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The Dynamics of Transition Layers in Solids with Discontinuous Chemical Potentials

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SUMMARY

We derive a two-phase segregation model in solids under isothermal conditions where due to plastic effects the number of vacancies changes when crossing a transition layer, i.e. a reconstitutive phase transition. We show the thermodynamic correctness of the model and review the existence of weak solutions in suitable spaces. By a formal asymptotic analysis we study the dynamics of the interface and its dependence on the unsymmetric vacancy distribution.

KEY WORDS: phase change problems; free boundary problems; coupling of solid mechanics with chemical and reactive effects

1 Introduction

The present article is devoted to the analysis of interface motion that arises during two-phase segregation in solids. It is motivated by recent experimental results in [20] and [21] on steels, where a jump of the chemical potential across the interface is observed that depends on the unsymmetric number of vacancies of the sub-lattices. These observations do not fit to existing mathematical and physical models for interface dynamics like the Allen-Cahn or phase field equations, [4], the Cahn-Hilliard system, [9], the Stefan problem, [16], or other recent models for phase transitions in solids, see for instance [10], [1] and [3].

Jumps of the chemical potential that depend on the particular structure of the sub-lattice were observed and studied before in [6] and [7] for models of Ga/As precipitates, where the defects are very important for the macroscopic properties of the material.

In [20] also some numerical simulations are done. They are based on the representation $f_l = \sum_{i=0}^{M} X_{li}\mu_{li}(X_{l1},\ldots,X_{lM})$ of the free energy density of Phase l and a formula for the mass flux J related to the Onsager relation, see (5) below. Both crucial identities thus depend on the vector μ of chemical potentials which in turn depends in a complicated way on the molar fractions X_{li}. This functional dependence is resolved with huge data bases like CALPHAD or

SGTE, see [14], [12], and `http:\\www.calphad.org`, `http:\\www.sgte.org`. In this way, the jump of the chemical potential is captured in the numerical computations in [20]. The objective of the present article is to explain this dynamic behaviour by going to a microscopic model, in this case of phase field type. Instead of studying transformations of the lattice to a chosen reference configuration which will not be possible in general, the creation and annihilation of vacancies are modelled formally by reactions, see Eq. (10). The jump in μ is the consequence of an unsymmetric generation of defects during the rearrangement of the atomic lattice. This leads to a local change of the number of available lattice positions N which is the reason for the local fluctuation of μ close to an interface.

The outline of this article is the following. In Section 2 we introduce some notation and derive the model. A thermodynamic validation is contained in Section 3 followed by a short review of existence results in Section 4. Finally, in Section 5 the kinetics of the transition layers by formally matched asymptotics are studied.

2 Derivation of the Model

We consider an isothermal regime where the temperature θ is kept constant. Let $\Omega \subset \mathbb{R}^D$ be a bounded domain with Lipschitz boundary containing $M \geq 1$ different species of molecules. By $C^k(\Omega)$ we denote the k-times continuously differentiable functions in Ω, by $C_0^k(\Omega)$ the functions in $C^k(\Omega)$ with compact support and by $H^{m,2}(\Omega)$ the Sobolev space of m-times weakly differentiable functions in the Hilbert space $L^2(\Omega)$. Finally, $H_0^{m,2}(\Omega)$ is the closure of $C_0^\infty(\Omega)$ w.r.t. $\|\cdot\|_{H^{m,2}(\Omega)}$.

Let $\varrho_i = \varrho_i(x,t)$ be the number of lattice sites per volume occupied by an atom of species i, $1 \leq i \leq M$, which are conserved quantities ($\int_\Omega \varrho_i(x,t)dx = \text{const}_i$ for all t), and let ϱ_0 denote the number of vacant lattice positions per volume, a quantity which may change locally in Ω. Set $\varrho := (\varrho_0, \ldots, \varrho_M)$.

If we assume that there are no interstitials, mass conservation leads to

$$\sum_{i=0}^{M} \varrho_i = N, \tag{1}$$

where N is the number of lattice sites per volume which is constant in each phase. As we assume that at most two coexisting phases are present we introduce a phase parameter $\chi = \chi(x,t) \in [0,1]$ as an indicator function of phase 1, say.

The free energy F of the system is

$$F = F(\varrho, \chi) = \int_\Omega f(\varrho, \chi, \nabla\chi)\, dx$$

with the free energy density $f(\varrho, \chi, \nabla\chi)$. For f we make the ansatz

$$f(\varrho, \chi, \nabla\chi) = \chi f_1(\varrho) + (1-\chi) f_2(\varrho) + \theta\Big(W(\chi) + \frac{\tilde{\gamma}}{2}|\nabla\chi|^2\Big) \tag{2}$$

where the last term is due to the entropy of mixing. Furthermore, $\tilde{\gamma} > 0$ determines the square root of the thickness of the boundary layer between the two phases, and

$$W(\chi) := \chi \ln \chi + (1-\chi)\ln(1-\chi) - \theta_c \chi^2$$

is a double well potential for a constant $\theta_c > 0$ chosen large. To simplify notation we set $\gamma := \theta\tilde{\gamma}$.

The unconserved order parameter χ is governed by the Allen-Cahn equation

$$\tau \partial_t \chi = -\frac{\partial F}{\partial \chi}(\varrho, \chi) = \gamma \triangle \chi + \omega(\varrho, \chi), \tag{3}$$

where $\tau = \tau(\theta)$ is a positive constant that adjusts the time scale of the propagation in χ and

$$\omega(\varrho, \chi) := (f_2 - f_1)(\varrho) - \theta W'(\chi).$$

The functions f_l in (2) denote the convex and smooth free energy densities of phase l. A possible choice on f_l is the entropic ansatz

$$f_l(\varrho) := k_B \theta \sum_{i=0}^{M} \varrho_i \Big(\ln \varrho_i - \ln N + \frac{E_i^l}{k_B \theta} \Big), \quad l = 1, 2, \tag{4}$$

where k_B is the Boltzmann constant, $E_i^l > 0$ are enthalpic energy terms, and the densities ϱ_i are defined as above. By

$$\mu_i(\varrho, \chi) := \frac{\partial f}{\partial \varrho_i}(\varrho, \chi, \nabla \chi), \quad 0 \leq i \leq M$$

we denote the i-th chemical potential and $\mu := (\mu_0, \ldots, \mu_M)$. Analogous to ϱ_0, the term μ_0 denotes the chemical potential with respect to the vacancy concentration.

The diffusion process is modelled by $\partial_t \varrho_i = -\mathrm{div}(J_i) + r_i$, $0 \leq i \leq M$, where the reaction terms r_i describe the creation/annihilation of vacant lattice sites due to plastic deformations close to a phase transition. For later use we define $r := (r_0, \ldots, r_M)$.

Onsager's law, [17], [18], postulates that every 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 [15], p.137,

$$J_i = -\sum_{j=0}^{M} L_{ij} \nabla \mu_j, \quad 0 \leq i \leq M, \tag{5}$$

with a mobility matrix $L \in \mathbb{R}^{(M+1)\times(M+1)}$ which for simplicity we assume to have constant coefficients. In order to be compatible with Condition (1) we demand $\sum_{i=0}^{M} J_i = 0$ or $\sum_{i=0}^{M} L_{ij} = 0$ for any $0 \leq j \leq M$. The Onsager reciprocity law, [17], [18], [15], states that L has to be symmetric which we assume in the following. This symmetry has its origin in the time reversibility of the underlying stochastic process which goes along with the symmetry of the corresponding Hamiltonian, see [19] for details. Thus the symmetry of L is an universal property. Additionally, L is positive semi-definite and we assume its kernel to be one-dimensional ($Le = 0$ for $e = (1, \ldots, 1) \in \mathbb{R}^{M+1}$).

Plastic deformations close to an interfacial layer lead to the creation and annihilation of vacant lattice positions. In the sequel we shall model the creation and annihilation formally by reactions. Geometrically, vacancies are created or destroyed by locally altering the lattice structure.

The explicit form of these reactions can be motivated by first considering a system without diffusion. We write

$$\partial_t \varrho_0 = r_{I} - r_{II},$$

where $r_{I} > 0$ is the creation rate of vacancies, $r_{II} > 0$ the annihilation rate of vacancies.

Led by the thermodynamic considerations of Section 3, we make the ansatz

$$\frac{r_{_{II}}}{r_{_I}} = \exp\Big(\frac{\mu_0}{k_B\theta}\Big). \tag{6}$$

The rates $r_{_I}$ and $r_{_{II}}$ are determined only up to a common positive factor. Therefore, we can only expect a condition on the ratio $r_{_{II}}/r_{_I}$.

For the annihilation rate we make the *Arrhenius* approach

$$r_{_{II}} = \varrho_0\, a(\varrho,\chi) \exp\Big(\frac{\chi E_0^1 + (1-\chi)E_0^2 - E_A(\chi)}{k_B\theta}\Big). \tag{7}$$

Equation (7) states that we have a thermal activation process. $E_A(\chi) > 0$ is the activation energy that has to be exceeded to start the process and $E_0^l > 0$ is the energy in phase l before the reaction. (7) further ensures that there is no annihilation if no vacancies are present ($\varrho_0 = 0$).

The thermodynamic validity of the model can be shown for arbitrary factors $a(\varrho,\chi) \geq 0$. For the physical situation considered here, a only depends on χ and we set

$$a(\varrho,\chi) = a(\chi) := \Big[\frac{1}{16} - \Big(\chi - \frac{1}{2}\Big)^2\Big]_+. \tag{8}$$

Here $[v]_+ := v$ if $v \geq 0$ and $[v] := 0$ if $v < 0$ denotes the positive part of an argument v. The setting (8) guarantees $a \geq 0$. It is chosen such that $a(\chi) = 0$ for $\chi \leq \frac{1}{4}$ and $\chi \geq \frac{3}{4}$, in particular $a(\chi) = 0$ in the bulk phases where $\chi = 1$ or $\chi = 0$. This is because vacancies are created or annihilated only in the interfacial layer, but not in the bulk.

We introduce the symbol

$$\beta_0 := \exp\Big(\frac{\chi E_0^1 + (1-\chi)E_0^2 - E_A(\chi)}{k_B\theta}\Big) > 0. \tag{9}$$

Ansatz (6) and the Arrhenius law (7) imply

$$r_0(\varrho,\chi) = r_{_I} - r_{_{II}} = a(\varrho,\chi)\beta_0\varrho_0\Big[\exp\Big(\frac{-\mu_0}{k_B\theta}\Big) - 1\Big], \quad r_i(\varrho,\chi) = 0,\ 1 \leq i \leq M. \tag{10}$$

The derivation of the model is now complete. To sum up, for $0 \leq i \leq M$ we are concerned with the system of equations

$$\begin{aligned} \partial_t\varrho_i &= \operatorname{div}\Big(\sum_{j=0}^{M} L_{ij}\nabla\mu_j\Big) + r_i, && (11)\\ \mu_i &= \frac{\partial f}{\partial\varrho_i}(\varrho,\chi), && (12)\\ \tau\partial_t\chi &= \gamma\triangle\chi + \omega(\varrho,\chi) && (13) \end{aligned}$$

combined with the initial conditions

$$\varrho_i(\cdot,0) = \varrho_{i0}, \quad \chi(\cdot,0) = \chi_0 \qquad \text{in } \Omega, \tag{14}$$

and the Neumann- and no-flux boundary conditions

$$\nabla\varrho_i\cdot n_{\partial\Omega} = [L\nabla\mu]_i\cdot n_{\partial\Omega} = \nabla\chi\cdot n_{\partial\Omega} = 0 \qquad \text{on } \partial\Omega,\ t > 0. \tag{15}$$

In this formulation, ϱ_{i0} and χ_0 are initial values for ϱ_i and χ, and $n_{\partial\Omega}$ denotes the outer normal to $\partial\Omega$. As a consequence to the reaction terms r_i, the number of vacant lattice positions ϱ_0 is different for each phase and this influences the jump of μ_i at an interface.

3 Thermodynamic validation

We shortly verify the second law of thermodynamics for the equations (11)-(15). As the temperature θ is kept constant it is enough to show that for a closed system the free energy of the system decreases with time.

The chain rule yields $\frac{d}{dt}F(\varrho,\chi)=\int_\Omega\big(\sum_{j=0}^{M}\frac{\partial F}{\partial\varrho_j}\partial_t\varrho_j+\frac{\partial F}{\partial\chi}\partial_t\chi\big)$. Thus we have to test $(11)_i$ with $\frac{\partial F}{\partial\varrho_i}$ and (13) with $\frac{\partial F}{\partial\chi}$. After summing up, integration over Ω and one integration by parts the result is

$$\frac{d}{dt}\int\limits_\Omega f(\varrho,\chi,\nabla\chi)+\int\limits_{\partial\Omega}\sum_{i=0}^{M}\mu_i J_i\cdot n_{\partial\Omega}-\int\limits_\Omega\Big[\sum_{i=0}^{M}\nabla\mu_i\cdot J_i+\sum_{i=0}^{M}\mu_i r_i+\frac{\partial F}{\partial\chi}\partial_t\chi\Big]=0.$$

The crucial estimate is $\sum_{i=0}^{M}\mu_i r_i\le 0$. This is equivalent to showing that

$$r_0\mu_0=(r_{_I}-r_{_{II}})\mu_0\le 0$$

or equivalently, since $r_{_I}$ is positive,

$$\Big(1-\frac{r_{_{II}}}{r_{_I}}\Big)\mu_0\le 0.$$

The left hand side can by Ansatz (6) be rewritten as

$$\Big[1-\exp\Big(\frac{\mu_0}{k_B\theta}\Big)\Big]\mu_0$$

which yields the desired estimate and shows the thermodynamic correctness of the reactions.

With the help of (3) and (5) we thus find

$$\frac{d}{dt}\int\limits_\Omega f(\varrho,\chi,\nabla\chi)+\int\limits_{\partial\Omega}\sum_{i=0}^{M}\mu_i J_i\cdot n_{\partial\Omega}+\int\limits_\Omega\Big[L\nabla\mu:\nabla\mu+\frac{1}{\tau}(\partial_\chi F(\varrho,\chi))^2\Big]\le 0. \qquad (16)$$

(16) is the constitutive inequality for the Helmholtz free energy. $L\nabla\mu:\nabla\mu$ represents the entropy production due to mass fluxes of constituents 1 to M and vacancies, and $\frac{1}{\tau}(\partial_\chi F(\varrho,\chi))^2$ the production due to reorganisation of the phases. All production terms are positive yielding for a thermodynamically closed system the desired estimate $\frac{d}{dt}\int_\Omega f(\varrho(x,t),\chi(x,t),\nabla\chi(x,t))\,dx\le 0$.

4 Existence of weak solutions

This section shortly reviews the existence theory to (11)-(15).

In fact one can easily adapt the proof in [3]. For polynomial free energies that satisfy suitable growth conditions one considers a semi-implicit time discretisation with step size $h>0$ (which is the implicit time discretisation, except that the reaction term r is treated explicitly). Then uniform bounds independent of h are derived that allow to pass to the limit $h\searrow 0$. In a second step, by regularising the logarithmic free energy, one can extend the results of the first part to logarithmic free energies.

The following theorem is formulated for the case of homogeneous Dirichlet boundary conditions to (11)-(14), i.e. $\varrho_i=\chi=0$ on $\partial\Omega$ for $t>0$.

Notice that the uniqueness part of the theorem can only be applied if ϱ, χ and $(1-\chi)$ stay strictly positive.

Theorem 1 *Let Ω be a Lipschitz domain, f be given by (2), (4), and let the initial data fulfill $f(\varrho_0,\chi_0)<\infty$, $\omega(\varrho_0,\chi_0)<\infty$. Then there exists a weak solution (ϱ,μ,χ) of (11)-(14) such that*

(i) $\varrho \in C^{0,\frac{1}{4}}([0,T_0];\ L^2(\Omega;\mathbb{R}^M))$,
(ii) $\partial_t\varrho \in L^2(0,T_0;\ (H^1_0(\Omega;\mathbb{R}^M))')$,
(iii) $\chi \in C^{0,\frac{1}{2}}([0,T_0];\ L^2(\Omega))$,
(iv) $\partial_t\chi \in L^2(0,T_0;\ (H^1_0(\Omega))')$,
(v) *there exists a* $q>1$ *such that* $\ln\varrho_i \in L^q(\Omega_T)$ *for* $0\le i\le M$,
$\ln\chi,\ \ln(1-\chi)\in L^2(\Omega_T)$ *and in particular* $0<\chi,\varrho_i<1$ *almost everywhere.*

If $\partial_\varrho f$, $\partial_\chi f$ are Lipschitz continuous, the solution (ϱ,μ,χ) is unique in the spaces stated above.

5 Analysis of the boundary layer dynamics

This section is concerned with the behaviour of the transition layer between two phases in the limit $\gamma\searrow 0$ of a sharp interface. To this end we consider formal expansions of ϱ and χ.

The physically most interesting case is where bulk diffusion and movement of the transition layer are on the same time scale. Therefore we rescale the problem and set $\gamma=\varepsilon$, $\theta_c=\frac{1}{\varepsilon}$. The coefficient τ of $\partial_t\chi$ in (13) is normalised to 1 and we assume $L^\varepsilon_{ij}=\varepsilon L_{ij}$ such that the scaling of the diffusion is the same as in the Allen-Cahn equation. To emphasize the dependence of the solution on ε we write in the following ϱ_ε, χ_ε.

Thus we are concerned with the system

$$\partial_t\chi_\varepsilon = \varepsilon\triangle\chi_\varepsilon-\frac{1}{\varepsilon}W'(\chi_\varepsilon)+f_2(\varrho_\varepsilon)-f_1(\varrho_\varepsilon), \tag{17}$$

$$\partial_t\varrho_\varepsilon = \varepsilon L\triangle(\chi_\varepsilon\partial_\varrho f_1(\varrho_\varepsilon)+(1-\chi_\varepsilon)\partial_\varrho f_2(\varrho_\varepsilon))+\frac{1}{\varepsilon}r(\varrho_\varepsilon,\chi_\varepsilon) \tag{18}$$

with initial values (14) and boundary conditions (15). In Equation (18) we used for a vector $v=(v_0,\dots,v_M)$ the notation $\triangle v=(\triangle v_0,\dots,\triangle v_M)$.

In this paragraph all functions/functionals as ϱ_ε, χ_ε and W are supposed to be sufficiently smooth.

The interface dynamics is studied in t, the fast time scale s, and the slow time scale h,

$$s:=\frac{1}{\varepsilon}t,\qquad h:=\varepsilon t.$$

First we study the bulk regions away from $\partial\Omega$ and choose expansions

$$\varrho_\varepsilon(x,t)=\overline{\varrho}(x,t)+\varepsilon\overline{\overline{\varrho}}(x,t)+\mathcal{O}(\varepsilon^2), \tag{19}$$

$$\chi_\varepsilon(x,t)=\overline{\chi}(x,t)+\varepsilon\overline{\overline{\chi}}(x,t)+\mathcal{O}(\varepsilon^2). \tag{20}$$

Substituting this into (17), (18) we find to leading order $\mathcal{O}(\varepsilon^{-1})$

$$W'(\overline{\chi})=0,\qquad r(\overline{\varrho},\overline{\chi})=0. \tag{21}$$

For the rest of this section we shall deal with the asymptotic behaviour of ϱ_ε and χ_ε close to an interface away from $\partial\Omega$. The interface $\Gamma(t)$ of χ_ε shall be parametrised by $\{x\in\Omega\mid p(x,t,h)=0\}$ where p is the signed distance function in direction to the normal of Γ.

The front $\Gamma(t=0)$ is preset by

$$p(x,0,0)=p_0 \tag{22}$$

for a given function p_0. For ϱ_ε and χ_ε we consider the expansions

$$\begin{aligned} \varrho_\varepsilon(x,t) &= \varrho^0(u,x,s,t,h) + \varepsilon\varrho^1(u,x,s,t,h) + \mathcal{O}(\varepsilon^2), && (23)\\ \chi_\varepsilon(x,t) &= \chi^0(u,x,s,t,h) + \varepsilon\chi^1(u,x,s,t,h) + \mathcal{O}(\varepsilon^2) && (24) \end{aligned}$$

which are valid close to $\Gamma(t)$ and

$$u := \frac{1}{\varepsilon}p(x,t,h). \tag{25}$$

If we insert (23), (24) in (17) and equate the terms of power ε^{-1} this yields

$$\partial_s\chi^0 + \partial_t p\partial_u\chi^0 - |\nabla p|^2\partial_{uu}\chi^0 + W'(\chi^0) = 0. \tag{26}$$

From differentiating $\chi^0(0,x,s,t,h) = \frac{1}{2}$ with respect to t it follows

$$\partial_t p(x,t,h)\,\partial_u\chi^0(0,x,s,t,h) = 0. \tag{27}$$

Similarly, when using (23), (24) in (18), the matching of terms with ε^{-1} yields

$$\partial_s\varrho^0 + \partial_t p\,\partial_u\varrho^0 + r(\varrho^0,\chi^0) = |\nabla p|^2 L\partial_{uu}\mu(\varrho^0,\chi^0), \tag{28}$$

with $\mu(\varrho^0,\chi^0) = \chi^0\partial_\varrho f_1(\varrho^0) + (1-\chi^0)\partial_\varrho f_2(\varrho^0)$.

Equations (26), (28) govern the evolution of $\varrho^0(u,s)$ and $\chi^0(u,s)$. Here the coefficient $\partial_t p$ only depends on x, t, h and $|\nabla p|^2 = 1$.

Under the assumption $\partial_u\chi^0(0,x,s,t,h) \neq 0$ which is compatible with the a-priori estimates, (26)-(28) simplifies to

$$\begin{aligned} \partial_s\chi^0 + W'(\chi^0) &= |\nabla p|^2\partial_{uu}\chi^0, && (29)\\ \partial_s\varrho^0 + r(\varrho^0,\chi^0) &= |\nabla p|^2 L\partial_{uu}\mu(\varrho^0,\chi^0). && (30) \end{aligned}$$

So, after an initial layer, we get

$$\partial_t p = 0 \tag{31}$$

and

$$\begin{aligned} \partial_{uu}\chi^0 &= W'(\chi^0), && (32)\\ L\partial_{uu}\mu(\varrho^0,\chi^0) &= r(\varrho^0,\chi^0). && (33) \end{aligned}$$

Motion of Γ in h

Now we consider the motion of the interface Γ for slow time h.

The first order expansion of χ_ε is

$$\begin{aligned} &\partial_s\chi^1 + \partial_t p\,\partial_u\chi^1 - |\nabla p|^2\partial_{uu}\chi^1 + W''(\chi^0)\chi^1 \\ &= -\partial_t\chi^0 + (\triangle p)\partial_u\chi^0 + 2\nabla p\cdot\nabla\partial_u\chi^0 - \partial_h p\,\partial_u\chi^0 + f_2(\varrho^0) - f_1(\varrho^0) \end{aligned}$$

which simplifies to

$$\partial_s\chi^1 - |\nabla p|^2\partial_{uu}\chi^1 + W''(\chi^0)\chi^1 = (\triangle p - \partial_h p)\partial_u\chi^0 + 2\nabla p\cdot\nabla\partial_u\chi^0 + f_2(\varrho^0) - f_1(\varrho^0). \tag{34}$$

We assume that ϱ^0, χ^0, ϱ^1, χ^1 approach travelling waves in u for large h, i.e. for $l = 1, 2$

$$\begin{aligned} \varrho^l(u,x,s,t,h) &\sim R^l(u - \tilde{c}h, x, t, h) \qquad &&\text{as } h \to \infty, \\ \chi^l(u,x,s,t,h) &\sim X^l(u - ch, x, t, h) \qquad &&\text{as } h \to \infty. \end{aligned}$$

These travelling waves satisfy the boundary conditions

$$\begin{aligned} R^l(u) &\to \overline{\varrho}_- \quad \text{for } u \to -\infty, \qquad & R^l(u) &\to \overline{\varrho}_+ \quad \text{for } u \to +\infty, \\ X^l(u) &\to \overline{\chi}_- \quad \text{for } u \to -\infty, \qquad & X^l(u) &\to \overline{\chi}_+ \quad \text{for } u \to +\infty. \end{aligned}$$

The limits $\overline{\varrho}_\pm$, $\overline{\chi}_\pm$ solve (21). In particular, $\overline{\chi}_\pm$ are minimisers of W.

Away from an initial layer, (34) becomes

$$-|\nabla p|^2 \partial_{uu} X^1 + W''(X^0) X^1 = (\triangle p) \partial_u X^0 + 2 \nabla p \cdot \nabla \partial_u X^0 - \partial_h p \, \partial_u X^0 + f_2(R^0) - f^1(R^0). \tag{35}$$

Differentiating (29) with respect to u we find

$$-|\nabla p|^2 \partial_{uuu} X^0 + W''(X^0) \partial_u X^0 = 0. \tag{36}$$

Now we multiply (35) with $\partial_u X^0$ and integrate from $u = -\infty$ to $u = +\infty$. For the left hand side after integration by parts we find with (36)

$$\int\limits_{-\infty}^{+\infty} -|\nabla p|^2 \partial_{uu} X^1 \partial_u X^0 + W''(X^0) X^1 \partial_u X^0 du = \int\limits_{-\infty}^{+\infty} \Big[-|\nabla p|^2 \partial_{uuu} X^0 + W''(X^0) \partial_u X^0 \Big] X^1 = 0.$$

We define

$$\overline{p}(R^0) := \int\limits_{-\infty}^{+\infty} (f_2(R^0) - f_1(R^0)) \partial_u X^0 du.$$

The remaining terms on the right hand side yield

$$\partial_h p = \triangle p + \frac{\nabla p \cdot \nabla \left(\int_{-\infty}^{+\infty} (\partial_u X^0)^2 du \right) + \overline{p}(R^0)}{\int_{-\infty}^{+\infty} (\partial_u X^0)^2 du}. \tag{37}$$

In general, $\overline{p}(R^0) \neq 0$. Let us consider for illustration the case $\overline{p}(R^0) = 0$. Then we may rewrite $\partial_u X^0$ as $\partial_\sigma \hat{X}^0 / |\nabla p|$ where $\sigma := \frac{u - ch}{|\nabla p|}$ and $\hat{X}^0(\sigma) := X^0(u - ch, x, t, h)$. We obtain

$$\partial_h p = \triangle p - \frac{\nabla p \cdot \nabla |\nabla p|}{|\nabla p|} = |\nabla p| \kappa_p, \tag{38}$$

where κ_p denotes the mean curvature of the level set $p = \text{const}$. By (38) we recover the well-known motion by mean curvature of level sets of Γ. In general due to the presence of $\overline{p}(R^0)$, this law is perturbed.

Finally we study the behaviour of $\partial_t N_\varepsilon$ at the interface. To this end we introduce the interfacial region

$$I_\varepsilon(t) := \{x \in \Omega \,|\, a(\chi_\varepsilon(x,t)) > 0\}$$

and define sets Γ_1, $\Gamma_2 \subset \Omega$ such that

$$\Omega \cap \partial I_\varepsilon = \Gamma_1 \cup \Gamma_2.$$

Let $\dot{\alpha}$ denote the velocity of Γ_1 in normal direction with $\alpha = \alpha(x,t,h)$.

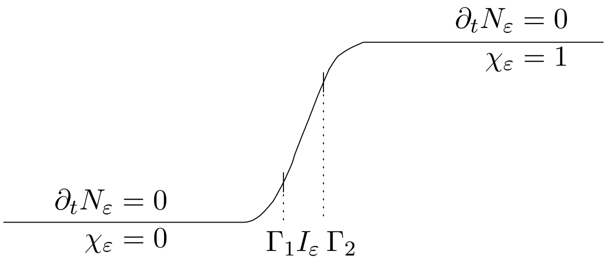

Figure 1: Graph of χ_ε and interfacial region

Summing the equations (11) for $0 \leq i \leq M$ we obtain

$$\partial_t N_\varepsilon = \frac{r_I - r_{II}}{\varepsilon}. \tag{39}$$

Since N_ε jumps in the variable u, we introduce the new scale

$$v := \frac{u + \alpha(t)}{\varepsilon}.$$

For N_ε we consider the expansion

$$N_\varepsilon(x,t) = N^0(v,x,t) + \varepsilon^2 N^1(v,x,t) + \mathcal{O}(\varepsilon^4), \tag{40}$$

where N^0, N^1 are supposed to be differentiable in v. With (40) we find

$$\partial_t N_\varepsilon = \partial_t N^0 + \frac{\dot{\alpha}}{\varepsilon}\partial_v N^0.$$

With (39), by comparing the terms of order ε^{-1}, we find the ordinary differential equation

$$\partial_v N^0 \dot{\alpha} + r_{II} - r_I = 0. \tag{41}$$

Depending on $\mathrm{sgn}(\dot{\alpha})$, the initial conditions to (41) are given either at Γ_1 (for $v = -\infty$) or at Γ_2 (for $v = +\infty$).

From the minimality of the free energy, when differentiating f with respect to t, we find with Equation (39)

$$\begin{aligned} 0 &= \partial_v f \, \partial_t v + \partial_{N_\varepsilon} f \, \partial_t N_\varepsilon \\ &= \partial_v f \frac{\dot{\alpha}}{\varepsilon} + \partial_{N_\varepsilon} f \, \frac{r_I - r_{II}}{\varepsilon}. \end{aligned}$$

Using ansatz (40) we thus obtain

$$\partial_v f + \frac{r_I - r_{II}}{\dot{\alpha}} \partial_{N^0} f = 0. \tag{42}$$

From the unboundedness of the interfacial region I_ε in the variable v we infer the minimality of f with respect to N^0 in I_ε.

It remains to investigate the behaviour of N^0 in the interfacial region. For $k = 1, 2$, $z \in \Gamma_k$ and $\delta = (\delta_1, \dots, \delta_D) \in \mathbb{R}^D$ let

$$(N^0_+)|_{\Gamma^k}(z) := \lim_{\delta \searrow 0} N^0(z + \delta), \quad (N^0_-)|_{\Gamma^k}(z) := \lim_{\delta \searrow 0} N^0(z - \delta).$$

Since $\partial_v f \leq 0$, Equation (42) yields for $k = 1, 2$

$$\operatorname{sgn}(\dot\alpha)\Big[f((N^0_+)|_{\Gamma_k}) - f((N^0_-)|_{\Gamma_k})\Big] \geq 0. \tag{43}$$

As f is minimal with respect to N^0 in I_ε, we obtain

$$f((N^0_-)|_{\Gamma_1}) = f((N^0_+)|_{\Gamma_1}) \quad \text{for } \operatorname{sgn}(\dot\alpha) > 0, \tag{44}$$

whereas $f(N^0)$ and hence N^0 jumps at Γ_2.

In the same way, the condition (43) evaluated on Γ_2 implies

$$f((N^0_-)|_{\Gamma_2}) = f((N^0_+)|_{\Gamma_2}) \quad \text{for } \operatorname{sgn}(\dot\alpha) < 0, \tag{45}$$

and f jumps at Γ_1.

Obviously, with the two conditions (44), (45) we have found the characteristic influx condition for the bulk equation $\partial_t N^0 = 0$.

6 Discussion

This article studied a situation where the number of vacancies varies locally, thereby changing the densities of the chemical constituents. This is usually not taken into account in standard segregation models.

After stating the model, the main objective was to study the influence of the unsymmetric vacancy distribution to the behaviour of the interface. We want to shortly comment on the found results and point out the differences to the existing theory.

Due to (29) and (30), we find that ϱ^0 and χ^0 are standing waves with respect to time t, whereas they are travelling waves in the slow time variable h.

As (37) shows, the motion by mean curvature of the interface Γ does no longer hold as the movement of the front depends now on two variables χ and ϱ.

Let us comment on the spatial variation of N. Due to ansatz (7), (8), the reactions vanish if $\chi = 0$ or $\chi = 1$ and hence $\partial_t N = 0$ in the bulk phases. If we assume constant initial conditions for N at $t = 0$, the number of available lattice sites per volume only changes whenever an interface passes as explained by (43).

In fact, $N(x, t)$ is determined by the last front that passed through x, i.e.

$$\begin{aligned} N(x,t) &= N(x, \tau(x,t)), \\ \tau(x,t) &= \max\{s \,|\, 0 \leq s \leq t,\ a(\chi(x,s)) > 0\}. \end{aligned}$$

Finally, there is a deep connection between the jump of the chemical potential and nucleation, in particular the size of nuclei, see [13]. We make no attempt to exploit this relationship here, but it may be of great technological importance for understanding the properties of the material. In the context of nucleation, it is noteworthy to observe that the use of reactions driven by Arrhenius kinetics to model structural changes in the lattice is not new, as the growth or shrinking of nucleation clusters is usually modelled by reactions (the so-called *Szilard mechanism*).

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