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Diffusional phase transitions in multicomponent systems with a concentration dependent mobility matrix

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Abstract

A model for phase separation in multicomponent systems is studied. In particular the possibility of a concentration dependence of the mobility matrix is taken into account. This leads to a system of fourth-order degenerate parabolic partial differential equations. We derive these equations from balance laws, show some properties of the model and prove a global existence result for the degenerate system.

Keywords: Multicomponent diffusion; Degenerate parabolic systems; Phase separation; Cahn–Hilliard equation

1. Introduction

Many phenomena in the theory of phase transitions can be modeled by diffusion equations for multicomponent systems. In this paper we consider systems described by a set of conserved order parameters $\mathbf{u} = (u_1, \ldots, u_N)$ ($N \in \mathbb{N}$) which fulfill the constraints

$$\sum_{i=1}^{N} u_i = 1 \text{ and } u_i \geq 0 \quad \text{for } i = 1, \ldots, N.$$

This includes systems with constant molar volume in which case the order parameter u_i describes the molar fraction of the ith component, or systems with constant molar mass density where we define u_i to be the mass fraction of the component i. Such assumptions are reasonable in many condensed systems on account of molecular or site conservation (for example this is true for many polymer systems and alloys).

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Since we want to model phase transition phenomena we choose a Helmholtz free energy $\mathcal{E}$ of a generalized Ginzburg–Landau form

$$\mathcal{E}(\mathbf{u}) = \int_\Omega (\Psi(\mathbf{u}) + \tfrac{1}{2}\nabla\mathbf{u} \cdot \boldsymbol{\Gamma}\nabla\mathbf{u}), \tag{1.1}$$

where Ω is an open bounded domain in $\mathbb{R}^n (n \in \mathbb{N})$. The homogeneous free energy Ψ and the gradient part of the free energy are defined as

$$\Psi(\mathbf{u}) = k_B\theta \sum_{i=1}^{N} \alpha_i u_i \ln u_i + \tfrac{1}{2}\mathbf{u} \cdot \mathbf{A}\mathbf{u}, \tag{1.2}$$

$$\nabla\mathbf{u} \cdot \boldsymbol{\Gamma}\nabla\mathbf{u} = \sum_{i,j=1}^{N} \Gamma_{ij}\nabla u_i \cdot \nabla u_j, \tag{1.3}$$

where k_B is the Boltzmann constant, θ is the absolute temperature, the A_{ij}'s are the interaction parameters and the Γ_{ij}'s are gradient energy parameters. Both $\boldsymbol{\Gamma}$ and $\mathbf{A}$ are assumed to be symmetric $(N \times N)$ matrices with constant entries and furthermore $\boldsymbol{\Gamma}$ is assumed to be positive definite. Similar free energies were proposed by De Fontaine [9,10], Hoyt [19–21] and Elliott and Luckhaus [14]. A typical choice is $\mathbf{A} = \chi(\mathbf{e}\mathbf{e}^t - \mathbf{Id})$ with $\mathbf{e} = (1, \ldots, 1)^t$, which is the case when the interaction between all components has the same magnitude χ (where $\chi \in \mathbb{R}^+$). The simplest choice for $\boldsymbol{\Gamma}$ is $\boldsymbol{\Gamma} = \gamma\mathbf{Id}$ where $\gamma > 0$ is a small interfacial parameter. We point out that if $\mathbf{A}$ has negative eigenvalues then Ψ becomes a nonconvex function for θ less than a critical temperature. For simplicity we rescale such that $k_B = 1$.

Having defined the Helmholtz free energy we get the chemical potentials μ_i as variational derivatives of $\mathcal{E}$ with respect to the ith component. We obtain

$$\mu_i = \partial_i\Psi(u) - (\boldsymbol{\Gamma}\Delta\mathbf{u})_i = \theta\alpha_i(\ln u_i + 1) + (\mathbf{A}\mathbf{u})_i - (\boldsymbol{\Gamma}\Delta\mathbf{u})_i, \tag{1.4}$$

where $(\mathbf{A}\mathbf{u})_i$ and $(\boldsymbol{\Gamma}\Delta\mathbf{u})_i$ are the ith component of the vectors $\mathbf{A}\mathbf{u}$ and $\boldsymbol{\Gamma}\Delta\mathbf{u}$. This identity is supplemented with the natural boundary condition $(\boldsymbol{\Gamma}\nabla\mathbf{u})_i \cdot \vec{n} = 0$ for all $i = 1, \ldots, N$, on $\partial\Omega \times (0, T)$, where $\vec{n}$ is the outer normal vector to $\partial\Omega$. Now we assume the thermodynamical principle that the fluxes $\vec{J}_i$ are linear and homogeneous functions of the forces $\nabla\mu_j$ (see [22, p. 136]) and make the ansatz

$$\vec{J}_i = -\sum_{j=1}^{N} L_{ij}(\mathbf{u})\nabla\mu_j \tag{1.5}$$

with Onsager coefficients L_{ij} which may depend on $\mathbf{u} = (u_1, \ldots, u_N)$ (see [16, Postulate II; 25,26]). In order to fulfill Onsager's reciprocity law we require that $\mathbf{L} = (L_{ij})_{i,j=1,\ldots,N}$ is symmetric [22, p. 137; 25,26].

With these definitions we can formulate the balance laws for the order parameters u_i as

$$\partial_t u_i = -\nabla \cdot \vec{J}_i, \quad i = 1, \ldots, N \tag{1.6}$$

together with the no-flux boundary condition $\vec{J}_i \cdot \vec{n} = 0$ for $i = 1, \ldots, N$ on $\partial\Omega \times (0, T)$. In the case that the order parameter $\mathbf{u}$ describes the molar fraction of components in a system of constant molar volume, these equations are a consequence of mass conservation (see [22]). We also refer to de Groot and Mazur [12] for a derivation of Eqs. (1.6) in systems of constant mass density. In order to ensure that the constraint $\sum_{i=1}^{N} u_i = 1$ is fulfilled during the evolution we assume

$$\sum_{i=1}^{N} L_{ij}(\mathbf{v}) = 0 \quad \text{for all } \mathbf{v} \in \mathbb{R}^N \text{ with } \sum_{i=1}^{N} v_i = 1 \text{ and for } j = 1, \ldots, N.$$

Hence

$$\partial_t \left(\sum_{i=1}^{N} u_i \right) = -\nabla \cdot \left(\sum_{i=1}^{N} \vec{J}_i \right) = \nabla \cdot \left(\sum_{i,j=1}^{N} L_{ij}(\mathbf{u}) \nabla \mu_j \right) = 0$$

so that the u_i sum up to one at time $t > 0$ if they did at time zero.

In this paper we consider an Onsager matrix $\mathbf{L}$ which can depend on the order parameters. This is necessary for many applications and was for the binary case first pointed out by Cahn [4] and Hilliard [18] and later by Langer, Bar-On and Miller [23] and de Gennes [11]. For example in the case that the mobility in the interface is larger than in the pure phase, one needs a concentration dependent mobility matrix (see [5,7,8]).

In the binary case (i.e. $N = 2$) we recover the Cahn–Hilliard equation (for $c := u_1 - u_2$)

$$\partial_t c = \nabla \cdot B(c) \nabla \left(\theta (\ln(1+c) - \ln(1-c)) - \chi c - \gamma \Delta c \right)$$

upon choosing

$$\boldsymbol{\Gamma} = \tfrac{1}{2}\gamma \mathbf{Id}, \quad \mathbf{A} = \tfrac{1}{2}\chi(\mathbf{e}\mathbf{e}^{\mathrm{t}} - \mathbf{Id}), \quad \alpha_1 = \alpha_2 = \tfrac{1}{2}$$

and using the facts $u_2 = 1 - u_1$ and $L_{12} = -L_{11}$. In this case $B(c) := L_{11}((1+c)/2, (1-c)/2)$ is called the mobility and has been proposed to be proportional to $1 - c^2$ (cf. [7,8,13,18,23]).

But what is an appropriate generalization of the mobility $B(c) = 1 - c^2$ to systems of more than two components? Ziya Akcasu and Tombakoglu [28] used the dynamic random phase approximation (or mean field theory) to determine the Onsager mobility matrix. Their simplest prototype is

$$L_{ij}(\mathbf{u}) = u_i(\delta_{ij} - u_j) \quad \text{for } i, j = 1, \ldots, N.$$

This is the case when there are no hydrodynamic interactions and when all components have the same diffusion coefficient. See also [27] for a numerical study based on the above mobility.

In this paper we allow more general mobility matrices

$$L_{ij}(\mathbf{u}) = l_i(u_i)(\delta_{ij} - (\mathbf{e} \cdot \mathbf{l}(\mathbf{u}))^{-1} l_j(u_j))$$

with $\mathbf{l}(\mathbf{u}) = (l_1(u_1), \ldots, l_N(u_N))^{\mathrm{t}}$ and bare mobilities $l_i \in C^1([0,1], \mathbb{R}_0^+)$ which vanish in 0 linearly, i.e. there exist positive constants c_1, C_1 such that

$$c_1 u_i \le l_i(u_i) \le C_1 u_i \quad \text{for } u_i \in [0,1].$$

In the case $l_i(u_i) = d_i u_i$, with positive constants d_i, we recover the prototype mobility matrix of Ziya Akcasu and Tombakoglu [28] if we take $d_i = 1$.

With the definitions above the system fulfills an isothermal version of the second principle of thermodynamics, namely the Clausius–Duhem inequality which in this case is an inequality for the total energy density $\Psi(\mathbf{u}) + \frac{1}{2}\nabla \mathbf{u} \cdot \boldsymbol{\Gamma} \nabla \mathbf{u}$. The local form of the inequality can formally be derived as follows:

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}(\Psi(\mathbf{u}) + \tfrac{1}{2}\nabla \mathbf{u} \cdot \boldsymbol{\Gamma} \nabla \mathbf{u}) \\
&\quad = D\Psi(\mathbf{u}) \cdot \mathbf{u}_t + \nabla \mathbf{u}_t \cdot \boldsymbol{\Gamma} \nabla \mathbf{u} = (D\Psi(\mathbf{u}) - \boldsymbol{\Gamma} \Delta \mathbf{u}) \cdot \mathbf{u}_t + \nabla \cdot (\mathbf{u}_t \cdot \boldsymbol{\Gamma} \nabla \mathbf{u}) \\
&\quad = -\boldsymbol{\mu} \cdot \nabla \cdot \vec{\mathbf{J}} + \nabla \cdot (\mathbf{u}_t \cdot \boldsymbol{\Gamma} \nabla \mathbf{u}) = -\nabla \cdot (\boldsymbol{\mu} \cdot \vec{\mathbf{J}}) + \nabla \boldsymbol{\mu} \cdot \vec{\mathbf{J}} + \nabla \cdot (\mathbf{u}_t \cdot \boldsymbol{\Gamma} \nabla \mathbf{u}) \\
&\quad \le -\nabla \cdot (\boldsymbol{\mu} \cdot \vec{\mathbf{J}} - \mathbf{u}_t \cdot \boldsymbol{\Gamma} \nabla \mathbf{u}).
\end{aligned}$$

The last inequality holds because $\mathbf{L}$ is positive semi-definite on the Gibbs-simplex

$$Q^N := \left\{ v \in \mathbb{R}^N \;\middle|\; \sum_{i=1}^{N} v_i = 1 \text{ and } v_i \geq 0 \text{ for } i = 1, \ldots, N \right\},$$

which will be proved in Section 2. Above and in the following sections we use the notations

$$D\Psi(\mathbf{u}) = (\partial_1 \Psi(\mathbf{u}), \ldots, \partial_N \Psi(\mathbf{u}))^{\mathrm{t}},$$
$$\boldsymbol{\mu} = (\mu_1, \ldots, \mu_N)^{\mathrm{t}}, \qquad \vec{\mathbf{J}} = (\vec{J}_1, \ldots, \vec{J}_N)^{\mathrm{t}},$$
$$\boldsymbol{\nabla} \cdot \vec{\mathbf{J}} = (\nabla \cdot \vec{J}_1, \ldots, \nabla \cdot \vec{J}_N)^{\mathrm{t}}, \qquad \boldsymbol{\mu} \cdot \vec{\mathbf{J}} = \sum_{i=1}^{N} \mu_i \vec{J}_i.$$

Although the scalar product $\cdot$ is used in different contexts it will be clear from the multiplicands which meaning it will have in a particular situation. The term $\mathbf{u}_t \cdot \boldsymbol{\Gamma} \nabla \mathbf{u}$ appearing in the Clausius–Duhem inequality can be interpreted as interface flux. In this context we refer to Gurtin [17] who first derived a version of the second law for binary systems with capillarity (or interface) contributions. In his paper the interface term is interpreted as the product of a capillarity potential $\mathbf{u}$ and a capillarity flux $\boldsymbol{\Gamma} \nabla \mathbf{u}$. We also refer to Elliott and Luckhaus [14] who extended Gurtin's inequality to multicomponent systems and Alt and Pawlow [1] for a nonisothermal version of an entropy inequality for multicomponent systems.

The aim of this paper is to develop an existence theory for multicomponent diffusion when the mobility matrix depends on the order parameter $\mathbf{u}$. A main difficulty in this task is the degeneracy of the matrix $\mathbf{L}(\mathbf{u})$. If we interpret $\mathbf{L}$ as a mapping from $\mathbb{R}^N$ into $\mathbb{R}^N$, we always have a zero eigenvalue. On the other hand if we restrict $\mathbf{L}(\mathbf{u})$ to

$$\mathbf{e}^{\perp} = \{\mathbf{v} \in \mathbb{R}^N \mid \mathbf{v} \cdot \mathbf{e} = 0\}$$

then we will show in Section 2 that $\mathbf{L}(\mathbf{u})$ is positive definite as long as $\mathbf{u}$ lies in the interior of the Gibbs simplex Q^N, but degenerates on the boundary of Q^N.

Now we state an existence theorem for the initial boundary value problem for (1.4)–(1.6) which will be proved in the following sections. From now on we assume either Ω is convex or has a $C^{1,1}$-boundary and use the notation $\Omega_T = \Omega \times (0, T)$.

Theorem A. Assume the initial data $\mathbf{u}_0 \in H^1(\Omega, \mathbb{R}^N)$ fulfills $\mathbf{u}_0 \in Q^N$ almost everywhere. Then there exists a function $\mathbf{u} : \Omega_T \to Q^N$ with $\mathbf{u} \in L^2(0, T; H^2(\Omega, \mathbb{R}^N)) \cap H^1(0, T; (H^1(\Omega, \mathbb{R}^N))')$ and fluxes $\vec{J}_i \in L^2(\Omega_T, \mathbb{R}^n)$ for $i = 1, \ldots, N$, such that

(1) $\mathbf{u}(0) = \mathbf{u}_0$ and $(\boldsymbol{\Gamma} \nabla u)_i \cdot \vec{n} = 0$, $i = 1, \ldots, N$,

(2) $\partial_t u_i = -\nabla \cdot \vec{J}_i$ in $L^2(0, T; (H^1(\Omega))')$,

(3) $\vec{\mathbf{J}} = -\mathbf{L}(\mathbf{u}) \nabla (-\boldsymbol{\Gamma} \Delta \mathbf{u} + D\Psi(\mathbf{u}))$ in the sense that

$$\int_{\Omega_T} \vec{\mathbf{J}} \cdot \vec{\eta} = -\int_{\Omega_T} \boldsymbol{\Gamma} \Delta \mathbf{u} \cdot (\nabla \cdot (\mathbf{L}(\mathbf{u}) \vec{\eta})) - \int_{\Omega_T} ((\mathbf{L}\, D^2 \Psi)(\mathbf{u}) \nabla \mathbf{u}) \cdot \vec{\eta}$$

for all $\vec{\eta} \in L^2(0, T; H^1(\Omega, (\mathbb{R}^n)^N)) \cap L^\infty(\Omega_T, (\mathbb{R}^n)^N)$ which fulfill $\vec{\eta}_i \cdot \vec{n} = 0$, for $i = 1, \ldots, N$ on $\partial\Omega \times (0, T)$.

This theorem will be proved in the following sections. First we prove some basic facts for the mobility matrix (Section 2). Then we formulate approximate equations with a smooth homogeneous free energy and a strictly positive definite mobility matrix and show existence of solutions to this set of equations (Section 3). For these

approximate solutions we show energy estimates which enable us to pass to the limit in the approximate equations (Section 4). The limit equation will be satisfied in a sense similar to the notion of a solution in the binary case defined in [13]. We finish with some conclusions.

2. Some properties of the mobility matrix

In this section we prove that the matrix $\mathbf{L}(\mathbf{u})$ is positive semi-definite for all $\mathbf{u} \in Q^N$.

Lemma 1. Let $\mathbf{a}, \mathbf{b} \in \mathbb{R}^d$ $(d \in \mathbb{N})$ and $\mathbf{Id}_d$ be the identity on $\mathbb{R}^d$. Then

$$\det(\mathbf{Id}_d - \mathbf{a}\mathbf{b}^{\mathrm{t}}) = 1 - \mathbf{a} \cdot \mathbf{b}.$$

Proof. Without loss of generality we assume $|\mathbf{b}| = 1$. The mapping $\mathbf{Id}_d - \mathbf{a}\mathbf{b}^{\mathrm{t}}$ is the identity on all vectors orthogonal to $\mathbf{b}$ and therefore we have 1 as an eigenvalue of multiplicity $(d-1)$. Hence the determinant of $\mathbf{Id}_d - \mathbf{a}\mathbf{b}^{\mathrm{t}}$ is determined by the remaining eigenvalue. Since

$$(\mathbf{Id}_d - \mathbf{a}\mathbf{b}^{\mathrm{t}})\mathbf{a} = (1 - \mathbf{a} \cdot \mathbf{b})\mathbf{a}$$

we conclude that $\mathbf{a}$ is an eigenvector to the eigenvalue $1 - \mathbf{a} \cdot \mathbf{b}$ and the lemma is proved provided $\mathbf{a} \cdot \mathbf{b} \neq 0$. In the case $\mathbf{a} \cdot \mathbf{b} = 0$ the lemma follows because the determinant is continuous. □

Lemma 2. Let $\mathbf{M} = (M_{ij})_{i,j=1,\dots,d}$ $(d \in \mathbb{N})$ be a matrix defined as

$$M_{ij} = m_i(\delta_{ij} - n_j) \quad (i, j = 1, \dots, d).$$

Then it holds

$$\det \mathbf{M} = m_1 \cdots m_d \left(1 - \sum_{k=1}^{d} n_k\right).$$

Proof. Since

$$\mathbf{M} = \operatorname{diag}(m_1, \dots, m_d)(\mathbf{Id} - \mathbf{e}\mathbf{n}^{\mathrm{t}})$$

with $\mathbf{e} = (1, \dots, 1)^{\mathrm{t}}$ and $\mathbf{n} = (n_1, \dots, n_d)^{\mathrm{t}}$ the conclusion follows from Lemma 1. □

Lemma 3. The matrix $\mathbf{L}(\mathbf{u}) = (L_{ij}(\mathbf{u}))_{i,j=1,\dots,N}$ with

$$L_{i,j}(\mathbf{u}) = l_i(u_i)(\delta_{i,j} - (\mathbf{e} \cdot \mathbf{l}(\mathbf{u}))^{-1} l_j(u_j)), \quad i, j = 1, \dots, N,$$

where the l_i are as in Section 1, is positive semi-definite for all $\mathbf{u} \in Q^N$.

Proof. Let $\mathbf{L}_d(\mathbf{u}) = (L_{ij}(\mathbf{u}))_{i,j=1,\dots,d}$ be an upper left sub-matrix of $\mathbf{L}$. Lemma 2 yields

$$\det \mathbf{L}_d = l_1 \cdots l_d \left(1 - (\mathbf{e} \cdot \mathbf{l}(\mathbf{u}))^{-1} \sum_{k=1}^{d} l_k\right),$$

which is nonnegative. The assertion now follows from an application of Hurwitz's theorem for symmetric matrices. □

Now we want to calculate the determinant of the linear mapping which we get when we restrict $\mathbf{L}(\mathbf{u})$ on $\mathbf{e}^\perp$. Let us denote this mapping by $\mathcal{L}_{\mathbf{e}^\perp}$. Since $\mathbf{L}(\mathbf{u})\mathbf{e}^\perp \perp \mathbf{e}$ we have

$$\mathcal{L}_{\mathbf{e}^\perp} : \mathbf{e}^\perp \longrightarrow \mathbf{e}^\perp.$$

Lemma 4. It holds that

$$\det \mathcal{L}_{\mathbf{e}^\perp} = N \cdot \frac{l_1 \cdots l_N}{\sum_{i=1}^N l_i}.$$

Proof. We choose a basis $\{\mathbf{f}_i\}_{i=1}^{N-1}$ of $\mathbf{e}^\perp$ with $\mathbf{f}_i := \mathbf{e}_i - \mathbf{e}_N$, where $\mathbf{e}_i$ is the ith unit vector. Then we get

$$\mathbf{L}\mathbf{f}_i = \sum_{j=1}^{N} (L_{ji} - L_{jN})\,\mathbf{e}_j = \sum_{j=1}^{N} (L_{ji} - L_{jN})(\mathbf{e}_j - \mathbf{e}_N) + \underbrace{\sum_{j=1}^{N} (L_{ji} - L_{jN})\mathbf{e}_N}_{=0}$$

$$= \sum_{j=1}^{N-1} (L_{ji} - L_{jN})\mathbf{f}_j,$$

where we omitted the argument $\mathbf{u}$. Therefore, the matrix $\hat{\mathbf{L}}$ which expresses the linear mapping $\mathcal{L}_{\mathbf{e}^\perp}$ with respect to the basis $(\mathbf{f}_1, \ldots, \mathbf{f}_{N-1})$ is

$$\hat{\mathbf{L}} = (\hat{\mathbf{L}}_1 - \hat{\mathbf{L}}_N, \ldots, \hat{\mathbf{L}}_{N-1} - \hat{\mathbf{L}}_N)$$

with the $(N-1)$ vectors $\hat{\mathbf{L}}_1, \ldots, \hat{\mathbf{L}}_{N-1}$ defined as $\hat{\mathbf{L}}_i = (L_{1i}, \ldots, L_{N-1\,i})^{\mathrm{t}}$. Hence we can calculate the determinant of $\hat{\mathbf{L}}$ as

$$\det \hat{\mathbf{L}} = \det(\hat{\mathbf{L}}_1, \ldots, \hat{\mathbf{L}}_{N-1}) + \sum_{i=1}^{N-1} \det(\hat{\mathbf{L}}_1, \ldots, \hat{\mathbf{L}}_{i-1}, -\hat{\mathbf{L}}_N, \hat{\mathbf{L}}_{i+1}, \ldots, \hat{\mathbf{L}}_{N-1}).$$

Since

$$\sum_{i=1}^{N-1} \hat{\mathbf{L}}_i = -\hat{\mathbf{L}}_N$$

we get

$$\det \hat{\mathbf{L}} = N \det(\hat{\mathbf{L}}_1, \ldots, \hat{\mathbf{L}}_{N-1}).$$

But Lemma 2 yields

$$\det(\hat{\mathbf{L}}_1 \cdots \hat{\mathbf{L}}_{N-1}) = l_1 \cdots l_{N-1} \left(1 - \sum_{i=1}^{N-1} l_i \left(\sum_{i=1}^{N} l_i\right)^{-1}\right) = \frac{l_1 \cdots l_N}{\sum_{i=1}^N l_i}$$

which proves Lemma 4. □

As a consequence of Lemma 4 we can determine when $\mathbf{L}(\mathbf{u})$ degenerates.

Corollary 5. The mobility matrix $\mathbf{L}(\mathbf{u})$ degenerates on Q^N, i.e. has more than one vanishing eigenvalue, if and only if

$$u_i = 0 \quad \text{for some } i \in \{1, \ldots, N\}.$$

Proof. Since l_i is zero if and only if $u_i = 0$ this result is an immediate consequence of Lemma 4. □

Remark 6. Lemmas 3 and 4 remain true for arbitrary nonnegative l_i's. In particular the assumption that $l_i(0) = 0$ is of course not necessary.

3. An approximating problem

As we have seen in Section 2 the mobility matrix $\mathbf{L}$ degenerates on the boundary of Q^N. In this section we replace the mobility by a modified mobility matrix $\mathbf{L}^\varepsilon$ having positive eigenvalues when restricted on $\mathbf{e}^\perp$ which for fixed ε are uniformly in $\mathbf{u}$ bounded away from zero.

First of all we define modified bare mobilities as

$$l_i^\varepsilon(u_i) := \begin{cases} l_i(\varepsilon) & \text{for } u_i \le \varepsilon, \\ l_i(u_i) & \text{for } u_i > \varepsilon, \end{cases}$$

where we extended l_i to all of $\mathbb{R}^+$ such that l_i and l_i' are bounded. With this definition the l_i^ε are Lipschitz continuous and uniformly bounded away from zero. Having defined the modified bare mobilities we get the modified mobility matrix $\mathbf{L}^\varepsilon(\mathbf{u})$ as

$$L_{ij}^\varepsilon(\mathbf{u}) := l_i^\varepsilon(\delta_{ij} - (\mathbf{e}\cdot\mathbf{l}^\varepsilon(\mathbf{u}))^{-1} l_j^\varepsilon)$$

with $\mathbf{l}^\varepsilon(\mathbf{u}) := (l_1^\varepsilon(u_1), \dots, l_N^\varepsilon(u_N))^{\mathrm{t}}$.

This new mobility matrix is uniformly positive definite on $\mathbf{e}^\perp$. Let $\boldsymbol{\pi}$ be the orthogonal projection from $\mathbb{R}^N$ onto the subspace $\mathbf{e}^\perp$.

Lemma 7. There exists a positive constant $c(\varepsilon)$ such that

$$\mathbf{v}\cdot\mathbf{L}^\varepsilon(\mathbf{u})\mathbf{v} \ge c(\varepsilon)|\boldsymbol{\pi}\mathbf{v}|^2 \tag{3.1}$$

for all $\mathbf{u}, \mathbf{v} \in \mathbb{R}^N$. Furthermore, $\mathbf{L}^\varepsilon(u)\mathbf{e} = 0$. But when restricted to $\mathbf{e}^\perp$ the linear mapping $\mathbf{L}^\varepsilon(\mathbf{u})$ has positive real eigenvalues.

Proof. Let $\mathcal{L}_{\mathbf{e}^\perp}^\varepsilon(\mathbf{u})$ be the restriction of the linear mapping defined by $\mathbf{L}^\varepsilon(\mathbf{u})$ on $\mathbf{e}^\perp$. Lemma 4 implies (cf. Remark 6)

$$\det \mathcal{L}_{\mathbf{e}^\perp}^\varepsilon(\mathbf{u}) = N\frac{l_1^\varepsilon\cdots l_N^\varepsilon}{\sum_{i=1}^N l_i^\varepsilon} \ge N\frac{c_1^N\varepsilon^N}{\sum_{i=1}^N \|l_i\|_{L^\infty(\mathbb{R}_0^+)}} \ge c_0\varepsilon^N,$$

where $c_0 > 0$. Furthermore, $\mathbf{L}^\varepsilon(\mathbf{u})$ is bounded independently of $\mathbf{u}$ in any matrix norm. This implies that the eigenvalues of $\mathcal{L}_{\mathbf{e}^\perp}^\varepsilon(\mathbf{u})$ are bounded.

Since $\det \mathcal{L}_{\mathbf{e}^\perp}^\varepsilon(\mathbf{u})$ is the product of all eigenvalues of $\mathcal{L}_{\mathbf{e}^\perp}^\varepsilon(\mathbf{u})$ and the magnitude of the eigenvalues is bounded we get an estimate on the smallest eigenvalue from below by a constant $c(\varepsilon)$ independent of $\mathbf{u}$. A simple calculation yields

$$\mathbf{L}^\varepsilon(\mathbf{u})\mathbf{e} = \sum_{i=1}^N\sum_{j=1}^N l_i^\varepsilon(\delta_{ij} - l_j^\varepsilon(\mathbf{e}\cdot\mathbf{l}^\varepsilon(\mathbf{u}))^{-1})\mathbf{e}_i = \sum_{i=1}^N l_i^\varepsilon \underbrace{\left(1 - \sum_{j=1}^N l_j^\varepsilon\left(\mathbf{e}\cdot\mathbf{l}^\varepsilon(\mathbf{u})\right)^{-1}\right)}_{=0}\mathbf{e}_i = 0.$$

Now (3.1) follows because $\mathbf{L}^\varepsilon$ is symmetric. □

In order to regularize the problem we replace the homogeneous free energy Ψ by

$$\Psi^\varepsilon(\mathbf{u}) = \theta \sum_{i=1}^{N} \alpha_i \Psi^\varepsilon(u_i) + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{A}\mathbf{u}$$

with

$$\psi^\varepsilon(r) := \begin{cases} r\ln r & \text{for } r \geq \varepsilon, \\ \left(r\ln\varepsilon - \dfrac{\varepsilon}{2} + \dfrac{r^2}{2\varepsilon}\right) & \text{for } r < \varepsilon. \end{cases}$$

This is the same modification of the free energy which was used by Elliott and Luckhaus [14] in their existence proof for the case of a constant mobility matrix. For Ψ^ε they proved the following lemma which we shall need later.

Lemma 8. There exists an $\varepsilon_0 > 0$ and a $K > 0$ such that for all $\varepsilon < \varepsilon_0$

$$\Psi^\varepsilon(\mathbf{u}) \geq -K \quad \text{for all } \mathbf{u} \in \mathbb{R}^N \text{ with } \mathbf{u}\cdot\mathbf{e} = 1.$$

The regularized problem now becomes to find functions $\mathbf{u}^\varepsilon, \mathbf{w}^\varepsilon : \Omega_T \longrightarrow \mathbb{R}^N$ such that

$$\partial_t \mathbf{u}^\varepsilon = \nabla\cdot[\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\nabla\mathbf{w}^\varepsilon],$$
$$w_i^\varepsilon = \frac{1}{N}\sum_{j=1}^{N}(-(\boldsymbol{\Gamma}\Delta\mathbf{u}^\varepsilon)_i + \partial_i\Psi^\varepsilon(\mathbf{u}^\varepsilon) + (\boldsymbol{\Gamma}\Delta\mathbf{u}^\varepsilon)_j - \partial_j\Psi^\varepsilon(\mathbf{u}^\varepsilon)) \quad \text{for } i = 1,\dots,N$$

together with the initial condition $\mathbf{u}^\varepsilon(0) = \mathbf{u}_0$, the no-flux condition $(\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\nabla\mathbf{w}^\varepsilon)\cdot\vec{n} = 0$ and the natural boundary condition $\boldsymbol{\Gamma}\nabla\mathbf{u}^\varepsilon\cdot\vec{n} = 0$.

Above we defined generalized chemical potential differences

$$w_i^\varepsilon := (\boldsymbol{\pi}\boldsymbol{\mu}^\varepsilon)_i = \frac{1}{N}\sum_{j=1}^{N}(\mu_i^\varepsilon - \mu_j^\varepsilon) = \frac{1}{N}\sum_{j=1}^{N}(-(\boldsymbol{\Gamma}\Delta\mathbf{u}^\varepsilon)_i + \partial_i\Psi^\varepsilon(\mathbf{u}^\varepsilon) + (\boldsymbol{\Gamma}\Delta\mathbf{u}^\varepsilon)_j - \partial_j\Psi^\varepsilon(\mathbf{u}^\varepsilon)).$$

These generalized chemical potential differences have been introduced by Elliott and Luckhaus [14]. This set of equations is the variational derivative of the free energy $\mathcal{E}$ when one allows variations subject to the constraint $\sum_{i=1}^{N} u_i = 1$ (cf. [1]). As we shall see later $\mathbf{w}^\varepsilon$ rather than $\boldsymbol{\mu}^\varepsilon$ is the quantity one gets estimates for. This is due to the fact that $\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)$ has the vector $\mathbf{e} = (1,\dots,1)^t$ in its kernel.

The next proposition states an existence result for the regularized problem.

Proposition B. Assume $\mathbf{u}_0 \in H^1(\Omega,\mathbb{R}^N)$ such that $\mathbf{u}_0\cdot\mathbf{e} = 1$ almost everywhere in Ω. Then for all $\varepsilon \in (0,\varepsilon_0]$ there exist functions $\mathbf{u}^\varepsilon \in L^2(0,T;H^1(\Omega,\mathbb{R}^N))\cap H^1(0,T;(H^1(\Omega,\mathbb{R}^N))')$ and $\mathbf{w}^\varepsilon \in L^2(0,T;H^1(\Omega,\mathbb{R}^N))$ such that

(1) $\partial_t\mathbf{u}^\varepsilon = \nabla\cdot[\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\nabla\mathbf{w}^\varepsilon]$ holds in $L^2(0,T;(H^1(\Omega,\mathbb{R}^N))')$,
(2) $\mathbf{w}^\varepsilon = \boldsymbol{\pi}(-\boldsymbol{\Gamma}\Delta\mathbf{u}^\varepsilon + D\Psi^\varepsilon(\mathbf{u}^\varepsilon))$ holds in $L^2(0,T;(H^1(\Omega,\mathbb{R}^N))')$,
(3) $\mathbf{u}^\varepsilon(0) = \mathbf{u}_0$ and $\mathbf{u}^\varepsilon\cdot\mathbf{e} = 1$ almost everywhere in Ω_T.

Proof. The proposition is proved by a Galerkin approximation. For the binary case this method is described in detail in [13]. Therefore, we only sketch the proof here and concentrate on the new difficulties which arise due to the fact that we consider multicomponent systems.

As Galerkin spaces for $\mathbf{u}^\varepsilon$ and $\mathbf{w}^\varepsilon$ we use

$$W_k^N := \underbrace{W_k \times \cdots \times W_k}_{N\text{-times}}$$

with $W_k = span\{\phi_1, \ldots, \phi_k\}$ where the ϕ_k are the eigenfunctions of the Laplace operator on Ω with Neumann boundary conditions. In particular we choose the ϕ_k such that they are orthonormal with respect to the L^2 scalar product and such that $\phi_1 \equiv$ const.

The proof is based on a free energy estimate. In the following estimate we omit the index k in $\mathbf{u}^{\varepsilon k}$ which stands for the kth Galerkin solution. We want to point out that the energy estimate can be made rigorous for the solution of the Galerkin approximation as well for the limit $(\mathbf{u}^\varepsilon, \mathbf{w}^\varepsilon)$:

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega (\Psi^\varepsilon(\mathbf{u}^\varepsilon) + \tfrac{1}{2}\nabla\mathbf{u}^\varepsilon \cdot \boldsymbol{\Gamma}\nabla\mathbf{u}^\varepsilon) \\
&\quad = \int_\Omega \left(D\Psi(\mathbf{u}^\varepsilon)\mathbf{u}_t^\varepsilon + \nabla\mathbf{u}^\varepsilon \cdot \boldsymbol{\Gamma}\nabla\mathbf{u}_t^\varepsilon\right) = \int_\Omega \left(D\Psi^\varepsilon(\mathbf{u}^\varepsilon)\mathbf{u}_t^\varepsilon - \boldsymbol{\Gamma}\Delta\mathbf{u}^\varepsilon \cdot \mathbf{u}_t^\varepsilon\right) \\
&\quad = \int_\Omega \mathbf{w}^\varepsilon \cdot (\nabla \cdot (\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\nabla\mathbf{w}^\varepsilon)) = -\int_\Omega \nabla\mathbf{w}^\varepsilon \cdot (\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\nabla\mathbf{w}^\varepsilon) \le -c(\varepsilon)\int_\Omega |\nabla\mathbf{w}^\varepsilon|^2,
\end{aligned}$$

where we used that $\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\mathbf{e} = 0$ and estimate (3.1). Since $\boldsymbol{\Gamma}$ is positive definite there exists a constant $\gamma > 0$ such that

$$\nabla\mathbf{u}^\varepsilon \cdot \boldsymbol{\Gamma}\nabla\mathbf{u}^\varepsilon \ge \gamma|\nabla\mathbf{u}^\varepsilon|^2.$$

Since Ψ^ε is bounded from below (Lemma 8) we get

$$\operatorname{ess\,sup}_{0<t<T}\int_\Omega |\nabla\mathbf{u}^\varepsilon(t)|^2 + c(\varepsilon)\int_{\Omega_T} |\nabla\mathbf{w}^\varepsilon|^2 \le C.$$

This estimate implies that $\partial_t\mathbf{u}^{\varepsilon k}$ is bounded in $L^2(0, T; (H^1(\Omega, \mathbb{R}^N))')$ uniformly with respect to k. Now the fact that $\int_\Omega u_i^{\varepsilon k}(t) = m_i$ with constants $m_i \in \mathbb{R}$ implies that the $\mathbf{u}^{\varepsilon k}$ are uniformly in k bounded in the norm of $L^\infty(0, T; H^1(\Omega, \mathbb{R}^N))$. Furthermore, the boundary condition $\boldsymbol{\Gamma}\nabla\mathbf{u}^\varepsilon \cdot \vec{n} = 0$ and the sub-linear growth of $D\Psi^\varepsilon$ implies that the $\mathbf{w}^{\varepsilon k}$ lie in a bounded set of $L^2(0, T; H^1(\Omega, \mathbb{R}^N))$ (for fixed ε).

Using compactness results these estimates are enough to pass to the limit as k tends to infinity (see [13] for the binary case). We just want to show that $\sum_{i=1}^N u^{\varepsilon k}(t, x) = 1$ is true for all $\varepsilon \in (0, \varepsilon_0]$ and $k \in \mathbb{N}$. For all test functions $\zeta(t, x) = \eta(t)\phi(x)$ with $\phi \in W_k$ and $\eta : [0, T] \to \mathbb{R}$ smooth such that $\eta(T) = 0$ we have for all $i \in \{1, \ldots, N\}$ that

$$-\int_{\Omega_T} \partial_t\zeta u_i^{\varepsilon k} + \int_\Omega u_{0i}^k\zeta(0) + \int_{\Omega_T}\sum_{j=1}^N L_{ij}^\varepsilon(\mathbf{u}^{\varepsilon k})\nabla w_j^{\varepsilon k}\nabla\zeta = 0,$$

where $u_{0i}^k = \sum_{j=1}^k (u_{0i}, \phi_j)_{L^2}\phi_j$. If we take the sum over $i \in \{1, \ldots, N\}$, we obtain

$$-\int_{\Omega_T} \partial_t\zeta \sum_{i=1}^N u_i^{\varepsilon k} + \int_\Omega \zeta(0)\sum_{i=1}^N u_{0i}^k + \int_{\Omega_T}\sum_{j=1}^N \underbrace{\sum_{i=1}^N L_{ij}^\varepsilon(\mathbf{u}^{\varepsilon k})}_{=0}\nabla w_j^{\varepsilon k}\nabla\zeta = 0.$$

Therefore,

$$\int_{\Omega_T} \zeta\, \partial_t \left(\sum_{i=1}^{N} u_i^{\varepsilon k} \right) = 0$$

for all ζ as above. This implies that $\partial_t(\sum_{i=1}^{N} u_i^{\varepsilon k})$ is for all t orthogonal to W_k in the L^2 scalar product. Hence $\partial_t(\sum_{i=1}^{N} u_i^{\varepsilon k}) = 0$. Since $u_{0i}^k = \sum_{j=1}^{k} (u_{0i}, \phi_j)_{L^2(\Omega)} \phi_j$ we have

$$\sum_{i=1}^{N} u_{0i}^k = \sum_{j=1}^{k} \left(\underbrace{\sum_{i=1}^{N} u_{0i}, \phi_j}_{=1} \right)_{L^2(\Omega)} \phi_j = 1.$$

This shows that $\sum_{i=1}^{N} u_i^{\varepsilon k} = 1$ for all $\varepsilon \in (0, \varepsilon_0]$ and $k \in \mathbb{N}$. Thus we obtain (3) in the limit as k tends to infinity which finishes the proof of Proposition B. □

Remark 9. Using the facts that $\mathbf{w}^\varepsilon \in L^2(0, T; (H^1(\Omega, \mathbb{R}^N))$ and that $D\Psi^\varepsilon$ is sub-linear we can apply elliptic regularity theory to conclude that $\nabla \Delta \mathbf{u}^\varepsilon \in L^2(\Omega_T)$.

But we want to stress that in general no in ε uniform estimates for third-order derivatives can be established. This is due to the fact that $\mathbf{L}^\varepsilon$ degenerates as ε tends to 0. In order to pass to the limit we shall establish estimates on second spatial derivatives which hold uniformly in ε. To establish these estimates we need to define

$$\Phi^\varepsilon(\mathbf{z}) := \sum_{i=1}^{N} \phi_i^\varepsilon(z_i) \quad \text{for all } \mathbf{z} \in \mathbb{R}^N$$

with

$$(\phi_i^\varepsilon)''(z_i) = \frac{1}{l_i^\varepsilon(z_i)} \quad \text{and} \quad \phi_i^\varepsilon(1) = 0,\ (\phi_i^\varepsilon)'(1) = 0 \ \text{ for } i = 1, \ldots, N.$$

The function $D\Phi^\varepsilon(\mathbf{u})$ will be the test function which enables us to establish the uniform estimates for second-order spatial derivatives.

In the next lemma we collect estimates which hold uniformly in ε.

Lemma 10. We assume $\mathbf{u}_0 \in H^1(\Omega, \mathbb{R}^N)$ with $u_0 \in Q^N$ almost everywhere and $\varepsilon \in (0, \varepsilon_0]$. Then the solutions $(\mathbf{u}^\varepsilon, \mathbf{w}^\varepsilon)$ of Proposition B fulfill the following properties. There exists a constant C such that

(1) $\operatorname{ess\,sup}_{0<t<T} \int_\Omega |\nabla \mathbf{u}^\varepsilon(t)|^2 + \int_{\Omega_T} (\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon) \nabla \mathbf{w}^\varepsilon \cdot \nabla \mathbf{w}^\varepsilon) \le C$,

(2) $\operatorname{ess\,sup}_{0<t<T} \int_\Omega \Phi^\varepsilon(\mathbf{u}^\varepsilon(t)) + \int_{\Omega_T} \Delta \mathbf{u}^\varepsilon \cdot \Gamma \Delta \mathbf{u}^\varepsilon \le C$,

(3) $\operatorname{ess\,sup}_{0<t<T} \int_\Omega \sum_{i=1}^{N} (\min(u_i^\varepsilon, 0))^2 \le C\varepsilon$.

Furthermore, the fluxes $\vec{\mathbf{J}}^\varepsilon = \mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon) \nabla \mathbf{w}^\varepsilon$ are uniformly bounded in $L^2(\Omega_T, \mathbb{R}^{Nn})$ and the time derivatives $\partial_t \mathbf{u}^\varepsilon$ are uniformly in ε bounded in $L^2(0, T; (H^1(\Omega, \mathbb{R}^N))')$.

Proof. The first estimate has been proven in Proposition B. Since $\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)$ has eigenvalues which are nonnegative and uniformly in ε bounded we conclude from estimate (1)

$$\int_{\Omega_T} (\vec{\mathbf{J}}^\varepsilon)^2 = \int_{\Omega_T} (\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon) \nabla \mathbf{w}^\varepsilon) \cdot (\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon) \nabla \mathbf{w}^\varepsilon) \le \tilde{C} \int_{\Omega_T} (\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon) \nabla \mathbf{w}^\varepsilon) \cdot \nabla \mathbf{w}^\varepsilon \le C\,.$$

Since $\partial_t \mathbf{u}^\varepsilon = -\nabla \cdot \vec{\mathbf{J}}^\varepsilon$ the estimate on $\vec{\mathbf{J}}^\varepsilon$ implies that $\partial_t \mathbf{u}^\varepsilon$ is uniformly bounded in $L^2(0,T;(H^1(\Omega,\mathbb{R}^N))')$.

Next we are going to prove (2). Therefore, we use $D\Phi^\varepsilon(\mathbf{u}^\varepsilon)$ as a test function in the weak formulation of the identity $\partial_t \mathbf{u}^\varepsilon = \nabla \cdot [\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\nabla \mathbf{w}^\varepsilon]$. By a standard approximation argument one can show (see [13] for details)

$$\int_0^t \langle D\Phi^\varepsilon(\mathbf{u}^\varepsilon), \partial_t \mathbf{u}^\varepsilon \rangle_{H^1,(H^1)'} = \int_\Omega \Phi^\varepsilon(\mathbf{u}^\varepsilon(t)) - \int_\Omega \Phi^\varepsilon(\mathbf{u}_0)$$

for almost all $t \in [0,T]$. On the other hand we have

$$\begin{aligned}
&\int_{\Omega_t} \nabla D\Phi^\varepsilon(\mathbf{u}^\varepsilon) \cdot \mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\nabla \mathbf{w}^\varepsilon \\
&\quad = \int_{\Omega_t} \sum_{i=1}^N \left((\phi_i^\varepsilon)''(u_i^\varepsilon)\nabla u_i^\varepsilon \cdot \sum_{j=1}^N L_{ij}^\varepsilon(u_i^\varepsilon)\nabla w_j^\varepsilon \right) \\
&\quad = \int_{\Omega_t} \sum_{i=1}^N \frac{1}{l_i^\varepsilon(u_i^\varepsilon)} \nabla u_i^\varepsilon \cdot \sum_{j=1}^N l_i^\varepsilon(u_i^\varepsilon)(\delta_{ij} - (\mathbf{e}\cdot\mathbf{l}^\varepsilon)^{-1} l_j^\varepsilon(u_j^\varepsilon))\nabla w_j^\varepsilon \\
&\quad = \int_{\Omega_t} \sum_{i=1}^N \nabla u_i^\varepsilon \cdot \nabla w_i^\varepsilon - \int_{\Omega_t} \underbrace{\sum_{i=1}^N \nabla u_i^\varepsilon}_{=0} \cdot \sum_{j=1}^N (\mathbf{e}\cdot\mathbf{l}^\varepsilon)^{-1} l_j^\varepsilon \nabla w_j^\varepsilon \\
&\quad = \int_{\Omega_t} \sum_{i=1}^N \nabla u_i^\varepsilon \cdot \nabla(-(\boldsymbol{\Gamma}\Delta \mathbf{u}^\varepsilon)_i + (\psi^\varepsilon)'(u_i^\varepsilon) + (\mathbf{A}\mathbf{u}^\varepsilon)_i) \\
&\quad = \int_{\Omega_t} \Delta \mathbf{u}^\varepsilon \cdot \boldsymbol{\Gamma}\Delta \mathbf{u}^\varepsilon + \int_{\Omega_t} \sum_{i=1}^N \nabla u_i^\varepsilon \underbrace{(\psi^\varepsilon)''(u_i^\varepsilon)}_{\geq 0} \nabla u_i^\varepsilon + \int_{\Omega_t} \nabla \mathbf{u}_\varepsilon \cdot \mathbf{A}\nabla \mathbf{u}_\varepsilon .
\end{aligned}$$

Altogether we obtain

$$\int_\Omega \Phi^\varepsilon(\mathbf{u}^\varepsilon(t)) + \int_{\Omega_t} \Delta \mathbf{u}^\varepsilon \cdot \boldsymbol{\Gamma}\Delta \mathbf{u}^\varepsilon \leq \int_\Omega \Phi^\varepsilon(\mathbf{u}_0) - \int_{\Omega_t} \nabla \mathbf{u}^\varepsilon \cdot \mathbf{A}\nabla \mathbf{u}^\varepsilon .$$

Since the Φ^ε are on Q^N bounded by a constant which does not depend on ε the first term on the right-hand side is bounded. The second term is quadratic in $\nabla \mathbf{u}^\varepsilon$ and is therefore bounded by estimate (1). Hence we have proved (2).

It remains to prove (3). Since $|l_i(w)| \leq C_1 w$ for all $w \in \mathbb{R}^+$ we get for all $z < 0$

$$\begin{aligned}
\phi_i^\varepsilon(z) &= \int_z^1 \int_v^1 \frac{1}{l_i^\varepsilon(w)} \,\mathrm{d}w \,\mathrm{d}v \geq \int_z^\varepsilon \int_v^\varepsilon \frac{1}{l_i(\varepsilon)} \,\mathrm{d}w \,\mathrm{d}v \\
&\geq \int_z^\varepsilon \int_v^\varepsilon \frac{1}{C_1\varepsilon} \,\mathrm{d}w \,\mathrm{d}v = \frac{1}{2C_1\varepsilon}(\varepsilon - z)^2 \geq \frac{1}{2C_1\varepsilon} z^2 .
\end{aligned}$$

Hence the estimate on Φ^ε implies (3). Therefore, the proof of Lemma 10 is complete. □

Remark 11. In the case $l_i(u_i) = u_i$ we get for $u \in Q^N$ that

$$\Phi^0(\mathbf{u}) := \lim_{\varepsilon \to 0} \Phi^\varepsilon(\mathbf{u}) = \sum_{i=1}^{N} u_i \ln u_i + \text{const},$$

which is up to a constant the logarithmic part of the free energy. Therefore, the estimate (2) can be seen as an estimate for the logarithmic part of the free energy.

Now we are in a position to prove Theorem A. By well-known compactness arguments (see [13]) we can subtract a subsequence of $\{\mathbf{u}^\varepsilon\}_{\varepsilon>0}$ which converges to a limit $\mathbf{u}$ almost everywhere in Ω_T as $\varepsilon \to 0$. Furthermore, the subsequence can be chosen such that the following convergence properties hold:

$$\begin{aligned}
&\mathbf{u}^\varepsilon \longrightarrow \mathbf{u} && \text{strongly in} && L^2(0,T; H^1(\Omega, \mathbb{R}^N)),\\
&\Delta\mathbf{u}^\varepsilon \longrightarrow \Delta\mathbf{u} && \text{weakly in} && L^2(\Omega_T, \mathbb{R}^N),\\
&\partial_t\mathbf{u}^\varepsilon \longrightarrow \partial_t\mathbf{u} && \text{weakly in} && L^2(0,T; (H^1(\Omega, \mathbb{R}^N))'),\\
&\vec{\mathbf{J}}^\varepsilon \longrightarrow \vec{\mathbf{J}} && \text{weakly in} && L^2(\Omega_T, \mathbb{R}^{Nn}).
\end{aligned}$$

Furthermore, estimate (3) in Lemma 10 together with the fact that $\sum_{i=1}^N u_i^\varepsilon = 1$ for all $\varepsilon \in (0, \varepsilon_0]$ gives in the limit that $\mathbf{u} \in Q^N$ almost everywhere in Ω_T. It remains to pass to the limit in the equations

$$\partial_t \mathbf{u}^\varepsilon = -\nabla \cdot \vec{\mathbf{J}}^\varepsilon, \tag{3.2}$$

$$\vec{\mathbf{J}}^\varepsilon = -\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\nabla(-\boldsymbol{\Gamma}\Delta\mathbf{u}^\varepsilon + D\Psi^\varepsilon(\mathbf{u}^\varepsilon)) \,. \tag{3.3}$$

Since Eqs. (3.2) is linear, passing to the limit in this equation follows from the weak convergence of $\partial_t\mathbf{u}^\varepsilon$ and $\vec{\mathbf{J}}^\varepsilon$.

The more difficult part is to pass to the limit in (3.3). First we show how to pass to the limit in the highest-order term. Therefore, we choose a test function $\vec{\eta}$ as in the formulation of Theorem A. We get

$$\begin{aligned}
&\int_{\Omega_T} \boldsymbol{\Gamma}\Delta\mathbf{u}^\varepsilon \cdot (\nabla \cdot (\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\vec{\eta}))\\
&\quad = \int_{\Omega_T} \sum_{i=1}^{N} \left(\sum_{k=1}^{N} \Gamma_{ik}\Delta u_k^\varepsilon \right) \left(\sum_{j=1}^{N} L_{ij}^\varepsilon(\mathbf{u}^\varepsilon)\nabla \cdot \vec{\eta}_j + \sum_{j=1}^{N} \nabla(L_{ij}^\varepsilon(\mathbf{u}^\varepsilon)) \cdot \vec{\eta}_j \right)\\
&\quad = \int_{\Omega_T} \sum_{i,j,k=1}^{N} \Gamma_{ik}\Delta u_k^\varepsilon [L_{ij}^\varepsilon(\mathbf{u}^\varepsilon)\nabla \cdot \vec{\eta}_j + \nabla(L_{ij}^\varepsilon(\mathbf{u}^\varepsilon)) \cdot \vec{\eta}_j].
\end{aligned}$$

Since Δu_k^ε converges weakly in $L^2(\Omega_T)$, $\mathbf{u}^\varepsilon$ converges pointwise everywhere and L_{ij}^ε converges uniformly it is enough to show

$$\nabla L_{ij}^\varepsilon(\mathbf{u}^\varepsilon) \longrightarrow \nabla L_{ij}(\mathbf{u}) \quad \text{in } L^2(\Omega_T) \,. \tag{3.4}$$

A closer examination of this term gives

$$\begin{aligned}
\nabla L_{ij}^\varepsilon(\mathbf{u}) &= \nabla \left[l_i^\varepsilon(u_i^\varepsilon) \left(\delta_{ij} - \left(\sum_{k=1}^{N} l_k^\varepsilon(u_k^\varepsilon) \right)^{-1} l_j^\varepsilon(u_j^\varepsilon) \right) \right]\\
&= \nabla(l_i^\varepsilon(u_i^\varepsilon)) \left(\delta_{ij} - \left(\sum_{k=1}^{N} l_k^\varepsilon(u_k^\varepsilon) \right)^{-1} l_j^\varepsilon(u_j^\varepsilon) \right)
\end{aligned}$$

$$+ l_i^\varepsilon(u_i^\varepsilon)\left(-\left(\sum_{k=1}^N l_k^\varepsilon(u_k^\varepsilon)\right)^{-1}\nabla l_j^\varepsilon(u_j^\varepsilon) + l_j^\varepsilon(u_j^\varepsilon)\left(\sum_{k=1}^N l_k^\varepsilon(u_k^\varepsilon)\right)^{-2}\sum_{k=1}^N \nabla l_k^\varepsilon(u_k^\varepsilon)\right).$$

The facts that $u_i^\varepsilon \to u_i$ converges pointwise everywhere and that $l_i^\varepsilon \to l_i$ converges uniformly imply that $l_i^\varepsilon(u_i^\varepsilon)$ converges to $l_i(u_i)$ pointwise almost everywhere. Therefore, it is enough to show that

$$\nabla l_i^\varepsilon(u_i^\varepsilon) \to \nabla l_i(u_i) \quad \text{in } L^2(\Omega_T).$$

In order to show this we calculate

$$\int_{\Omega_T} |\nabla l_i^\varepsilon(u_i^\varepsilon) - \nabla l_i(u_i)|^2 = \int_{\Omega_T\cap\{u_i>0\}} |(l_i^\varepsilon)'(u_i^\varepsilon)\nabla u_i^\varepsilon - (l_i)'(u_i)\nabla u_i|^2 + \int_{\Omega_T\cap\{u_i=0\}} |(l_i^\varepsilon)'(u_i^\varepsilon)\nabla u_i^\varepsilon - (l_i)'(u_i)\nabla u_i|^2 = \mathrm{I} + \mathrm{II}. \tag{3.5}$$

On $\{u_i > 0\}$ we have $(l_i^\varepsilon)'(u_i^\varepsilon)\nabla u_i^\varepsilon \longrightarrow (l_i)'(u_i)\nabla u_i$ almost everywhere. Using the fact that $\nabla u_i^\varepsilon \to \nabla u_i$ in $L^2(\Omega_T)$ we can apply the generalized dominated convergence theorem of Lebesgue to conclude that the term I in (3.5) converges to zero. In addition we use the fact that $\nabla u_i = 0$ on $\{u_i = 0\}$ almost everywhere to compute

$$\int_{\Omega_T\cap\{u_i=0\}} |(l_i^\varepsilon)'(u_i^\varepsilon)\nabla u_i^\varepsilon - (l_i)'(u_i)\nabla u_i|^2 = \int_{\Omega_T\cap\{u_i=0\}} |(l_i^\varepsilon)'(u_i^\varepsilon)\nabla u_i^\varepsilon|^2 \le C\int_{\Omega_T\cap\{u_i=0\}} |\nabla u_i^\varepsilon|^2 \longrightarrow C\int_{\Omega_T\cap\{u_i=0\}} |\nabla u_i|^2 = 0.$$

This proves (3.4) and therefore the convergence of the highest-order term.

It remains to pass to the limit in the term containing the homogeneous free energy. Therefore, we have to show

$$\int_{\Omega_T} ((\mathbf{L}^\varepsilon D^2\Psi^\varepsilon)(\mathbf{u}^\varepsilon)\nabla\mathbf{u}^\varepsilon)\cdot\vec{\eta} \longrightarrow \int_{\Omega_T} ((\mathbf{L}D^2\Psi)(\mathbf{u})\nabla\mathbf{u})\cdot\vec{\eta}. \tag{3.6}$$

Since $\nabla\mathbf{u}^\varepsilon \longrightarrow \nabla\mathbf{u}$ in the strong topology of $L^2(\Omega_T, \mathbb{R}^N)$ it remains to show that $\left(\mathbf{L}^\varepsilon D^2\Psi^\varepsilon\right)(\mathbf{u}^\varepsilon)$ converges almost everywhere. Noting that $\mathbf{L}^\varepsilon$ converges to $\mathbf{L}$ uniformly the convergence of $(\mathbf{L}^\varepsilon\mathbf{A})(\mathbf{u}^\varepsilon)$ follows from the pointwise convergence of $\mathbf{u}^\varepsilon$. The difficult part is to show convergence of

$$\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\,\mathrm{diag}(\alpha_1(\psi^\varepsilon)''(u_1^\varepsilon), \ldots, \alpha_N(\psi^\varepsilon)''(u_N^\varepsilon)).$$

Therefore, we show: *For all $i, j = 1, \ldots, N$ we have*

$$\left(\sum_{k=1}^N l_k^\varepsilon(u_k^\varepsilon)\right)^{-1}(l_i(\psi^\varepsilon)'')(u_i^\varepsilon) \longrightarrow \left(\sum_{k=1}^N l_k(u_k)\right)^{-1}(l_i\psi'')(u_i)$$

as $\varepsilon \to 0$ almost everywhere in Ω_T.

Above and in the following we use the notation $\psi(r) = r\ln r$ for all $r \in \mathbb{R}^+$. Since $l_k^\varepsilon(\cdot)$ converges to $l_k(\cdot)$ uniformly the convergence of the term $(\sum_{k=1}^N l_k^\varepsilon(u_k^\varepsilon))^{-1} l_j^\varepsilon(u_j^\varepsilon)$ is obvious. We are left to show

$$(l_i^\varepsilon(\psi^\varepsilon)'')(u_i^\varepsilon) \longrightarrow (l_i\psi'')(u_i) \quad \text{almost everywhere.}$$

For (t, x) with $u_i(t, x) > 0$ this convergence follows from the fact that $l_i^\varepsilon(z) = l_i(z)$ and $\psi^\varepsilon(z) = \psi(z)$ for $z \ge \varepsilon$.

Now we consider points (t, x) with $\lim_{\varepsilon\to 0} u_i^\varepsilon(t,x) = 0$. For subsequences $\{\varepsilon_k\}_{k\in\mathbb{N}}$ such that $\varepsilon_k \to 0$ and $u_i^{\varepsilon_k}(t,x) \geq \varepsilon_k$ we have

$$(l_i^{\varepsilon_k}(\psi^{\varepsilon_k})'')(u_i^{\varepsilon_k}) = (l_i\psi'')(u_i^{\varepsilon_k}) \to (l_i\psi'')(0)$$

as ε_k tends to zero. Besides that for subsequences $\{\varepsilon_k\}_{k\in\mathbb{N}}$ with $\varepsilon_k \to 0$ and $u_i^{\varepsilon_k}(t,x) \leq \varepsilon_k$ we have

$$(l_i^{\varepsilon_k}(\psi^{\varepsilon_k})'')(u_i^{\varepsilon_k}) = (l_i\psi'')(\varepsilon_k) \to (l_i\psi'')(0)$$

as ε_k tends to zero. In both cases we define $(l_i\psi'')(0) := \lim_{z\searrow 0}(l_i\psi'')(z)$. Since $\psi''(z) = \frac{1}{z}$ and $l_i \in C^1([0,1])$ we get $(l_i\psi'')(0) = l_i'(0)$.

We remark that the term $(\mathbf{L}D^2\Psi)(\mathbf{u})$ on the boundary of Q^N has to be interpreted as above, i.e. the term is defined as the limit from the interior of Q^N. To be precise let us derive the term which we get from the logarithmic part of Ψ:

$$(\mathbf{L}\,\mathrm{diag}(\alpha_1\psi'',\ldots,\alpha_N\psi''))(\mathbf{u}) = \left(\mathbf{Id} - \left(\sum_{k=1}^N l_k(u_k)\right)^{-1}\mathbf{l}(\mathbf{u})\mathbf{e}^{\mathrm{t}}\right)\mathrm{diag}\left(\alpha_1\frac{l_1(u_1)}{u_1},\ldots,\alpha_N\frac{l_N(u_N)}{u_N}\right)$$

with $\mathbf{l}(\mathbf{u}) = (l_1(u_1),\ldots,l_N(u_N))^{\mathrm{t}}$ and $l_i(u_i)/u_i := l_i'(0)$ if $u_i = 0$. Since we proved convergence almost everywhere for all entries of the matrix

$$\mathbf{L}^\varepsilon(\mathbf{u}^\varepsilon)\,\mathrm{diag}((\alpha_1\psi^\varepsilon)''(u_1^\varepsilon),\ldots,(\alpha_N\psi^\varepsilon)''(u_N^\varepsilon))$$

we can apply the generalized dominated convergence theorem of Lebesgue to conclude

$$\int_{\Omega_T}((\mathbf{L}^\varepsilon D^2\Psi^\varepsilon)(\mathbf{u}^\varepsilon)\nabla\mathbf{u}^\varepsilon)\cdot\vec{\eta} \longrightarrow \int_{\Omega_T}((\mathbf{L}D^2\Psi)(\mathbf{u})\nabla\mathbf{u})\cdot\vec{\eta}$$

for all test functions $\vec{\eta}$ which fulfill the requirements of Theorem A.

This completes the proof of Theorem A. □

4. Conclusions

We derived a model for phase separation in multicomponent systems which takes a concentration dependence of the mobility matrix into account. This is physically reasonable because in many applications the mobility in the pure components is much smaller than in the interfacial regions.

In this paper we study mobility matrices which are generalizations of a mobility matrix introduced by Ziya Akcasu and Tombakoglu [28]. We show that these mobilities degenerate only on the boundary of the Gibbs simplex. The main part of the paper is dedicated to the proof of an existence theorem for the resulting fourth-order degenerate parabolic system. Existence of a solution is shown by approximation with nondegenerate problems.

Uniqueness of solutions is still an open problem. To our best knowledge there is no proof of uniqueness for fourth-order degenerate parabolic equations. Beretta et al. [2] gave examples of nonuniqueness for the initial boundary value problem for the equation $h_t + (h^n h_{xxx})_x = 0$ $(0 < n < 3)$. But due to the applications they had in mind they used a weaker notion of a solution than we did. In particular they did not require $h \in L^2(0,T;H^2(\Omega))$. Therefore, there is still some hope that there is only one solution which fulfills the requirements of Theorem A.

We want to point out that other homogeneous free energies are possible. For example a polynomial which generalizes the quartic double well potential $W(c) = c^2(1-c)^2$ to the case of multicomponent systems. With some

minor modifications our theory is applicable in this case as well. Finally it is possible to pass to the limit $\theta \searrow 0$ to get the deep quench limit (see [13,14]). In our paper [13] we showed how to pass to the limit $\theta \searrow 0$ in the binary case and since the alterations are straightforward we do not carry out the proof for the multicomponent case.

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