such that

$$|\partial_c f^1(c, \chi)| + |\partial_\chi f^1(c, \chi)| \leq \delta f^1(c, \chi) + C_\delta \quad \text{for all } c \in \Sigma,\ \chi \in \mathbb{R}.$$

(A3) The initial data (c_0, χ_0) fulfils

$$f(c_0, \chi_0) < \infty,\ \omega(c_0, \chi_0) < \infty.$$

(A4.1) The diffusion tensor L is symmetric and positive definite.
(A4.2) $\gamma > 0$ is a constant, $0 < \lambda < \lambda_0$ where λ_0 is a small constant such that the estimate $\partial_t F \leq 0$ is valid.
(A5) The reaction term r is chosen in correspondence to f such that

$$\int_\Omega \mu \cdot r \leq 0. \tag{50}$$

(A6) The coefficients $\alpha_i > 0$ satisfy Condition (40). Furthermore $0 < \kappa \leq 1$, $k > 0$ and $0 < b^1, b^2 \leq 1$. The initial values c_0 of c and κ, b^1, b^2 fulfil (compare with (39))

$$\kappa^{1/\max(b^1,b^2)} < \frac{\sigma_2^2}{\sigma_1 \sigma_3}. \tag{51}$$

By Assumption (A2) any polynomial growth is allowed for f^1, whereas exponential growth is not. For the non-convex part, sublinear growth of $\partial_c f^2$ in c and $\partial_\chi f^2$ in χ is prescribed.

If we approximate a logarithmic free energy function f by a polynomial, we also have to replace the reaction term by a suitable approximation. This is the gist of (A5). In Section 15 it is shown how a suitable r can be constructed for approximations f^δ of f.

If one chooses $\lambda > 0$ small enough, one can guarantee $\partial_t F(c(t), \chi(t)) \leq 0$ because then the term with the possibly 'wrong' sign $\lambda \triangle c r_1$ can be compensated by $(\alpha_1 - 2\alpha_2 + \alpha_3) Q(c) r_1(c) < 0$. From now on we assume without further stating that the assumptions (A1)-(A6) hold.

11 Existence of solutions to the time discrete scheme

For the treatment of the diffuse interface model we introduce the energy functional

$$F(c,\chi) := \int_\Omega \Big(f(c,\chi) + \frac{\lambda}{2}|\nabla c|^2 + \frac{\gamma}{2}|\nabla \chi|^2 \Big). \tag{52}$$

Additionally, for each time step m in the semi-implicit time discretisation (49), given step size $h > 0$ and given (c^{m-1}, χ^{m-1}) we define the discrete energy functional

$$F^{m,h}(c,\chi) := F(c,\chi) + \frac{1}{2h}\|c - c^{m-1} - hr^{m-1}\|_L^2 + \frac{\tau}{2h}\|\chi - \chi^{m-1}\|_{L^2}^2. \tag{53}$$

Lemma 1 *Let* $(c^{m-1}, \chi^{m-1}) \in X_1 \times X_2$ *be given. Then for* $0 < h < \min\{\frac{\tau}{2C_1}, \frac{\lambda}{8C_1^2 C_L}\}$ *the functional* $F^{m,h}$ *possesses a minimiser in* $X_1 \times X_2$*.*

Proof: We will show that $F^{m,h}$ is coercive and weakly lower semicontinuous. Using Assumptions (A2.1) and (A2.2) we find

$$\begin{aligned} F^{m,h}(c,\chi) \;&\geq\; \frac{\lambda}{2}\|\nabla c\|_{L^2}^2 + \frac{\gamma}{2}\|\nabla \chi\|_{L^2}^2 - C_1(\|c\|_{L^2}^2 + \|\chi\|_{L^2}^2) - C \\ &\quad + \frac{1}{2h}\Big(\|c - c^{m-1} - hr^{m-1}\|_L^2 + \tau\|\chi - \chi^{m-1}\|_{L^2}^2\Big) \\ &\geq\; \Big(\frac{\lambda}{2} - \delta C_1\Big)\|\nabla c\|_{L^2}^2 + \Big(\frac{1}{2h} - \frac{C_1 C_L}{\delta}\Big)\|c - c^{m-1} - hr^{m-1}\|_L^2 \\ &\quad + \frac{\gamma}{2}\|\nabla\chi\|_{L^2}^2 + \Big(\frac{\tau}{2h} - C_1\Big)\|\chi - \chi^{m-1}\|_{L^2}^2 - C, \end{aligned}$$

where in the second estimate (44) was used and $C = C(c^{m-1}, \chi^{m-1}, r)$. Now, for $0 < h < \min\{\frac{\tau}{2C_1}, \frac{\lambda}{8C_1^2 C_L}\}$ by choosing $\delta = \frac{\lambda}{4C_1}$, we conclude with the help of the Poincaré inequality that $F^{m,h}$ is coercive on $X_1 \times X_2$. Let

$$d := \inf\{F^{m,h}(c,\chi) \mid c \in X_1,\, \chi \in X_2\}, \quad d < \infty.$$

If we now consider a minimising sequence $(c_l, \chi_l)_{l\in\mathbb{N}} \subset X_1 \times X_2$ with $F^{m,h}(c_l, \chi_l) \to d$, the coercivity of $F^{m,h}$ implies the boundedness of (c_l, χ_l) uniformly in l. Passing to a subsequence if necessary, by the reflexivity of $X_1 \times X_2$ we may assume

$$(c_l, \chi_l) \rightharpoonup (c, \chi) \in X_1 \times X_2 \quad \text{for } l \to \infty$$

and by Rellich's theorem or Sobolev's imbedding theorem,

$$(c_l, \chi_l) \to (c, \chi) \in L^2(\Omega, \mathbb{R}^4) \times L^2(\Omega, \mathbb{R}) \text{ for } l \to \infty$$

and $(c_l, \chi_l) \to (c, \chi)$ a.e. in Ω.

To verify the weak lower semicontinuity of $F^{m,h}$ in $X_1 \times X_2$ we first remark that this is true for all convex terms. For $\int_\Omega f^1(c, \chi)$ this follows from Assumption (A2) and for $\int_\Omega f^2(c,\chi)$ from (A2.2) and the dominated convergence theorem of Lebesgue. This implies $F^{m,h}(c,\chi) \leq \liminf_{l\to\infty} F^{m,h}(c_l, \chi_l)$. $\square$

Lemma 2 *The minimiser* (c^m, χ^m) *of* $F^{m,h}$ *fulfils*

$$\int_\Omega \frac{c^m - c^{m-1}}{h} \cdot \xi + \int_\Omega L\nabla\mu^m : \nabla\xi = \int_\Omega r^{m-1}\xi \quad \textit{for all } \xi \in Y, \tag{54}$$

$$\int_\Omega \Big(\lambda\nabla c^m \cdot \nabla\eta + \partial_c f(c^m, \chi^m) \cdot \eta\Big) = \int_\Omega \mu^m \cdot \eta \quad \textit{for } \eta \in Y \cap L^\infty(\Omega; \mathbb{R}^4), \tag{55}$$

$$\int_\Omega \Big[\tau\frac{\chi^m - \chi^{m-1}}{h} + \omega(c^m, \chi^m)\Big]\zeta + \int_\Omega \gamma\nabla\chi^m \cdot \nabla\zeta = 0 \quad \textit{for } \zeta \in H^1(\Omega). \tag{56}$$

Here, $\mu^m = \mathcal{G}\Big(\frac{c^m - c^{m-1}}{h} - r^{m-1}\Big)$.

Proof: We choose directions $\xi \in Y \cap L^\infty(\Omega; \mathbb{R}^4)$, $\zeta \in X_2 \cap L^\infty(\Omega; \mathbb{R})$ and determine the variations of $F^{m,h}(c, \chi)$ with respect to c and χ for ξ, ζ. We start with the variation w.r.t. c, i.e.

$$\lim_{s\to 0}\Big((F^{m,h}(c^m + s\xi, \chi^m) - F^{m,h}(c^m, \chi^m))s^{-1}\Big). \tag{57}$$

Since f^1 is convex in c, we have

$$f^1(c^m, \chi^m) \geq f^1(c^m + s\xi, \chi^m) - s\partial_c f^1(c^m + s\xi, \chi^m) \cdot \xi.$$

This implies

$$\begin{aligned} f^1(c^m + s\xi, \chi^m) &\leq f^1(c^m, \chi^m) + |s\partial_c f^1(c^m + s\xi, \chi^m)| \, \|\xi\|_{L^\infty} \\ &\leq f^1(c^m, \chi^m) + |s| \, f^1(c^m + s\xi, \chi^m) \, \|\xi\|_{L^\infty} + C|s|. \end{aligned}$$

The last is by Assumption (A2.3) with $\delta = 1$. Hence, for s small enough,

$$\Big|\frac{f^1(c^m + s\xi, \chi^m) - f^1(c^m, \chi^m)}{s}\Big| \leq C(f^1(c^m, \chi^m) + 1).$$

Assumption (A2.2) and Lebesgue's dominated convergence theorem imply

$$\lim_{s\to 0}\frac{1}{s}\Big(\int_\Omega f(c^m + s\xi, \chi^m) - f(c^m, \chi^m)\Big) = \int_\Omega \partial_c f(c^m, \chi^m) \cdot \xi.$$

The variation of the quadratic form $c \mapsto \frac{1}{2h}\|c^m - c^{m-1} - hr^{m-1}\|_L^2$ yields

$$\lim_{s\to 0}\Big(s^{-1}(2h)^{-1}\left(\|c^m + s\xi - c^{m-1} - hr^{m-1}\|_L^2 - \|c^m - c^{m-1} - hr^{m-1}\|_L^2\right)\Big)$$
$$= \Big(\frac{c^m - c^{m-1} - hr^{m-1}}{h}, \xi\Big)_L = \Big(\mathcal{G}\Big(\frac{c^m - c^{m-1}}{h} - r^{m-1}\Big), \xi\Big)_{L^2} = \Big(\mu^m, \xi\Big)_{L^2}$$

and finally

$$\begin{aligned}\frac{\lambda}{2}\lim_{s\to 0}\Big\{s^{-1}\Big[(\nabla(c+s\xi), \nabla(c+s\xi))_{L^2} - (\nabla c, \nabla c)_{L^2}\Big]\Big\} &= \lambda(\nabla c, \nabla\xi)_{L^2} \\ &= -\lambda(\triangle c, \xi)_{L^2}.\end{aligned}$$

Hence we obtain (54). The equality (55) follows because (c^m, χ^m) is a minimiser and thus the variation in (57) is 0. To derive (56), we consider the variation of $F^{m,h}(c^m, \chi^m)$ w.r.t. χ. As before,

$$\begin{aligned}\lim_{s\to 0}\Big(\tau s^{-1}(2h)^{-1}\left(\|\chi^m + s\zeta - \chi^{m-1}\|_{L^2}^2\right. &- \left.\|\chi^m - \chi^{m-1}\|_{L^2}^2\right)\Big) \\ &= \Big(\tau\frac{\chi^m - \chi^{m-1}}{h}, \zeta\Big)_{L^2}.\end{aligned}$$

It remains to prove

$$\lim_{s\to 0}\int_\Omega \Big(f(c^m, \chi^m + s\zeta) - f(c^m, \chi^m)\Big) = \int_\Omega \partial_\chi f(c^m, \chi^m)\zeta.$$

This limit can be justified in the same way as (57) and Identity (56) follows. □

12 Uniform estimates

In the preceding sections we proved the existence of a discrete solution (c^m, μ^m, χ^m) for $1 \le m \le M$ and arbitrary $M \in \mathbb{N}$. We define the piecewise constant extension (c_M, μ_M, χ_M) of $(c^m, \mu^m, \chi^m)_{1\le m\le M}$ by

$$(c_M(t), \mu_M(t), \chi_M(t)) := (c_M^m, \mu_M^m, \chi_M^m) := (c^m, \mu^m, \chi^m) \text{ for } t \in ((m-1)h, mh]$$

and $c_M(0) = c_0$, $\chi_M(0) = \chi_0$, $\mu_M(0)$ obtained from Eq. (55).

The piecewise linear extension $(\overline{c}_M, \overline{\mu}_M, \overline{\chi}_M)$ for $t = (\beta m + (1-\beta)(m-1))h$ with appropriate $\beta \in [0,1]$ is given by the interpolation

$$(\overline{c}_M, \overline{\mu}_M, \overline{\chi}_M)(t) := \beta(c_M^m, \mu_M^m, \chi_M^m) + (1-\beta)(c_M^{m-1}, \mu_M^{m-1}, \chi_M^{m-1}).$$

Lemma 3 *For sufficiently small h the following a-priori estimates are valid.*
(a) For all $M \in \mathbb{N}$ and all $t \in [0, T_0]$ we have the dissipation inequality

$$F(c_M, \chi_M)(t) + \frac{1}{2} \int\limits_{\Omega_t} (L\nabla\mu_M : \nabla\mu_M + |\partial_t \chi_M|^2) \leq F(c_0, \chi_0).$$

(b) There exists a constant $C > 0$ such that

$$\sup_{0 \leq t \leq T_0} \Big\{ \|c_M(t)\|_{H^1} + \|\chi_M(t)\|_{H^1} \Big\} \leq C, \quad (58)$$

$$\sup_{0 \leq t \leq T_0} \int\limits_{\Omega} f^1(c_M(t), \chi_M(t)) + \|\nabla\mu_M\|_{L^2(\Omega_{T_0})} + \|\partial_t \chi_M\|_{L^2(\Omega_{T_0})} \leq C. \quad (59)$$

Proof: The idea of the proof is to use the decay of $t \mapsto F(c(t), \chi(t))$. Here, a modification of the standard proof becomes necessary which reveals that the treatment of the reaction term in (49) is natural.

As (c^m, χ^m) is a minimiser of $F^{m,h}$,

$$F(c^m, \chi^m) + \frac{1}{2h}\|c^m - c^{m-1} - hr^{m-1}\|_L^2 + \frac{\tau}{2h}\|\chi^m - \chi^{m-1}\|_{L^2}^2 \leq F(c^{m-1} + hr^{m-1}, \chi^{m-1}). \quad (60)$$

A direct calculation yields

$$\frac{1}{2h}\|c^m - c^{m-1} - hr^{m-1}\|_L^2 = \frac{h}{2}(\nabla\mu^m, L\nabla\mu^m)_{L^2}.$$

To bring the right hand side of (60) in a form suitable for recursion, we remark that for sufficiently small h

$$F(c^{m-1} + hr^{m-1}, \chi^{m-1}) \leq F(c^{m-1}, \chi^{m-1}).$$

This is equivalent to

$$\frac{F(c^{m-1} + hr^{m-1}, \chi^{m-1}) - F(c^{m-1}, \chi^{m-1})}{h} \leq 0 \quad \text{for all } h > 0.$$

By Lebesgue's dominated convergence theorem, a sufficient condition for the last inequality is $\partial_c F(c^{m-1}, \chi^{m-1}) \cdot r^{m-1} \leq 0$ which holds due to (A5).

By iterating (60) with the estimated right hand side, we find

$$F(c_M^m, \chi_M^m) + \frac{1}{2}\int\limits_0^{mh} \Big((\nabla \mu_M^m, L\nabla \mu_M^m)_{L^2} + (\partial_t \chi_M^m, \partial_t \chi_M^m)_{L^2} \Big)\, dt \le F(c_0, \chi_0).$$

Using the assumptions and with the help of the Poincaré inequality this proves the lemma. □

We extend c_M by the initial value c_0 of c for $t \in (-h, 0]$. Now, for the linear interpolation $\overline{c}_M$ of c_M^m, the Euler-Lagrange equation (54) can be rewritten as

$$\int\limits_\Omega \partial_t \overline{c}_M(t) \cdot \xi + \int\limits_\Omega L\nabla \mu_M(t) : \nabla \xi = \int\limits_\Omega r(c_M(t-h), \chi_M(t-h)) \cdot \xi \quad \text{for all } \xi \in Y \tag{61}$$

which holds for almost all $t \in (0, T_0)$. Together with the uniform estimates of Lemma 3, (61) allows to show compactness in time.

Lemma 4 *There exists a constant $C > 0$ such that for all $t_1, t_2 \in [0, T_0]$*

$$\|\overline{c}_M(t_2) - \overline{c}_M(t_1)\|_{L^2} \le C|t_2 - t_1|^{\frac{1}{4}}.$$

Furthermore, there is a subsequence $(c_M)_{M\in\mathcal{N}}$ and a subsequence $(\mu_M)_{M\in\mathcal{N}}$ with $\mathcal{N} \subset \mathbb{N}$ and there are $c \in L^\infty(0, T_0; Y)$, $\mu \in L^2(0, T_0; Y)$ such that

- *(i)* $\overline{c}_M \to c$ *in* $C^{0,\alpha}([0, T_0]; L^2(\Omega; \mathbb{R}^4))$ *for all* $\alpha \in (0, \frac{1}{4})$,
- *(ii)* $c_M \to c$ *in* $L^\infty(0, T_0; L^2(\Omega; \mathbb{R}^4))$,
- *(iii)* $c_M \to c$ *almost everywhere in* Ω_{T_0},
- *(iv)* $c_M \overset{*}{\rightharpoonup} c$ *in* $L^\infty(0, T_0; H_0^1(\Omega; \mathbb{R}^4))$,
- *(v)* $\mu_M \rightharpoonup \mu$ *in* $L^2(0, T_0; H_0^1(\Omega; \mathbb{R}^4))$

as $M \in \mathcal{N}$ tends to infinity.

Proof: We test Eq. (61) with $\xi := \overline{c}_M(t_2) - \overline{c}_M(t_1)$, where $t_1, t_2 \in [0, T_0]$ with $t_1 < t_2$. After integration in time from t_1 to t_2, we obtain

$$\begin{aligned} \|\overline{c}_M(t_2) - \overline{c}_M(t_1)\|_{L^2}^2 \; &+ \int\limits_{t_1}^{t_2}\int\limits_\Omega L\nabla \mu_M(t) : \nabla(\overline{c}_M(t_2) - \overline{c}_M(t_1))\, dt \\ &= \int\limits_{t_1}^{t_2}\int\limits_\Omega r(c_M(t-h), \chi_M(t-h))(\overline{c}_M(t_2) - \overline{c}_M(t_1))\, dt. \end{aligned}$$

The c_M^m are uniformly bounded in Y, therefore the linear interpolants $\overline{c}_M$ are uniformly bounded in $L^\infty(0,T_0;\,Y)$. Thus we obtain

$$\begin{aligned}
&\|\overline{c}_M(t_2)-\overline{c}_M(t_1)\|_{L^2}^2 \\
&\le\ C\|\overline{c}_M\|_{L^\infty(H^1)}\int_{t_1}^{t_2}\Big(\|\nabla\mu_M(t)\|_{L^2}+\|r(c_M(t-h),\chi_M(t-h))\|_{L^2}\Big)\,dt \\
&\le\ C\|\overline{c}_M\|_{L^\infty(H^1)}\Big[(t_2-t_1)^{\frac{1}{2}}\|\nabla\mu\|_{L^2(\Omega_{T_0})}+(t_2-t_1)\|r(c_M,\chi_M)\|_{L^\infty(L^2)}\Big].
\end{aligned}$$

Employing the a-priori estimates (58) and (59) we have shown

$$\|\overline{c}_M(t_2)-\overline{c}_M(t_1)\|_{L^2}\le C|t_2-t_1|^{\frac{1}{4}}\quad\text{for all } t_1,t_2\in[0,T_0]$$

for a positive constant C. This is the equicontinuity of $(\overline{c}_M)_{M\in\mathbb{N}}$. The boundedness of $(\overline{c}_M)$ in $L^\infty(0,T_0;\,H_0^{1,2}(\Omega))$ and the fact that H^1 is compactly imbedded in L^2 yields (i) as a consequence of the Arzelà-Ascoli theorem. The claims (ii),(iii) and (iv) follow exactly as in [7]. We choose for $t\in[0,T_0]$ values $m\in\{1,\dots,M\}$ and $\beta\in[0,1]$ such that $t=(\beta m+(1-\beta)(m-1))h$. From the definition of $\overline{c}$ we get at once

$$\begin{aligned}
\|\overline{c}_M(t)-c_M(t)\|_{L^2} &= \|\beta c_M^m+(1-\beta)c_M^{m-1}-c_M^m\|_{L^2}\\
&= (1-\beta)\|c_M^m-c_M^{m-1}\|_{L^2}\\
&\le Ch^{\frac{1}{4}}.
\end{aligned}$$

This tends to zero as M becomes infinite. With the help of (i), this proves (ii). Since for a subsequence we have convergence almost everywhere, (iii) is proved, too. Claim (iv) is a direct consequence of Estimate (58) which gives the boundedness of c_M in $L^\infty(0,T_0;\,Y)$.

For the proof of (v) we notice that due to Estimate (59), the $(\nabla\mu_M)$ are uniformly bounded in $L^2(\Omega_{T_0})$. By the Poincaré inequality the (μ_M) are uniformly bounded in $L^2(0,T_0;\,H_0^1(\Omega))$. With the Banach-Alaoglu theorem (v) follows. □

Lemma 5 *For a suitable subsequence $\mathcal{N}\subset\mathbb{N}$, we have*

(i)	$\overline{\chi}_M$	$\to$	χ *in* $C^{0,\alpha}([0,T_0];\,L^2(\Omega))$ *for all* $\alpha\in(0,\frac{1}{2})$,
(ii)	χ_M	$\to$	χ *in* $L^\infty(0,T_0;\,L^2(\Omega))$,
(iii)	χ_M	$\to$	χ *almost everywhere in* Ω_{T_0},

$$\begin{array}{llll} \textit{(iv)} & \chi_M & \overset{*}{\rightharpoonup} & \chi \textit{ in } L^\infty(0,T_0;\, H^1(\Omega)), \\ \textit{(v)} & \partial_c f(c_M,\chi_M) & \to & \partial_c f(c,\chi) \textit{ in } L^1(\Omega_{T_0}), \\ \textit{(vi)} & \partial_\chi f(c_M,\chi_M) & \to & \partial_\chi f(c,\chi) \textit{ in } L^1(\Omega_{T_0}) \end{array}$$

as $M \in \mathcal{N}$ tends to infinity.

Proof: Similar to Eq. (61) we can reformulate Identity (56) to

$$\tau \int_\Omega \partial_t \overline{\chi}_M(t)\zeta + \int_\Omega \gamma \nabla \chi_M(t) \cdot \nabla \zeta + \int_\Omega \omega(c_M(t), \chi_M(t))\zeta = 0 \quad \text{for all } \zeta \in H^1(\Omega) \tag{62}$$

which holds for almost all $t \in [0, T_0]$.

We test (62) with $\zeta := \overline{\chi}_M(t_2) - \overline{\chi}_M(t_1)$, where $t_1, t_2 \in [0, T_0]$, $t_2 > t_1$. After integration in time from t_1 to t_2 we get

$$\begin{aligned} \tau \|\overline{\chi}_M(t_2) - \overline{\chi}_M(t_1)\|_{L^2}^2 \; &+ \int_{t_1}^{t_2} \int_\Omega \gamma \nabla \chi_M(t) \cdot \nabla (\overline{\chi}_M(t_2) - \overline{\chi}_M(t_1)) \, dt \\ &+ \int_{t_1}^{t_2} \omega(c_M(t), \chi_M(t)) \, (\overline{\chi}_M(t_2) - \overline{\chi}_M(t_1)) \, dt = 0. \end{aligned}$$

From the uniform boundedness of $\overline{\chi}_M$ in $L^\infty(0, T_0;\, H^1(\Omega))$ and in $L^\infty(\Omega_{T_0})$ we obtain:

$$\int_{t_1}^{t_2} \int_\Omega \gamma \nabla \chi_M(t) \cdot \nabla (\overline{\chi}_M(t_2) - \overline{\chi}_M(t_1)) \, dt \le c \|\overline{\chi}_M\|_{L^\infty(H^1)} \int_{t_1}^{t_2} \|\nabla \chi_M(t)\|_{L^2} \, dt,$$

$$\int_{t_1}^{t_2} \omega(c_M(t), \chi_M(t)) \, (\overline{\chi}_M(t_2) - \overline{\chi}_M(t_1)) \, dt \le c \|\overline{\chi}_M\|_{L^\infty(\Omega_{T_0})} \int_{t_1}^{t_2} \omega(c_M(t), \chi_M(t)) dt.$$

With the continuity of ω, these estimates imply

$$\|\overline{\chi}_M(t_2) - \overline{\chi}_M(t_1)\|_{L^2} \le C|t_2 - t_1|^{\frac{1}{2}} \quad \text{for all } t_1, t_2 \in [0, T_0]$$

and exactly as in Lemma 4 this yields statements (i)-(iv).

In order to prove (v) and (vi), we first notice that by Assumption (A2), $\partial_c f$ and $\partial_\chi f$ are continuous functions. Hence, by (iii) and Lemma 4(iii),

$$\begin{aligned} \partial_c f(c_M, \chi_M) &\to \partial_c f(c, \chi) \quad \text{almost everywhere in } \Omega_{T_0}, \\ \partial_\chi f(c_M, \chi_M) &\to \partial_\chi f(c, \chi) \quad \text{almost everywhere in } \Omega_{T_0}. \end{aligned}$$

The growth condition of Assumption (A2.3) on f^1 now yields that for arbitrary $\delta > 0$ and all measurable $E \subset \Omega$

$$\int\limits_E |\partial_c f^1(c_M, \chi_M)| \leq \delta \int\limits_E f^1(c_M, \chi_M) + C_\delta |E| \leq \delta C + C_\delta |E|.$$

Therefore, $\int\limits_E |\partial_c f^1(c_M, \chi_M)| \to 0$ as $|E| \to 0$ uniformly in M and by Vitali's theorem, $f^1(c_M, \chi_M) \to f^1(c, \chi)$ in $L^1(\Omega_{T_0})$ as $M \in \mathcal{N}$ tends to infinity. The same result for f^2 follows directly from (A2.2) and the dominated convergence theorem of Lebesgue. The proof of $\partial_\chi f(c_M, \chi_M) \to \partial_\chi f(c, \chi)$ exploiting (A2.3) and (A2.2) is similar. $\square$

13 Global existence of solutions for polynomial free energy

We are now in the position to state one of the main results.

Theorem 1 *Let the assumptions of Section 10 hold. Then, there exists a weak solution (c, μ, χ) of the diffuse interface equations in the sense of (46)-(48) such that*

(i) $c \in C^{0,\frac{1}{4}}([0, T_0];\ L^2(\Omega; \mathbb{R}^4))$,
(ii) $\partial_t c \in L^2(0, T_0;\ (H^1_0(\Omega; \mathbb{R}^4))')$,
(iii) $\chi \in C^{0,\frac{1}{2}}([0, T_0];\ L^2(\Omega))$,
(iv) $\partial_t \chi \in L^2(0, T_0;\ (H^1_0(\Omega))')$.

Proof: We are going to prove that (c, μ, χ) introduced in Lemmata 4 and 5 is the desired weak solution in the sense of (46)-(48). From Eq. (61) we learn

$$-\int\limits_{\Omega_{T_0}} \partial_t \xi (\overline{c}_M - c_0) + \int\limits_{\Omega_{T_0}} L \nabla \mu_M : \nabla \xi + \int\limits_{\Omega_{T_0}} r(c_M, \chi_M) = 0$$

for all $\xi \in L^2(0,T_0;Y)$ with $\partial_t\xi \in L^2(\Omega_{T_0})$ and $\xi(T_0)=0$. Passing to the limit $M\to\infty$ together with Lemma 4 this implies (46). Now we show (47). From (55) we see

$$\int_\Omega \lambda\nabla c_M\cdot\nabla\eta + \partial_c f(c_M,\chi_M)\cdot\eta = \int_\Omega \mu_M\cdot\eta \quad \text{for all } \eta\in Y\cap L^\infty(\Omega;\mathbb{R}^4).$$

The convergence of

$$\int_\Omega \lambda c_M\cdot\nabla\eta \to \int_\Omega \lambda c\cdot\nabla\eta$$

as $M\to\infty$ is clear by linearity and the convergence

$$\int_\Omega \partial_c f(c_M,\chi_M)\cdot\eta \to \int_\Omega \partial_c f(c,\chi)\cdot\eta$$

is again evident by Vitali's theorem similar to the proof of Lemma 5 by using the almost everywhere convergence of c_M and χ_M, the growth condition (A2.3), Estimate (59) on f^1 and the boundedness of η.

In the same way, we obtain (48) from (62). □

14 Uniqueness of the diffuse interface model

To show uniqueness of (42), we use an integration in time method. The proof requires the validity of the free energy inequality and the validity of (A6).

Theorem 2 *The solution (c,μ,χ) of the diffuse interface equations obtained in Theorem 1 is unique in the spaces stated in this theorem.*

Proof: Assume that (c^i,χ^i,μ^i), $i=1,2$ are two solutions of System (42). Now, let $c:=c^2-c^1$, $\chi:=\chi^2-\chi^1$, $\mu:=\mu^2-\mu^1$, $r:=r(c^2,\chi^2)-r(c^1,\chi^1)$, $\omega:=\partial_\chi f(c^2,\chi^2)-\partial_\chi f(c^1,\chi^1)$. The difference (c,χ,μ) solves the weak formulation

$$-\int_{\Omega_{T_0}} \partial_t\xi\cdot c + \int_{\Omega_{T_0}} L\nabla\mu : \nabla\xi - \int_{\Omega_{T_0}} r\cdot\xi \;=\; 0, \tag{63}$$

$$\int_{\Omega_{T_0}} \Big[(\partial_c f(c^2,\chi^2)-\partial_c f(c^1,\chi^1))\cdot\eta + \lambda\nabla c\cdot\nabla\eta\Big] \;=\; \int_{\Omega_{T_0}} \mu\cdot\eta, \tag{64}$$

$$-\int_{\Omega_{T_0}} \tau\partial_t\zeta\chi + \int_{\Omega_{T_0}} \gamma\nabla\chi\cdot\nabla\zeta - \int_{\Omega_{T_0}} \omega\cdot\zeta \;=\; 0. \tag{65}$$

For given $\eta \in L^2(0,T_0;\, H_0^1(\Omega,\mathbb{R}^4))$ and $t_0 \in (0,T_0)$ we define

$$\xi(\cdot,t) := \begin{cases} \int\limits_t^{t_0} \eta(\cdot,s)ds & \text{if } t \le t_0, \\ 0 & \text{if } t > t_0. \end{cases} \tag{66}$$

Using this test function in (63) we find after integration by parts in time

$$\begin{aligned} 0 &= \int\limits_{\Omega_{t_0}} c\cdot\eta + \int\limits_{\Omega_{t_0}} L\nabla\mu : \nabla\Big(\int\limits_t^{t_0} \eta(s)ds\Big) - \int\limits_{\Omega_{t_0}} r\cdot\Big(\int\limits_t^{t_0} \eta(s)\,ds\Big) \\ &= \int\limits_{\Omega_{t_0}} c\cdot\eta + \int\limits_{\Omega_{t_0}} L\nabla\Big(\int\limits_0^t \mu(s)ds\Big) : \nabla\eta - \int\limits_{\Omega_{t_0}} \Big(\int\limits_0^t r(s)ds\Big)\cdot\eta. \end{aligned} \tag{67}$$

This implies

$$\mathcal{G}\Big(c - \int\limits_0^t r(s)ds\Big) = -\int\limits_0^t \mu(s)\,ds \quad \text{and} \quad \partial_t\mathcal{G}\Big(c - \int\limits_0^t r(s)ds\Big) = -\mu.$$

By choosing $\eta := \mu$ in (67) we obtain

$$\begin{aligned} 0 &= \int\limits_{\Omega_{t_0}} c\cdot\mu + \int\limits_{\Omega_{t_0}} L\nabla\Big(\mathcal{G}\Big(\int\limits_0^t r(s)ds - c\Big)\Big) : \nabla\Big(\partial_t\mathcal{G}\Big(\int\limits_0^t r(s)ds - c\Big)\Big) \\ &\quad - \int\limits_{\Omega_{t_0}} \Big(\int\limits_0^t r(s)ds\Big)\cdot\mu \end{aligned}$$

and consequently

$$\begin{aligned} 0 &= \int\limits_{\Omega_{t_0}} c\cdot\mu + \int\limits_{\Omega} L\nabla\mathcal{G}\Big(\int\limits_0^{t_0} r(s)ds - c(t_0)\Big) : \nabla\mathcal{G}\Big(\int\limits_0^{t_0} r(s)ds - c(t_0)\Big) \\ &\quad - \int\limits_{\Omega_{t_0}} \Big(\int\limits_0^t r(s)ds\Big)\cdot\mu. \end{aligned} \tag{68}$$

In Eq. (64) we test with $\eta := \mathcal{X}_{[0,t_0]}c$. Hence we have

$$\int\limits_{\Omega_{t_0}} c \cdot \mu = \int\limits_{\Omega_{t_0}} \lambda |\nabla c|^2 + (\partial_c f(c^2, \chi^2) - \partial_c f(c^1, \chi^1)) \cdot c. \tag{69}$$

From (68) and (69) we learn

$$\begin{aligned} \Big\| \Big(\int\limits_0^{t_0} r \Big) - c(t_0) \Big\|_L^2 + \int\limits_{\Omega_{t_0}} \lambda |\nabla c|^2 \; - \int\limits_{\Omega_{t_0}} (\int\limits_0^t r(s) ds) \cdot \mu & \\ = \; - \int\limits_{\Omega_{t_0}} (\partial_c f(c^2, \chi^2) - \partial_c f(c^1, \chi^1)) \cdot c. & \quad (70) \end{aligned}$$

From the free energy estimate we infer that if conditions (40), (51) and (A4.2) hold (i.e. if $\lambda < \lambda_0$), then

$$\int\limits_{\Omega_{t_0}} \Big(\int\limits_0^t r(s) ds \Big) \cdot \mu \leq 0. \tag{71}$$

This holds because $r(t) \cdot \mu(t) = r_1(t)(\mu_1(t) - 2\mu_2(t) + \mu_3(t))$ and $(\mu_1(t) - 2\mu_2(t) + \mu_3(t)) < 0$, $\int_0^L r(s) ds \geq r_1(t) > 0$ for almost every $t \in \Omega_{T_0}$, see Section 5. Therefore we obtain as a consequence of (70)

$$\lambda \int\limits_{\Omega_{t_0}} |\nabla c|^2 \leq - \int\limits_{\Omega_{t_0}} (\partial_c f(c^2, \chi^2) - \partial_c f(c^1, \chi^1)) \cdot c. \tag{72}$$

In (65) we choose the test function $\mathcal{X}_{[0,t_0]}\chi$ analoguos to (66). This leads to

$$\frac{\tau}{\gamma} \int\limits_{\Omega_{t_0}} \chi \eta + \int\limits_{\Omega_{t_0}} \nabla \Big(\int\limits_0^t \chi(s)\, ds \Big) : \nabla \eta(t) - \frac{1}{\gamma} \int\limits_{\Omega_{t_0}} \eta(t) \int\limits_0^t \omega(s)\, ds = 0. \tag{73}$$

This implies because of $\chi(0) = 0$

$$\begin{aligned} (-\triangle)^{-1} \Big(\frac{\tau}{\gamma} \chi - \frac{1}{\gamma} \int\limits_0^t \omega(s)\, ds \Big) &= - \int\limits_0^t \chi(s)\, ds, \\ \partial_t (-\triangle)^{-1} \Big(\frac{\tau}{\gamma} \chi - \frac{1}{\gamma} \int\limits_0^t \omega(s)\, ds \Big) &= -\chi(t). \end{aligned}$$

We set $\eta := \chi$ in (73). As in the treatment of Eq. (63) this yields

$$0 = \gamma\tau \int_{\Omega_{t_0}} |\chi|^2 + \Big\|\tau\chi(t_0) - \Big(\int_0^{t_0} \omega(s)\Big)\Big\|_{L^2}^2 - \gamma \int_{\Omega_{t_0}} \chi(t) \int_0^t \omega(s)\, ds$$

and consequently with Young's inequality

$$\tau \int_{\Omega_{t_0}} |\chi|^2 \le \delta \int_{\Omega_{t_0}} |\chi|^2 + \frac{C}{\delta} \int_{\Omega_{t_0}} \Big(\int_0^t \omega(s)\, ds\Big)^2. \tag{74}$$

Now we add (72) and (74) and find

$$\begin{aligned}\lambda \int_{\Omega_{t_0}} |\nabla c|^2 + \tau \int_{\Omega_{t_0}} |\chi|^2 \ \le\ & \delta C \int_{\Omega_{t_0}} \big(|c|^2 + |\chi|^2\big) + \frac{C}{\delta} \int_{\Omega_{t_0}} \Big(\int_0^t \omega(s)\, ds\Big)^2 \\ & + |\partial_c f(c^2, \chi^2) - \partial_c f(c^1, \chi^1)|^2.\end{aligned}$$

For δ small the first integral on the right hand side can be absorbed on the left. As

$$|\partial_c f(c^2, \chi^2) - \partial_c f(c^1, \chi^1)|^2 + |\partial_\chi f(c^2, \chi^2) - \partial_\chi f(c^1, \chi^1)|^2 \le C_0 \left(|c|^2 + |\chi|^2\right)$$

where C_0 depends on the Lipschitz constant of $\partial_c f$ and $\partial_\chi f$, we find at last by exploiting the Poincaré inequality

$$\int_{\Omega_{t_0}} (|\nabla c|^2 + |\chi|^2) \le C \int_{\Omega_{t_0}} (|\nabla c|^2 + |\chi|^2) + \int_0^t \int_{\Omega_{t_0}} (|\nabla c|^2 + |\chi|^2).$$

With Gronwall's inequality this finally means $c = \chi = 0$ in Ω_{t_0} and with (64) $\mu = 0$ in Ω_{t_0}. By repeating the argument, as $t_0 > 0$, this holds in the whole of Ω_{T_0}. $\square$

15 Logarithmic free energy

In the following four sections we are going to extend Theorem 1 to logarithmic free energies. The results will in particular be taylor made for the free energy functional considered in Def. (8)

$$f(c,\chi)=\chi b^1\sum_{j=1}^{4}c_j\ln c_j+(1-\chi)b^2\sum_{j=1}^{4}c_j\ln c_j+\sum_{i=1}^{3}c_iE_i+\Big(\sum_{j=1}^{4}\alpha_jc_j\Big)^2+TW(\chi). \tag{75}$$

We will use the statements proved for polynomial free energies that can be regarded as a Taylor expansion.

For the proof of $0<c_j<1$, $1\le j\le 4$, we approximate f for $\delta>0$ by some f^δ that fulfils the requirements of Section 10 and find suitable a-priori estimates that put us in the position to pass to the limit $\delta\to 0$.

The logarithmic form of the free energy guarantees that the concentration vector c lies inside the transformed Gibbs simplex

$$G:=\Sigma\cap\{c\in\mathbb{R}^4\mid c_j\ge 0 \text{ for } 1\le j\le 4\}$$

and that $\chi\in(0,1)$. Therefore (c,χ) is physically meaningful.
The Assumptions (A2) and (A3) of Section 10 are replaced by
(A2') f is of the form (75) with constants $\alpha_j>0$, $b^1>0$, $b^2>0$, $T>0$.
(A3') The initial values $c_0\in X_1,\chi_0\in X_2$ fulfil $c_0\in G$, $\chi\in[0,1]$ almost everywhere and

$$\int_\Omega c_{0l}>0 \quad \text{for } 1\le l\le 4, \qquad \int_\Omega \chi>0,\ \int_\Omega(1-\chi)>0.$$

(A6') Additional to the conditions in (A6) we demand

$$\kappa^{1/\max(b^1,b^2)}<\frac{1}{e^2}. \tag{76}$$

The assumptions (A1) and (A4) remain unchanged and continue to hold.

To proceed, we define for $d>0$ the convex function

$$\psi(d):=d\ln d$$

and for $\delta>0$ its regularisation (defined for $d\in\mathbb{R}$)

$$\psi^\delta(d):=\begin{cases} d\ln d & \text{for } d\ge\delta,\\ d\ln\delta-\frac{\delta}{2}+\frac{d^2}{2\delta} & \text{for } d<\delta.\end{cases}$$

The regularised free energy functional is defined such that $\psi^\delta\in C^2$ and the derivative $(\psi^\delta)'$ is monotone increasing. This ansatz goes back to [5].

The free energy of the regularised δ-problem is found by replacing $\sum_i c_i \ln c_i$ by $\sum_i \psi^\delta(c_i)$ in (26). Since the convex combination

$$\bar{f}(c,\chi) := \chi f_1(c) + (1-\chi) f_2(c)$$

would define a non-convex functional in c if $\chi \notin [0,1]$, we consider the following penalisation ($f^\delta = f^{1,\delta} + f^2$, see Assumption A2)

$$f^{1,\delta}(c,\chi) := \begin{cases} \chi b^1 \sum_j \psi^\delta(c_j) + (1-\chi) b^2 \sum_j \psi^\delta(c_j) + T[\psi^\delta(\chi) + \psi^\delta(1-\chi)] \\ \qquad\qquad \text{if } \chi \in (0,1), \\ +\infty \qquad\quad \text{else} \end{cases}$$

$$f^2(c,\chi) := \Big(\sum_{j=1}^4 \alpha_j c_j \Big)^2.$$

Due to the expression $\psi^\delta(\chi) + \psi^\delta(1-\chi)$ in the definition of f^δ it is obvious that every minimiser χ fulfils $0 < \chi < 1$. This is proved rigorously in Lemma 8.

It can be easily checked that the functional $F^{m,h}$ of Section 11 still has a minimiser (c^m, χ^m) for every m and sufficiently small h. For $\chi \in (0,1)$, $f^{1,\delta}$ is still continuously differentiable. Since $f^{1,\delta}$, f^2 fulfil the assumptions of Section 10 the earlier existence results can be carried over.

The regularisation f^δ of f also implies that $\omega(c^\delta, \chi^\delta) = \partial_\chi f^\delta(c^\delta, \chi^\delta)$ depends on δ and therefore we will replace $\omega(c^m, \chi^m)$ in the implicit time discretisation (49) by $\omega^\delta(c^m, \chi^m)$ and the weak formulation (48) by

$$-\int_{\Omega_{T_0}} \tau \partial_t \zeta (\chi^\delta - \chi_0) + \int_{\Omega_{T_0}} \gamma \nabla \chi^\delta \cdot \nabla \zeta - \int_{\Omega_{T_0}} \omega^\delta(c^\delta, \chi^\delta) \zeta = 0 \qquad (77)$$

for all $\zeta \in L^2(0, T_0;\, H^1(\Omega; \mathbb{R}))$ with $\partial_t \zeta \in L^2(\Omega_{T_0})$, $\zeta(T_0) = 0$.
Later we will show that $\omega^\delta(c^\delta, \chi^\delta) \to \omega(c,\chi)$ in $L^1(\Omega_{T_0})$ as $\delta \searrow 0$.

The only assumption that needs further clarification is (A5). In order to verify (50), we have to construct an approximation $r^\delta = (r_1^\delta, -r_1^\delta, r_1^\delta, 0)$ of r and have to check that

$$\int_\Omega k_B T b_\chi \Big[(\psi^\delta)'(c_1) - 2(\psi^\delta)'(c_2) + (\psi^\delta)'(c_3) + \frac{E_1 - 2E_2 + E_3}{k_B T b_\chi} \Big] r_1^\delta \le 0.$$

We claim that a good choice for r_1^δ is

$$r_1^\delta(c,\chi) := k^{1/b_\chi} \Big(\max(c_2, \delta)^2 - \kappa^{1/b_\chi} \max(c_1, \delta) \max(c_3, \delta) \Big). \qquad (78)$$

To illustrate (78), let us consider three characteristic cases:
Case 1: $c_1 \geq \delta$, $c_2 \geq \delta$, $c_3 \geq \delta$:
Apparently $r^\delta = r$, and (50) follows verbatim as in the proof of the free energy inequality in Section 5.
Case 2: $c_1 < \delta$, $c_2 \geq \delta$, $c_3 \geq \delta$:
From the definition of ψ^δ we find that we have to estimate

$$\int_\Omega k_B T b_\chi \Big[\ln\delta + \frac{c_1}{\delta} - 2\ln c_2 - 2 + \ln c_3 + 1 + \frac{E_1 + E_3 - 2E_2}{k_B T b_\chi} \Big] r_1^\delta$$
$$= \int_\Omega k_B T b_\chi \Big[\ln\Big(\frac{\delta c_3 \kappa^{1/b_\chi}}{c_2^2} \Big) + \frac{c_1}{\delta} - 1 \Big] r_1^\delta.$$

The estimate follows now from $(\ln(\delta c_3 \kappa^{1/b_\chi}) - \ln(c_2^2)) r_1^\delta < 0$ and because of $\frac{c_1}{\delta} - 1 < 0$ and $r_1^\delta = k^{1/b_\chi}(c_2^2 - \kappa^{1/b_\chi}\delta c_3) > 0$ for δ sufficiently small. We emphasise that we need $r_1^\delta > 0$ in order to have $\int_\Omega (\alpha_1 - 2\alpha_2 + \alpha_3) Q(c^\delta) r_1^\delta < 0$ which allows to compensate the surface energy term for sufficiently small λ.
Case 3: $c_1 < \delta$, $c_2 < \delta$, $c_3 < \delta$:
Here we have to estimate

$$\int_\Omega k_B T b_\chi \Big[\ln\Big(\frac{\delta^2}{\delta^2} \Big) + \frac{c_1}{\delta} - 2\frac{c_2}{\delta} + \frac{c_3}{\delta} + \frac{E_1 - 2E_2 + E_3}{k_B T b_\chi} \Big] r_1^\delta.$$

We observe $r_1^\delta = k^{1/b_\chi}\delta^2(1 - \kappa^{1/b_\chi}) > 0$ due to Assumption (A6). Finally

$$\int_\Omega \Big(\frac{E_1 - 2E_2 + E_3}{k_B T b_\chi} + \frac{c_1 - 2c_2 + c_3}{\delta} \Big) \leq \int_\Omega (\ln(\kappa^{1/b_\chi}) + 2) < 0$$

if κ satisfies (76). The remaining cases can be treated similar to Case 2.

16 Uniform estimates

The following lemma was first stated and proved in Elliott and Luckhaus [5] for logarithmic free energies typical for the Cahn-Hilliard system.

Lemma 6 *For $\delta_0 = \frac{1}{e}$ there exists a $K > 0$ such that for all $\delta \in (0, \delta_0)$*

$$f^\delta(c, \chi) \geq -K \quad \text{for all } c \in \Sigma,\ \chi \in [0,1].$$

Proof: For $\delta_0 < \frac{1}{e}$ one has $\psi^\delta(d) \geq -\frac{1}{e}$ for all $\delta < \delta_0$. As $b^l, T > 0$, the proof is complete. $\square$

Lemma 7 *(a) For $\delta \in (0, \delta_0)$ there exists a weak solution $(c^\delta, \mu^\delta, \chi^\delta)$ of (42) with a logarithmic free energy that satisfies (A2')-(A6') in the sense of Section 8 with (48) replaced by (77).*
(b) There exists a constant $C > 0$ independent of δ such that for all $\delta \in (0, \delta_1)$ with some constant $\delta_1 \leq \delta_0$

$$\begin{aligned} \sup_{t\in[0,T_0]} \left\{ \|c^\delta(t)\|_{H^1} + \|\chi^\delta(t)\|_{H^1} \right\} &\leq C, \\ \sup_{t\in[0,T_0]} \int_\Omega f^{1,\delta}(c^\delta(t), \chi^\delta(t)) + \|\nabla\mu^\delta\|_{L^2(\Omega_{T_0})} &\leq C \end{aligned}$$

and

$$\begin{aligned} \|c^\delta(t_2) - c^\delta(t_1)\|_{L^2} &\leq C|t_2 - t_1|^{\frac{1}{4}}, \\ \|\chi^\delta(t_2) - \chi^\delta(t_1)\|_{L^2} &\leq C|t_2 - t_1|^{\frac{1}{2}} \end{aligned}$$

for all $t_1, t_2 \in [0, T_0]$.
(c) One can extract subsequences $(c^\delta)_{\delta\in\mathcal{R}}$, $(\mu^\delta)_{\delta\in\mathcal{R}}$ and $(\chi^\delta)_{\delta\in\mathcal{R}}$ where $\mathcal{R} \subset (0, \delta_1)$ is a countable set with zero as the only accumulation point such that

- *(i)* $c^\delta \to c$ *in* $C^{0,\alpha}([0,T_0];\, L^2(\Omega;\mathbb{R}^4))$ *for all* $\alpha \in (0, \frac{1}{4})$,
- *(ii)* $c^\delta \to c$ *almost everywhere in* Ω_{T_0},
- *(iii)* $c^\delta \stackrel{*}{\rightharpoonup} c$ *in* $L^\infty(0,T_0;\, H^1_0(\Omega;\mathbb{R}^4))$,
- *(iv)* $\chi^\delta \to \chi$ *in* $C^{0,\alpha}([0,T_0];\, L^2(\Omega))$ *for all* $\alpha \in (0, \frac{1}{2})$,
- *(v)* $\chi^\delta \to \chi$ *almost everywhere in* Ω_{T_0} *and* $0 \leq \chi^\delta, \chi \leq 1$ *a.e. in* Ω_{T_0},
- *(vi)* $\chi^\delta \stackrel{*}{\rightharpoonup} \chi$ *in* $L^\infty(0,T_0;\, H^1(\Omega))$,
- *(vii)* $\mu^\delta \rightharpoonup \mu$ *in* $L^2(0,T_0;\, H^1_0(\Omega;\mathbb{R}^4))$

as $\delta \in \mathcal{R}$ tends to zero.

Proof: Using Lemma 6, the regularised problem satisfies the assumptions of Section 10 and by Theorem 1, a weak solution for fixed $\delta \in (0, \delta_0)$ exists. This proves (a). The estimates in (b) are a direct consequence of Lemma 3 and Lemma 4, where due to Assumption (A4.2) we have to choose δ small enough for Lemma 3 to hold. From Lemma 3, it follows that $F^\delta(c_0, \chi_0)$ does not depend on δ, hence the constant on the right hand side does not depend on δ. (c) is proved by Lemmata 4 and 5. $\square$

17 Higher integrability for the logarithmic free energy

Since $\varphi^\delta := (\psi^\delta)'$ will be singular as $\delta \to 0$ we introduce for $r > 0$

$$\varphi_r^\delta(d) := \begin{cases} \varphi^\delta(d)|\varphi^\delta(d)|^{r-1} & \text{if } \varphi^\delta(d) \neq 0, \\ 0 & \text{if } \varphi^\delta(d) = 0. \end{cases}$$

By definition, $\varphi_r^\delta \in C^0(\mathbb{R})$.

For $0 < r < 1$, φ_r^δ is not differentiable at the zero point of φ^δ. To overcome this difficulty, for $\varrho > 0$ introduce the function $\varphi_r^{\delta,\varrho}$ with $\varphi_r^{\delta,\varrho} = \varphi_r^\delta$ in $\mathbb{R} \setminus [0,1]$ and define $\varphi_r^{\delta,\varrho}$ in $[0,1]$ such that $\varphi_r^{\delta,\varrho}$ is a C^1 function, monotone increasing and $\varphi_r^{\delta,\varrho} \to \varphi_r^\delta$ in $C^0(\mathbb{R})$ as $\varrho \searrow 0$.

For the approximation of $\varphi^\delta(\chi^\delta)$ in the modified Allen-Cahn equation it is more suitable to introduce the Dirac sequence

$$\varphi^{\delta,\varepsilon}(x) := (\varphi^\delta * J_\varepsilon)(x) := \varepsilon^{-D} \int\limits_{\mathbb{R}^D} \varphi^\delta(x) J((x-y)/\varepsilon)\, dy$$

where the kernal $J \in C^\infty(B^1(0))$ is a positive smooth polynomial (see Assumption A2). As is well known, $\varphi^{\delta,\varepsilon} \in C^\infty$ and $\varphi^{\delta,\varepsilon} \to \varphi^\delta$ in $L^p(\Omega)$ as $\varepsilon \searrow 0$ for any $p \geq 1$.

Even though by construction $0 < \chi^\delta < 1$ almost everywhere, it might still happen that for the limit the sets $\{x \in \Omega \,|\, \chi(x) = 0\}$ and $\{x \in \Omega \,|\, \chi(x) = 1\}$ have non-zero Lebesgue measure and that the entropic terms in the free energy density become singular. Now we will show that this is not the case.

Lemma 8 *There exists a constant $C > 0$ such that for all $\delta \in (0, \delta_0)$*

(i) $\|\varphi^\delta(c_l^\delta)\|_{L^q(\Omega_{T_0})} \leq C$ *for a suitable $q > 1$ and all $1 \leq l \leq 4$,*
(ii) $\|\varphi^\delta(\chi^\delta) + \varphi^\delta(1-\chi^\delta)\|_{L^2(\Omega_{T_0})} \leq C$.

Proof: The weak formulation (47) for the generalised chemical potential is

$$\begin{aligned} \int\limits_{\Omega_{T_0}} \mu^\delta \cdot \eta \;=\; & \int\limits_{\Omega_{T_0}} \Big\{ \lambda \sum_{l=1}^4 \nabla c_l^\delta \cdot \nabla \eta_l + 2\Big[\alpha_l \sum_{j=1}^4 \alpha_j c_j^\delta\Big]_{1\leq l\leq 4} \cdot \eta + \sum_{l=1}^3 E_l \eta_l \Big\} \\ & + \int\limits_{\Omega_{T_0}} (\chi^\delta b^1 + (1-\chi^\delta) b^2)[\varphi^\delta(c_l^\delta)]_{1\leq l\leq 4} \cdot \eta \qquad (79) \end{aligned}$$

for all $\eta \in L^2(0,T_0;\, H^1(\Omega;\mathbb{R}^4)) \cap L^\infty(\Omega_{T_0},\mathbb{R}^4)$. We choose $\eta := [\varphi_r^{\delta,\varrho}(c_l^\delta)]_{1\le l\le 4}$ in (79) which is an admissible test function because of the Sobolev imbedding theorem and because $\varphi_r^{\delta,\varrho} \in C^1$. We obtain

$$\int\limits_{\Omega_{T_0}} \sum_{l=1}^4 \mu_l^\delta \varphi_r^{\delta,\varrho}(c_l^\delta) = + \int\limits_{\Omega_{T_0}} \sum_{l=1}^4 \varphi_r^{\delta,\varrho}(c_l^\delta)\Big(2\alpha_l \sum_{j=1}^4 \alpha_j c_j^\delta + E_l\Big)$$
$$+ \int\limits_{\Omega_{T_0}} \lambda \sum_{l=1}^4 \nabla c_l^\delta \cdot \nabla \varphi_r^{\delta,\varrho}(c_l^\delta) + \int\limits_{\Omega_{T_0}} \sum_{l=1}^4 (\chi^\delta b^1 + (1-\chi^\delta)b^2)\varphi^\delta(c_l^\delta)\varphi_r^{\delta,\varrho}(c_l^\delta).$$

In the last formula we set for simplicity $E_4 := 0$. Due to $(\varphi_r^{\delta,\varrho})' \ge 0$ we find

$$\int\limits_{\Omega_{T_0}} \lambda \sum_{l=1}^4 \nabla c_l^\delta \cdot \nabla \varphi_r^{\delta,\varrho}(c_l^\delta) \ge 0.$$

This implies

$$\int\limits_{\Omega_{T_0}} \sum_{l=1}^4 (\chi^\delta b^1 + (1-\chi^\delta)b^2)\varphi^\delta(c_l^\delta))\varphi_r^{\delta,\varrho}(c_l^\delta)$$
$$\le \int\limits_{\Omega_{T_0}} \sum_{l=1}^4 \mu_l^\delta \varphi_r^{\delta,\varrho}(c_l^\delta) - \int\limits_{\Omega_{T_0}} \sum_{l=1}^4 \varphi_r^{\delta,\varrho}(c_l^\delta)\Big(2\alpha_l \sum_{j=1}^4 \alpha_j c_j + E_l\Big)$$
$$\le C \max_{1\le l\le 4} \|\varphi_r^{\delta,\varrho}(c_l^\delta)\|_{L^2(\Omega_{T_0})}\Big(\|\mu^\delta\|_{L^2(\Omega_{T_0})} + \|c^\delta\|_{L^2(\Omega_{T_0})}\Big)$$

where the constant C in the last line depends on $\alpha_1,\ldots,\alpha_4$ and on $E_1,\ldots,E_3$. For $\varrho \searrow 0$ employing Lemma 6 and Lemma 7 this proves

$$\int\limits_{\Omega_{T_0}} \sum_{l=1}^4 (\chi^\delta b^1 + (1-\chi^\delta)b^2)\varphi^\delta(c_l^\delta)\varphi_r^\delta(c_l^\delta) \le C. \tag{80}$$

A direct computation finally yields

$$\int\limits_{\Omega_{T_0}} \sum_{l=1}^4 (\chi^\delta b^1 + (1-\chi^\delta)b^2)\varphi^\delta(c_l^\delta))\varphi_r^\delta(c_l^\delta)$$
$$\ge \int\limits_{\Omega_{T_0}} \max_{1\le l\le 4} (\chi^\delta b^1 + (1-\chi^\delta)b^2)|\varphi^\delta(c_l^\delta)|^{r+1} \ge \int\limits_{\Omega_{T_0}} C \max_{1\le l\le 4} |\varphi^\delta(c_l^\delta)|^{r+1}$$

for a constant $C = C(b^1, b^2)$. The last is possible because $\chi^\delta b^1 + (1-\chi^\delta) b^2 > 0$ almost everywhere in Ω_{T_0}. Together with (80) this proves (i).

Next we consider the weak formulation (77)

$$- \int_{\Omega_{T_0}} \tau \partial_t \zeta (\chi^\delta - \chi_0) + \int_{\Omega_{T_0}} \gamma \nabla \chi^\delta \cdot \nabla \zeta - \int_{\Omega_{T_0}} (b^2 - b^1) \sum_{j=1}^{4} \psi^\delta (c_j^\delta) \zeta$$
$$+ \int_{\Omega_{T_0}} T(\varphi^\delta(\chi^\delta) + \varphi^\delta(1-\chi^\delta))\zeta = 0 \tag{81}$$

of the Allen-Cahn eq. We want to test Eq. (81) with $\zeta := \varphi^{\delta,\varepsilon}(\chi) + \varphi^{\delta,\varepsilon}(1-\chi)$. Since by Theorem 1 $\chi^\delta \in C^{0,\frac{1}{2}}(0, T_0;\, L^2(\Omega_{T_0}))$, we can use Fourier theory to formally shift a half time derivative from ζ to $\chi^\delta - \chi_0$. After this procedure we find with Lemma 7

$$\int_{\Omega_{T_0}} \tau \partial_t^{\frac{1}{2}} (\varphi^{\delta,\varepsilon}(\chi^\delta) + \varphi^{\delta,\varepsilon}(1-\chi^\delta)) \partial_t^{\frac{1}{2}} (\chi^\delta - \chi_0) \leq C.$$

To estimate the second integral in (81), we notice

$$\int_{\Omega_{T_0}} \gamma \nabla \chi^\delta \cdot \nabla(\varphi^{\delta,\varepsilon}(\chi^\delta) + \varphi^{\delta,\varepsilon}(1-\chi^\delta)) = \int_{\Omega_{T_0}} \gamma |\nabla \chi^\delta|^2 \left[(\varphi^{\delta,\varepsilon})'(\chi^\delta) - (\varphi^{\delta,\varepsilon})'(1-\chi^\delta)\right].$$

By Lemma 7, χ^δ is bounded in $L^\infty(0, T_0;\, H^1(\Omega))$ which implies the boundedness of the integral.

If we choose δ sufficiently small in (i) we find $c_j \in (0,1)$ for $1 \leq j \leq 4$, see also the proof of Theorem 3. This guarantees that $\psi^\delta(c_j)$ does not become singular and thus proves the boundedness of the third integral in (81) independently of δ. Finally, we have

$$\begin{aligned} 0 \;\leq\; & \int_{\Omega_{T_0}} (\varphi^\delta(\chi^\delta) + \varphi^\delta(1-\chi^\delta))(\varphi^{\delta,\varepsilon}(\chi^\delta) + \varphi^{\delta,\varepsilon}(1-\chi^\delta)) \\ & \to \|\varphi^\delta(\chi^\delta) + \varphi^\delta(1-\chi^\delta)\|_{L^2(\Omega_{T_0})} \quad \text{as } \varepsilon \searrow 0. \end{aligned}$$

By combining these results, (ii) follows. $\square$

18 Global existence of solutions for logarithmic free energies

Theorem 3 *Let the assumptions of Section 15 hold. Then there exists a weak solution* (c, μ, χ) *in the sense of Section 8 of the diffuse interface equations (42) with logarithmic free energy such that*

(i)	$c \in C^{0,\frac{1}{4}}([0,T_0];\ L^2(\Omega;\mathbb{R}^4))$,
(ii)	$\partial_t c \in L^2(0,T_0;\ (H_0^1(\Omega;\mathbb{R}^4))')$,
(iii)	$\chi \in C^{0,\frac{1}{2}}([0,T_0];\ L^2(\Omega))$,
(iv)	$\partial_t \chi \in L^2(0,T_0;\ (H_0^1(\Omega))')$,
(v)	*there exists a* $q > 1$ *such that* $\ln c_j \in L^q(\Omega_{T_0})$ *for* $1 \leq j \leq 4$, $\ln \chi,\ \ln(1-\chi) \in L^2(\Omega_{T_0})$ *and in particular* $0 < \chi, c_j < 1$ *a.e.*

Proof: We pass to the limit $\delta \searrow 0$ in the weak formulation (46)-(48) with f defined by (75) and have to show that (c, μ, χ) found in Lemma 7 is a solution.

For the limit in (47), the argumentation is an extension to [7]. In particular we must take care of the term

$$\chi^\delta b^1 \sum_{j=1}^{4} \varphi^\delta(c_j^\delta) + (1-\chi^\delta) b^2 \sum_{j=1}^{4} \varphi^\delta(c_j^\delta). \tag{82}$$

From the almost everywhere convergence of c_l^δ to c_l, Lemma 8(i) and the Lemma of Fatou we find

$$\int\limits_{\Omega_{T_0}} \liminf_{\delta\searrow 0} |\varphi^\delta(c_l^\delta)|^q \leq \liminf_{\delta\searrow 0} \int\limits_{\Omega_{T_0}} |\varphi^\delta(c_l^\delta)|^q \leq C.$$

Next we will show that

$$\lim_{\delta\searrow 0} \varphi^\delta(c_l^\delta) = \begin{cases} \varphi(c_l) & \text{if } \lim_{\delta\searrow 0} c_l^\delta = c_l > 0, \\ \infty & \text{if } \lim_{\delta\searrow 0} c_l^\delta = c_l \leq 0 \end{cases} \tag{83}$$

almost everywhere in Ω_{T_0}. For a point $(x,t) \in \Omega_{T_0}$ with $\lim_{\delta\searrow 0} c_l^\delta(x,t) = c_l(x,t) > 0$, we obtain from $\varphi^\delta(d) = \varphi(d)$ for $d \geq \delta$ that $\varphi^\delta(c^\delta(x,t)) \to \varphi(c(x,t))$. In the second case of a point $(x,t) \in \Omega_{T_0}$ with $\lim_{\delta\searrow 0} c_l^\delta(x,t) = c_l(x,t) \leq 0$, we have for δ small enough

$$|\varphi^\delta(c_l^\delta(x,t))| \geq \varphi(\max\{\delta, c_l^\delta(x,t)\}) \to \infty \quad \text{for } \delta \searrow 0.$$

This proves (83). A similar statement holds for $\psi^\delta(\chi^\delta)$.

From (83) and Lemma 8(i) we deduce $0 < c_l < 1$ a.e., $\int_{\Omega_{T_0}} |\varphi(c_l)|^q \le C$ and $\varphi^\delta(c_l^\delta) \to \varphi(c_l)$ a.e. With Vitali's theorem we find

$$\varphi^\delta(c_l^\delta) \to \varphi(c_l) \quad \text{in } L^1(\Omega_{T_0}).$$

This allows to pass to the limit in (47).

Let us now consider the limit in (77). The relation $0 < c_j < 1$ almost everywhere implies $b^l \sum_{j=1}^4 \psi^\delta(c_j^\delta) \to b^l \sum_{j=1}^4 \psi(c_j)$, $l = 1, 2$ almost everywhere in Ω_{T_0} like in the first case of (83). From $\varphi^\delta(c_j^\delta) \in L^q(\Omega_{T_0})$, the uniform boundedness of χ^δ and Vitali's theorem we obtain

$$\chi^\delta b^1 \sum_{j=1}^4 \psi^\delta(c_j^\delta) \to \chi b^1 \sum_{j=1}^4 \psi(c_j),\ (1-\chi^\delta) b^2 \sum_{j=1}^4 \psi^\delta(c_j^\delta) \to (1-\chi) b^2 \sum_{j=1}^4 \psi(c_j)$$

in $L^1(\Omega_{T_0})$ such that

$$\omega^\delta(c^\delta, \chi^\delta) \to \omega(c, \chi) \quad \text{in } L^1(\Omega_{T_0}) \text{ for } \delta \searrow 0.$$

By repeating the argumentation from above for $\varphi^\delta(\chi^\delta) + \varphi^\delta(1-\chi^\delta)$ we deduce $0 < \chi < 1$ almost everywhere in Ω_{T_0} which again with the help of Vitali's theorem and Lemma 8(ii) yields

$$\varphi^\delta(\chi^\delta) + \varphi^\delta(1-\chi^\delta) \to \varphi(\chi) + \varphi(1-\chi) \quad \text{in } L^1(\Omega_{T_0}).$$

So we can also pass to the limit in (77). The limit for (46) can be justified in the same way as in the proof of Theorem 1 if we additionally show

$$r^\delta(c^\delta, \chi^\delta) \to r(c, \chi) \quad \text{in } L^1(\Omega_{T_0}). \tag{84}$$

From the almost everywhere convergence of c_l^δ to c_l and $c_l > 0$ almost everywhere in Ω_{T_0} we obtain

$$\max(c_l^\delta, \delta) \to c_l \quad \text{almost everywhere in } \Omega_{T_0},\ \delta \searrow 0, \quad 1 \le l \le 3.$$

Since the functions $\chi \mapsto k^{1/b_\chi}$ and $\chi \mapsto \kappa^{1/b_\chi}$ are in C^1, we find

$$k^{1/b_{\chi^\delta}} \Big(\max(c_2^\delta, \delta)^2 - \kappa^{1/b_{\chi^\delta}} \max(c_1, \delta) \max(c_3, \delta) \Big) \to k^{1/b_\chi} \Big(c_2^2 - \kappa^{1/b_\chi} c_1 c_3 \Big)$$

almost everywhere in Ω_{T_0} as $\delta \searrow 0$. By Lebesgue's dominated convergence theorem we find (84), because $k^{1/b_{\chi^\delta}} \le k^{1/\min(b^1, b^2)}$ almost everywhere in Ω_{T_0}

if $k \geq 1$ respectively $k^{1/b_{\chi^\delta}} \leq k^{1/\max(b^1,b^2)}$ almost everywhere if $k < 1$ and the analogous estimate for the κ-term, hence

$$\int_{\Omega_{T_0}} |r_1^\delta| \leq C \int_{\Omega_{T_0}} \Big(|c_2^2| + |c_1 c_3| \Big)$$

for a constant C that depends on κ and k. $\square$

Uniqueness of the solution to Theorem 3 can be obtained in exactly the same way as in Theorem 2 if we replace (A6) by (A6').

19 The sharp interface model

It remains to perform the limit $\lambda \to 0$. This limit is carried out in the same way as before by showing a-priori estimates and compactness results.

Lemma 9 *(a) For $\lambda \in (0, \lambda_0)$ there exists a weak solution $(c^\lambda, \mu^\lambda, \chi^\lambda)$ of (42) with a logarithmic free energy that satisfies (A2')-(A6').*
(b) There is a constant $C > 0$ independent of λ such that for all $\lambda \in (0, \lambda_0)$

$$\begin{aligned} \sup_{t\in[0,T_0]} \Big\{ \|c^\lambda(t)\|_{H^1} + \|\chi^\lambda(t)\|_{H^1} \Big\} &\leq C, \\ \sup_{t\in[0,T_0]} \int_\Omega f^1(c^\lambda(t), \chi^\lambda(t)) + \|\nabla \mu^\lambda\|_{L^2(\Omega_{T_0})} &\leq C \end{aligned}$$

and for all $t_1, t_2 \in [0, T_0]$

$$\begin{aligned} \|c^\lambda(t_2) - c^\lambda(t_1)\|_{L^2} &\leq C|t_2 - t_1|^{\frac{1}{4}}, \\ \|\chi^\lambda(t_2) - \chi^\lambda(t_1)\|_{L^2} &\leq C|t_2 - t_1|^{\frac{1}{2}}. \end{aligned}$$

(c) One can extract subsequences $(c^\lambda)_{\lambda\in\mathcal{R}}$, $(\mu^\lambda)_{\lambda\in\mathcal{R}}$ and $(\chi^\lambda)_{\lambda\in\mathcal{R}}$ where $\mathcal{R} \subset (0, \lambda_0)$ is a countable set with zero as the only accumulation point such that

- *(i)* $c^\lambda \to c$ *in* $C^{0,\alpha}([0, T_0]; L^2(\Omega; \mathbb{R}^4))$ *for all* $\alpha \in (0, \frac{1}{4})$,
- *(ii)* $c^\lambda \to c$ *almost everywhere in* Ω_{T_0},
- *(iii)* $c^\lambda \overset{*}{\rightharpoonup} c$ *in* $L^\infty(0, T_0; H_0^1(\Omega; \mathbb{R}^4))$,
- *(iv)* $\chi^\lambda \to \chi$ *in* $C^{0,\alpha}([0, T_0]; L^2(\Omega))$ *for all* $\alpha \in (0, \frac{1}{2})$,
- *(v)* $\chi^\lambda \to \chi$ *almost everywhere in* Ω_{T_0} *and* $0 \leq \chi^\lambda$, $\chi \leq 1$ *a.e. in* Ω_{T_0},
- *(vi)* $\chi^\lambda \overset{*}{\rightharpoonup} \chi$ *in* $L^\infty(0, T_0; H^1(\Omega))$,
- *(vii)* $\mu^\lambda \rightharpoonup \mu$ *in* $L^2(0, T_0; H_0^1(\Omega; \mathbb{R}^4))$

as $\lambda \in \mathcal{R}$ tends to zero.

Proof: By Theorem 3, a weak solution for fixed $\lambda \in (0, \lambda_0)$ exists. This proves (a). The estimates in (b) are a direct consequence of Lemma 7, where due to Assumption (A4.2) we have to choose $\lambda < \lambda_0$ for Lemma 3 to hold. Since $F^\lambda(c_0, \chi_0)$ can be estimated independently of λ, the constant C on the right hand side does not depend on λ. (c) is proved by Lemma 7. $\square$

We make precise what we mean by a weak solution to the sharp interface model. We call a triple $(c, \mu, \chi) \in L^2(0, T_0;\, H_0^{1,2}(\Omega; \mathbb{R}^4)) \times L^2(0, T_0;\, H_0^{1,2}(\Omega; \mathbb{R}^4)) \times L^2(0, T_0;\, H^{1,2}(\Omega; \mathbb{R}))$ with $r(c, \chi), \omega(c, \chi) \in L^1(\Omega_{T_0})$ a *weak solution* of the sharp interface model (30) if

$$-\int\limits_{\Omega_{T_0}} \partial_t \xi \cdot (c - c_0) + \int\limits_{\Omega_{T_0}} L \nabla \mu : \nabla \xi - \int\limits_{\Omega_{T_0}} r(c, \chi) \xi = 0 \tag{85}$$

for all $\xi \in L^2(0, T_0;\, H_0^1(\Omega; \mathbb{R}^4))$ with $\partial_t \xi \in L^2(\Omega_{T_0})$, $\xi(T_0) = 0$, and

$$\int\limits_{\Omega_{T_0}} \mu \cdot \eta = \int\limits_{\Omega_{T_0}} \frac{\partial f}{\partial c}(c) \cdot \eta \tag{86}$$

for all $\eta \in L^2(0, T_0;\, H_0^1(\Omega; \mathbb{R}^4)) \cap L^\infty(\Omega_{T_0}; \mathbb{R}^4)$, and

$$-\int\limits_{\Omega_{T_0}} \tau \partial_t \zeta (\chi - \chi_0) + \int\limits_{\Omega_{T_0}} \gamma \nabla \chi \cdot \nabla \zeta - \int\limits_{\Omega_{T_0}} \omega(c, \chi) \zeta = 0 \tag{87}$$

for all $\zeta \in L^2(0, T_0;\, H^1(\Omega; \mathbb{R}))$ with $\partial_t \zeta \in L^2(\Omega_{T_0})$, $\zeta(T_0) = 0$.

Theorem 4 *Let the assumptions of Section 15 hold. Then, there exists a weak solution (c, μ, χ) in the sense of (85) of the sharp interface equations (30) with a logarithmic free energy that satisfies (A2')-(A6') such that*

- *(i)* $c \in C^{0,\frac{1}{4}}([0, T_0];\, L^2(\Omega; \mathbb{R}^4))$,
- *(ii)* $\partial_t c \in L^2(0, T_0;\, (H_0^1(\Omega; \mathbb{R}^4))')$,
- *(iii)* $\chi \in C^{0,\frac{1}{2}}([0, T_0];\, L^2(\Omega))$,
- *(iv)* $\partial_t \chi \in L^2(0, T_0;\, (H_0^1(\Omega))')$,
- *(v)* *there exists a* $q > 1$ *such that* $\ln c_j \in L^q(\Omega_{T_0})$ *for* $1 \le j \le 4$, $\ln \chi$, $\ln(1 - \chi) \in L^2(\Omega_{T_0})$ *and in particular* $0 < \chi, c_j < 1$ *a.e.*

Proof: We pass to the limit $\lambda \searrow 0$ in the weak formulation. In order to show that the limit (c, μ, χ) found in Lemma 9 is a solution we only have to observe that in (47) $\lambda \triangle \mu \to 0$ in $H_0^{1,2}(\Omega)$ as $\lambda \searrow 0$. $\square$

Theorem 5 *If $\partial_c f$, $\partial_\chi f$ are Lipschitz continuous, the solution (c, μ, χ) of the sharp interface equations obtained in Theorem 4 is unique in the spaces stated in this theorem.*

Proof: The proof of Theorem 2 can be reused after sharpening Estimate (71). We have according to (A4.2)

$$
\begin{aligned}
-\int_{\Omega_{t_0}} \Big(\int_0^t r(s)ds \Big) \cdot \mu \;&\geq\; \int_{\Omega_{t_0}} r_1(t)(\mu_1(t) - 2\mu_2(t) + \mu_3(t)) \\
&\geq\; \int_{\Omega_{t_0}} (\alpha_1 - 2\alpha_2 + \alpha_3) Q(c) r_1 \geq \lambda \int_{\Omega_{t_0}} |\nabla c|^2
\end{aligned}
$$

for an arbitrary constant $\lambda < \lambda_0$. Then one can proceed with the proof. $\square$

References

[1] H.W. Alt, S. Luckhaus, "Quasilinear elliptic parabolic differential equations", Math. Z.**183**, 311-338 (1983)

[2] K. Bente, T. Doering, "Diffusion Induced Segregation in Cu-In systems", Min. Petrol**53**, 285-305 (1995)

[3] T. Blesgen, "Modeling and Numerical Simulation of Diffusion Induced Segregation", Cryst. Res. Tech.**37**, 570-580 (2002)

[4] T. Blesgen, S. Luckhaus und K. Bente, "Diffusion Induced Segregation in the Case of the Ternary System Sphalerite, Chalcopyrite and Cubanite", Cryst. Res. Tech.**39**,969-979 (2004)

[5] C.M. Elliott and S. Luckhaus, "A generalised diffusion equation for phase separation of a multi-component mixture with interfacial free energy", Preprint SFB 256, University Bonn (1991)

[6] C.M. Elliott und Z. Songmu, "On the Cahn-Hilliard Equation", Arch. Ration. Mech. Anal.**96**, 339-357 (1986)

[7] H. Garcke, "On mathematical models for phase separation in elastically stressed solids", habilitation thesis, Bonn (2001)

[8] P. Grindrod, "The theory and application of reaction-diffusion equations, paterns and waves", 2nd Edition, Clarendon Press, Oxford 1996

[9] O'Keefe, "Structures and Bonding in Crystals", Academic Press 1981.

[10] J.S. Kirkaldy, D.J. Young, "Diffusion in the Condensed State", The Institute of Metals, London (1987)

[11] L. Onsager, "Reciprocal relations in irreversible processes I", Phys. Rev. **37**, 405-426 (1931)

[12] L. Onsager, "Reciprocal relations in irreversible processes II", Phys. Rev. **38**, 2265-2279 (1931)

[13] M.H. Protter, H.F. Weinberger, "Maximum Principle in Differential Equations", 2nd Edition Springer 1999

Symbol	Species	Ion Radius
α_1	Fe^{3+}	0.555Å
α_2	Fe^{2+}	0.660Å
α_3	Cu^{+}	0.635Å
α_4	Zn^{2+}	0.640Å

Table 1: Values of sulfide crystal radii taken from [9]

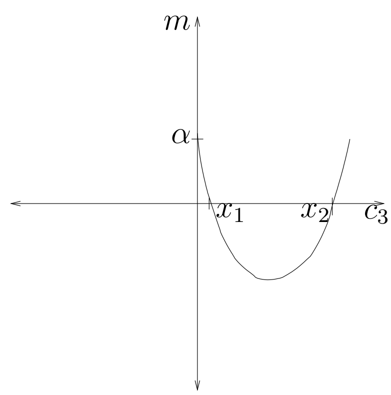

Figure 1: Plot of $m(c_3)$