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Upscaled phase-field models for interfacial dynamics in strongly heterogeneous domains

By Markus Schmuck[1,2,*], Marc Pradas[1], Grigorios A. Pavliotis[2,3] and Serafim Kalliadasis[1]

[1] *Department of Chemical Engineering, and* [2] *Department of Mathematics, Imperial College London, South Kensington Campus, SW7 2AZ London, UK*
[3] *CERMICS, École Nationale des Ponts et Chaussées, 6 and 8 Avenue Blaise Pascal, 77455 Marne La Vallée Cedex 2, France*

We derive a new, effective macroscopic Cahn–Hilliard equation whose homogeneous free energy is represented by fourth-order polynomials, which form the frequently applied double-well potential. This upscaling is done for perforated/strongly heterogeneous domains. To the best knowledge of the authors, this seems to be the first attempt of upscaling the Cahn–Hilliard equation in such domains. The new homogenized equation should have a broad range of applicability owing to the well-known versatility of phase-field models. The additionally introduced feature of systematically and reliably accounting for confined geometries by homogenization allows for new modelling and numerical perspectives in both science and engineering. Our results are applied to wetting dynamics in porous media and to a single channel with strongly heterogeneous walls.

Keywords: phase-field models; Cahn–Hilliard equation; multi-scale modelling; homogenization; porous media; wetting

1. Introduction

Consider the abstract energy density

$$e(\phi) := F(\phi) + \frac{\lambda^2}{2}|\nabla\phi|^2, \tag{1.1}$$

where ϕ is a conserved density that plays the role of an order parameter by taking appropriate equilibrium limiting values that represent different phases. The gradient term $\lambda^2|\nabla\phi|^2$ penalizes the interfacial area between these phases, and the bulk free energy F is defined as the polynomial

$$F(\phi) := \int_0^\phi f(s)\mathrm{d}s \quad \text{and} \quad f(s) := a_3 s^3 + a_2 s^2 + a_1 s. \tag{1.2}$$

In the Ginzburg–Landau/Cahn–Hilliard formulation, the total energy is defined by $E(\phi) := \int_\Omega e(\phi)\mathrm{d}\mathbf{x}$ with density (1.1) on a bounded $C^{1,1}$-domain $\Omega \subset \mathbb{R}^d$ with $1 \le d \le 3$ denoting the spatial dimension. In general, the local minima of F

*Author for correspondence (m.schmuck@imperial.ac.uk).

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correspond to the equilibrium limiting values of ϕ representing different phases separated by a diffuse interface whose spatial extension is governed by the gradient term.

It is well accepted that thermodynamic equilibrium can be achieved by minimizing the free energy E, here supplemented by a possible boundary contribution $\int_{\partial\Omega} g(\mathbf{x})\mathrm{d}o(\mathbf{x})$ for $g(\mathbf{x}) \in H^{3/2}(\partial\Omega)$, with respect to its gradient flow over the domain Ω, i.e.

$$\text{(homogeneous case)}\left\{\begin{array}{ll}\dfrac{\partial}{\partial t}\phi = \mathrm{div}(\hat{\mathrm{M}}\nabla(f(\phi) - \lambda^2\Delta\phi)) & \text{in } \Omega_T,\\ \nabla_n\phi := \mathbf{n}\cdot\nabla\phi = g(\mathbf{x}) & \text{on } \partial\Omega_T,\\ \nabla_n\Delta\phi = 0 & \text{on } \partial\Omega_T,\end{array}\right\} \tag{1.3}$$

where $\Omega_T := \Omega\times]0,T[$, $\partial\Omega_T := \partial\Omega\times]0,T[$, ϕ satisfies the initial condition $\phi(\mathbf{x},0) = \psi(\mathbf{x})$, and $\hat{\mathrm{M}} = \{\mathrm{m}_{ij}\}_{1\le i,j\le d}$ denotes a mobility tensor with real and bounded elements $\mathrm{m}_{ij} > 0$. Equation (1.3) is the gradient flow with respect to the H^{-1}-norm, here weighted by the mobility tensor $\hat{\mathrm{M}}$, and is referred to as the Cahn–Hilliard equation. This equation is a model prototype for interfacial dynamics (Fife 1991) and phase transformation (Cahn & Hilliard 1958) under homogeneous Neumann boundary conditions, i.e. $g = 0$, and a free energy F representing the phenomenological standard double-well potential $F(s) = \frac{1}{4}(s^2-1)^2$. The polynomial $f = F'$, defined in (1.2), encloses a set of free energies that allow for the same steps in the rigorous homogenization process leading to the main result of this paper, theorem 3.3. We emphasize that F represents a bulk free energy that is well accepted because it allows for stable numerics and captures phenomenologically the features of systematically derived free energies such as the regular solution model (Cahn & Hilliard 1958) based on the free energy of mixing, i.e.

$$f(\phi) = kT(\phi\ln\phi + (1-\phi)\ln(1-\phi)) + a\phi(1-\phi). \tag{1.4}$$

The mean free energy (1.4) can be derived by a thermodynamic limit from lattice gas models of filled and empty sites, for instance. Unfortunately, the energy (1.1) cannot be reduced to the atomistic Lennard-Jones potential. But (1.1) is related to the Lennard-Jones potential in the sense of the Lebowitz, Mazel and Presutti (LMP) theory (Presutti 2009). It is well known that formally, the energy (1.1) dissipates along solutions of the gradient flow (1.3), i.e. $E(\phi(\cdot,t)) \le E(\phi(\cdot,0)) =: E_0$. This follows immediately after differentiating (1.1) with respect to time and using (1.3) for $g = 0$.

Here, we study the energy density (1.1) with respect to a perforated domain $\Omega^\epsilon \subset \mathbb{R}^d$ instead of a homogeneous $\Omega \subset \mathbb{R}^d$. The dimensionless variable $\epsilon > 0$ defines the heterogeneity $\epsilon = \ell/L$, where ℓ represents the characteristic pore size and L is the characteristic length of the porous medium (figure 1). Hence, the porous medium is characterized by a reference cell $Y := [0,\ell_1]\times[0,\ell_2]\times\cdots\times[0,\ell_d]$, which represents a single, characteristic pore. For simplicity, we set $\ell_1 = \ell_2 = \cdots = \ell_d = 1$. A well-accepted approximation is then the periodic covering of the macroscopic porous medium by such a single reference cell ϵY

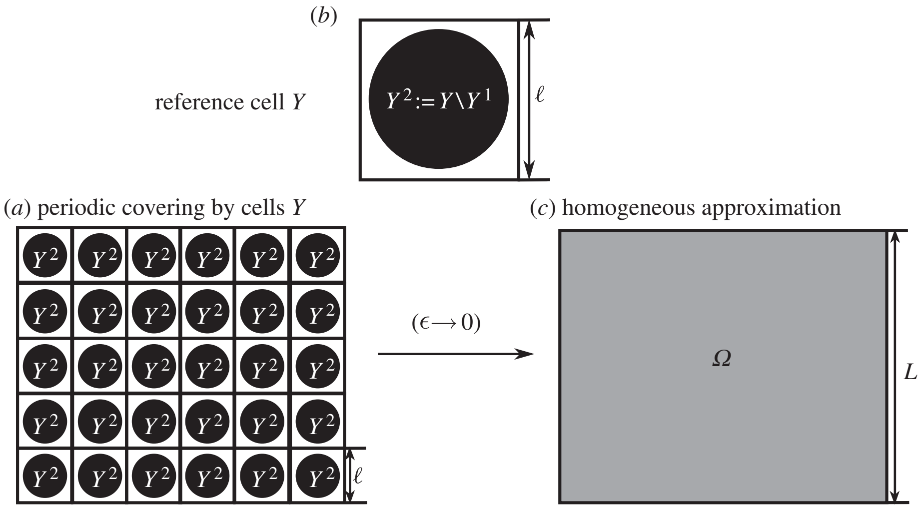

Figure 1. (a) Strongly heterogeneous/perforated material as a periodic covering of reference cells $Y := [0, \ell]^d$. (b) Definition of the reference cell $Y = Y^1 \cup Y^2$ with $\ell = 1$. (c) The 'homogenization limit' $\epsilon := \ell/L \to 0$ scales the perforated domain such that perforations become invisible in the macroscale.

(figure 1). The pore and the solid phase of the medium are denoted by Ω^ϵ and B^ϵ, respectively. These sets are defined by

$$\Omega^\epsilon := \bigcup_{\mathbf{z}\in\mathbb{Z}^d} \epsilon(Y^1 + \mathbf{z}) \cap \Omega \quad \text{and} \quad B^\epsilon := \bigcup_{\mathbf{z}\in\mathbb{Z}^d} \epsilon(Y^2 + \mathbf{z}) \cap \Omega = \Omega \setminus \Omega^\epsilon, \tag{1.5}$$

where the subsets Y^1, $Y^2 \subset Y$ are defined such that Ω^ϵ is a connected set. More precisely, Y^1 stands for the pore phase (e.g. liquid or gas phase in wetting problems; figure 1).

These definitions allow us to reformulate (1.3) by the following microscopic porous media problem:

$$\text{(microporous case)} \left\{ \begin{array}{ll} \partial_t \phi_\epsilon = \operatorname{div}(\hat{\mathrm{M}} \nabla(-\lambda^2 \Delta\phi_\epsilon + f(\phi_\epsilon))) & \text{in } \Omega^\epsilon_T, \\ \nabla_n \phi_\epsilon := \mathbf{n}\cdot\nabla\phi_\epsilon = 0 & \text{on } \partial\Omega^\epsilon_T, \\ \nabla_n \Delta\phi_\epsilon = 0 & \text{on } \partial\Omega^\epsilon_T, \\ \phi_\epsilon(\mathbf{x}, 0) = \psi(\mathbf{x}) & \text{on } \Omega^\epsilon. \end{array} \right\} \tag{1.6}$$

In the next section, we motivate our main goal of deriving a homogenized upscaled problem by passing to the limit $\epsilon \to 0$ in (1.6).

(a) *Physical motivation*

There is a large amount of literature available on multi-phase flows through porous media: e.g. the review by Sahimi (1993) on fluid flow in reservoir rocks and references therein; the experimental works on viscous fluid imbibition processes in a Hele–Shaw cell by Rubio *et al.* (1989), Hernández-Machado *et al.* (2001), Geromichalos *et al.* (2002) and Planet *et al.* (2007); or the study of fluid flow in sheets of paper in Balankin *et al.* (2003), to name a few. A physically complex problem of vapour sorption and desorption from nanoporous solids was studied by Bazant & Bazant (2011). Adler & Brenner (1988) provided a comprehensive review of the field of multi-phase flows and they outline in detail some of its fundamental concepts, such as volume averaging and extending Darcy's law towards two-phase flows, both of which are used often. Notably, the volume-averaging method requires a fictitious length scale defining the test volumes. These volumes cannot be chosen to be the characteristic pore scale as in homogenization theory in order to comply with the ergodic hypothesis required by the method. The review also addresses the frequently questioned approach of using phenomenological relative permeabilities (Muskat & Meres 1936).

Recently, Papatzacos (2002, 2010) applied a special type of volume averaging, Marle's averaging technique (Marle 1982), to a coupled system consisting of the continuity equation, a momentum and an energy balance. The effective model then turns via Darcy's law into a Cahn–Hilliard-type equation for a phenomenologically motivated transport parameter. This thermodynamic derivation of an effective macroscopic Cahn–Hilliard equation for mass transport starting from a microscopic continuity equation clearly demonstrates the relevance of phase-field type approaches in heterogeneous structures. In fact, the use of the Cahn–Hilliard equation to describe macroscopic fluid flows in porous media has received a lot of attention over the last few years. It has been shown that such a phase-field model adapted to imbibition reduces to Darcy's law in the sharp interface limit, i.e. when $\lambda \to 0$ (Alava *et al.* 2004). Therefore, it is an ideal candidate, particularly for numerical modelling, to study, for example, the statistical and dynamical properties of the kinetic roughening process that the interface undergoes as the liquid invades the porous medium (Dubé *et al.* 1999; Hernández-Machado *et al.* 2001; Laurila *et al.* 2005; Pradas & Hernández-Machado 2006).

However, up to now, no effective macroscopic equations have been derived for any microscopic porous media formulation (1.6). It should be noted that understanding rationally and systematically how microscopic details affect global macroscopic properties is a crucial point in a wide spectrum of multi-phase flow applications, from traditional ones, such as oil recovery, to more recent ones, such as micro- and nano-fluidics. The present study aims to address this issue and, at the same time, exemplify its physical relevance for the field of multi-phase flows by using as a paradigm the problem of wetting in heterogeneous domains such as imbibition. As far as the Cahn–Hilliard equation is concerned, it has a long history and enjoys a broad range of applicability, as discussed later. This is a major motivation for the first homogenization result derived here in the context of perforated or strongly heterogeneous domains. Moreover, the upscaled problem should allow for efficient and systematic low-dimensional computations in applications.

(*b*) *On the broad applicability of the Cahn–Hilliard equation*

As noted already, the Cahn–Hilliard equation has a wide applicability. The phase-field equation (1.3) was first introduced by Cahn & Hilliard (1958), where they suggested a free-energy formulation for non-uniform systems. Alternatively, Cahn–Hilliard-type equations can be obtained by square-gradient approximations to non-local free-energy functionals like those used in the statistical mechanics of non-homogeneous fluids (Miranville 2003; Pereira & Kalliadasis 2012). Since the work of Cahn and Hilliard, this formalism has become a fundamental modelling tool in both science and engineering. Cahn–Hilliard or more generally phase-field energy functionals are for example applied in image processing such as inpainting (Bertozzi *et al.* 2007). Wetting phenomena, of great interest in technological applications, especially motivated by recent developments in micro-fluidics, enjoy a wide-spread use of phase-field modelling (Pomeau 2001; Laurila *et al.* 2008; Queralt-Martin *et al.* 2011). Such phenomena have some intriguing features, including the appearance of hysteresis and non-locality, e.g. correlations between the contact line dynamics at each surface plate of a micro-channel (Wylock *et al.* 2012). Additional complexities in wetting include the presence of an electric field (electrowetting, e.g. Eck *et al.* (2009)). There are numerous other applications where phase-field models provide a powerful modelling tool. For example, in Lowengrub *et al.* (2009), a phase-field model is proposed to describe the dynamics of vesicles and associated phenomena, such as spinodal decomposition, coarsening, budding and fission. In this study, in addition to the Cahn–Hilliard equation, an Allen–Cahn equation (L^2-gradient flow of $E(\phi)$) is employed.

Clearly, there is a large amount of literature on phase-field/Cahn–Hilliard models on a wide variety of physical settings and applications, which cannot be fully reviewed here. That said, it is important to emphasize that the key to the versatility of phase-field/Cahn–Hilliard formulations is precisely the fact that many physical settings are characterized by simple energies of the form (1.1).

In §2, we introduce two relevant formulations of the Cahn–Hilliard equation. The main theorem, which states the new macroscopic Cahn–Hilliard equation, is given in §3, where we also provide the local equilibrium condition required for homogenization. In §4, we demonstrate the applicability of the new effective equation in the context of wetting and are able to connect it to physically suggested models in imbibition. Conclusions and suggestions for further work are presented in §5.

2. Two reformulations of the Cahn–Hilliard equation: zero mass and splitting

We present two equivalent formulations of the Cahn–Hilliard equation. The first helps to achieve solvability for Lipschitz inhomogeneities and the second, referred to as ‘splitting formulation’, decouples the Cahn–Hilliard equation into two second-order problems for a feasible upscaling by the multiple-scale method.

(*a*) *Zero mass formulation* (*for well-posedness*)

Novick-Cohen (1990) proves well-posedness of the Cahn–Hilliard problem (1.3) rewritten for $\Omega_T := \Omega\times]0,T[$ and $\partial\Omega_T := \partial\Omega\times]0,T[$ in the following zero mass formulation:

$$\text{(zero mass)}\left\{\begin{array}{ll}\partial_t v = \operatorname{div}(\hat{\mathrm{M}}\nabla(bv + h(v) - \lambda^2\Delta v)) & \text{in } \Omega_T,\\ \nabla_n v = \mathbf{n}\cdot\nabla\Delta v = 0 & \text{on } \partial\Omega_T,\\ v(\mathbf{x},0) = v_0(\mathbf{x}) = \psi(\mathbf{x}) - \bar{\phi} & \text{in } \Omega,\end{array}\right\} \tag{2.1}$$

where $v(\mathbf{x},t) := \phi(\mathbf{x},t) - \bar{\phi}$, $b := f'(\phi)$, $h(v) := f(\bar{\phi}+v) - bv$, and by mass conservation of (1.3), we define $(1/|\Omega|)\int_\Omega \phi\,\mathrm{d}\mathbf{x} := (1/|\Omega|)\int_\Omega \psi\,\mathrm{d}\mathbf{x} =: \bar{\phi}$. These definitions imply $bv + h(v) = f(\bar{\phi}+v)$. For $k \geq 0$, we introduce the family of spaces

$$H_E^k(\Omega) = \{\phi \in H^k(\Omega) | \nabla_n \phi = 0 \text{ and } \bar{\phi} = 0\}. \tag{2.2}$$

Novick-Cohen (1990) verifies local existence and uniqueness of solutions $v \in H_E^2(\Omega)$ of problem (2.1) for $f \in C^2_{Lip}(\mathbb{R})$ with $|f(s)| \to \infty$ as $s \to \pm\infty$ and $v(\mathbf{x},0) \in H_E^2(\Omega)$. Moreover, in Novick-Cohen (1990), one also finds necessary conditions on h leading to global existence.

(b) *Splitting (for homogenization)*

The existence result summarized in §2*a* enables us to give the following weak formulation of problem (1.3). There exists for all $\varphi \in H_E^2(\Omega)$ a weak solution $v \in H_E^2(\Omega)$ solving the equation

$$\frac{\mathrm{d}}{\mathrm{d}t}(v,\varphi) + \lambda^2(\Delta v, \mathrm{div}(\hat{\mathrm{M}}\nabla\varphi)) = (\mathrm{div}(\hat{\mathrm{M}}\nabla f(\bar{\phi}+v)), \varphi). \tag{2.3}$$

By identifying $v = (-\Delta)^{-1}w$ in the $H_E^2(\Omega)$-sense, together with solvability of equation (2.3), we are able to introduce the following problem:

$$\text{(splitting)}\ \left\{\begin{array}{ll} \partial_t(-\Delta)^{-1}w - \lambda^2\mathrm{div}(\hat{\mathrm{M}}\nabla w) = \mathrm{div}(\hat{\mathrm{M}}\nabla f(\bar{\phi}+v)) & \text{in } \Omega_T, \\ \nabla_n w = -\nabla_n \Delta v = 0 & \text{on } \partial\Omega_T, \\ -\Delta v = w & \text{in } \Omega_T, \\ \nabla_n v = g(\mathbf{x}) & \text{on } \partial\Omega_T, \\ v(\mathbf{x},0) = \psi(\mathbf{x}) - \bar{\phi} & \text{in } \Omega, \end{array}\right\} \tag{2.4}$$

which is equivalent to (1.3) in the H_E^2-sense and hence, when $g = 0$, is well-posed too (Novick-Cohen 1990). The advantage of (2.4) is that it allows us to base our upscaling approach on well-known results from elliptic/parabolic homogenization theory (Bensoussans *et al.* 1978; Zhikov *et al.* 1994; Pavliotis & Stuart 2008). Finally, we remark that the splitting (2.4) slightly differs from the strategy applied for computational purposes in Barrett & Blowey (1999), for instance.

3. Main results

Before we state our main result, the subsequent homogenization of the Cahn–Hilliard equation requires the assumption of local thermodynamic equilibrium.

Definition 3.1 (Local equilibrium). *We say that the phase field ϕ is in local thermodynamic equilibrium, if and only if*

$$\frac{\delta E(\phi)}{\delta\phi} = \mu(\phi) = f(\phi) - \lambda^2\Delta\phi = \text{const.}, \tag{3.1}$$

for each $\mathbf{x}/\epsilon = \mathbf{y}$ element of the same reference cell Y. μ stands for the chemical potential, which is only allowed to vary over the different reference cells.

The state of general conditions of equilibrium of heterogeneous substances seems to go back to the celebrated work of Gibbs (1876). The assumption of local thermodynamic equilibrium can be justified on physical and mathematical grounds by the assumed separation of macroscopic (size of the porous medium) and microscopic (characteristic pore size) length scales and the emerging difference in the associated characteristic time scales. This kind of equilibrium assumptions are widely applied to a variety of physical situations such as diffusion (Nelson & Auerbach 1999), macroscale thermodynamics in porous media (Bennethum *et al.* 1999) and ionic transport in porous media based on dilute solution theory (Schmuck 2012; Schmuck & Bazant 2012; Schmuck & Berg 2012), for instance. Local equilibrium assumptions as in definition 3.1 emerge as key requirements for the mathematical well-posedness of arising cell problems that define effective transport coefficients in homogenized, nonlinear (and coupled) problems.

The homogeneous free energy F in (1.2) enables upscaling under the following.

Assumption 3.2. *Assume that the homogeneous free energy F satisfies for real parameters $\alpha_2 > \alpha_1 > 0$, which define F as a double-well potential by $F(s) = (s-\alpha_1)^2(s-\alpha_2)^2$, such that*

$$25(\alpha_1+\alpha_2)^2 - 20(\alpha_1^2+\alpha_2^2+3\alpha_1\alpha_2) > \frac{(\alpha_1+\alpha_2)^2}{4}. \tag{3.2}$$

These considerations allow us to state the following main result of this study.

Theorem 3.3 (Upscaled Cahn–Hilliard equations). *Let $\hat{\mathrm{M}} = \{\mathrm{m}\delta_{ij}\}_{1\le i,j\le d}$ for $\mathrm{m} > 0$. We assume that the local equilibrium condition (3.1) is satisfied. Moreover, suppose that $\psi(\mathbf{x}) \in H^2_E(\Omega)$ and let F satisfy assumption 3.2. Then, the microscopic porous media formulation (1.6) can be effectively approximated by the following macroscopic problem:*

$$\left.\begin{aligned}
\theta_1\frac{\partial\phi_0}{\partial t} &= \operatorname{div}\left(\left[\theta_1 f'(\phi_0)\hat{\mathrm{M}} - \left(2\frac{f(\phi_0)}{\phi_0} - f'(\phi_0)\right)\hat{\mathrm{M}}_v\right]\nabla\phi_0\right)\\
&\qquad - f'(\phi_0)\operatorname{div}(\hat{\mathrm{M}}_v\nabla\phi_0) + \frac{\lambda^2}{\theta_1}\operatorname{div}(\hat{\mathrm{M}}_{\mathrm{w}}\nabla(\operatorname{div}(\hat{\mathrm{D}}\nabla\phi_0))) \quad \text{in } \Omega_T,\\
\nabla_n\phi_0 &= \mathbf{n}\cdot\nabla\phi_0 = 0 \quad \text{on } \partial\Omega_T,\\
\nabla_n\Delta\phi_0 &= 0 \quad \text{on } \partial\Omega_T\\
\text{and}\quad \phi_0(\mathbf{x},0) &= \psi(\mathbf{x}) \quad \text{in } \Omega,
\end{aligned}\right\} \tag{3.3}$$

where $\theta_1 := |Y^1|/|Y|$ *is the porosity, and the porous media correction tensors* $\hat{\mathrm{D}} := \{\mathrm{d}_{ik}\}_{1\le i,k\le d}$, $\hat{\mathrm{M}}_v = \{\mathrm{m}^v_{ik}\}_{1\le i,k\le d}$ *and* $\hat{\mathrm{M}}_w = \{\mathrm{m}^w_{ik}(\mathbf{x})\}_{1\le i,k\le d}$ *are defined by*

$$\left.\begin{aligned} \mathrm{d}_{ik} &:= \frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\mathrm{d}\mathbf{y},\\ \mathrm{m}^v_{ik} &:= \frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\mathrm{m}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\mathrm{d}\mathbf{y}\\ \text{and}\qquad \mathrm{m}^w_{ik}(\mathbf{x}) &:= \frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\mathrm{m}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_w^k(\mathbf{x})}{\partial y_j}\right)\mathrm{d}\mathbf{y}. \end{aligned}\right\} \tag{3.4}$$

The corrector functions $\xi_v^k \in H^1_{per}(Y^1)$ *and* $\xi_w^k \in L^2(\Omega; H^1_{\mathrm{per}}(Y^1))$ *for* $1 \le k \le d$ *solve in the distributional sense the following reference cell problems:*

$$\left.\begin{aligned} \xi_w^k &: \begin{cases} -\sum_{i,j,k=1}^{d}\dfrac{\partial}{\partial y_i}\left(\delta_{ik} - \delta_{ij}\dfrac{\partial \xi_w^k}{\partial y_j}\right) \\ \quad = \lambda^2\sum_{k,i,j=1}^{d}\dfrac{\partial}{\partial y_i}\left(\mathrm{m}_{ik} - \dfrac{f(\phi_0)}{f'(\phi_0)\phi_0}\mathrm{m}_{ij}\dfrac{\partial \xi_v^k}{\partial y_j}\right) & \text{in } Y^1,\\ \sum_{i,j,k=1}^{d}\mathrm{n}_i\left(\delta_{ij}\dfrac{\partial \xi_w^k}{\partial y_j} - \delta_{ik}\right) \\ \quad -\lambda^2\sum_{k,i,j=1}^{d}\dfrac{\partial}{\partial y_i}\left(\mathrm{m}_{ik} - \dfrac{f(\phi_0)}{f'(\phi_0)\phi_0}\mathrm{m}_{ij}\dfrac{\partial \xi_v^k}{\partial y_j}\right) = 0 & \text{on } \partial Y^1,\\ \xi_w^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_w^k) = 0 \end{cases}\\ \text{and}\qquad \xi_v^k &: \begin{cases} -\sum_{i,j=1}^{d}\dfrac{\partial}{\partial y_i}\left(\delta_{ik} - \delta_{ij}\dfrac{\partial \xi_v^k}{\partial y_j}\right) = 0 & \text{in } Y^1,\\ \sum_{i,j=1}^{d}\mathrm{n}_i\left(\delta_{ij}\dfrac{\partial \xi_w^k}{\partial y_j} - \delta_{ik}\right) = 0 & \text{on } \partial Y^1,\\ \xi_v^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_v^k) = 0. \end{cases} \end{aligned}\right\} \tag{3.5}$$

Remark 3.4.

- The reference cell problem $(3.5)_1$ for ξ_v^k can be solved numerically for example. For problem $(3.5)_2$, there are results in the literature (Auriault & Lewandowska 1997) in the case of straight or perturbed straight channels.
- The thermodynamic equilibrium (3.1) enables the derivation of the cell problem $(3.5)_1$ and assumption 3.2 is necessary for its well-posedness.

4. Applications to wetting

The freedom in defining the free energy $F(\phi)$ in the phase-field equation (1.3) enables us to apply the upscaling formalism developed in this paper to a variety of physical problems. Taking F as in assumption 3.2 includes the phenomenological double-well form that is generally applied for the homogeneous free energy.

Herewith, we can immediately describe the evolution of two phases such as liquid–gas through a porous medium, for instance. The quantity of interest in describing wetting phenomena is the contact angle, defined as the angle between the liquid–gas interface and the wetted area of the substrate.

In the phase-field model (1.3), it is well accepted to account for wetting properties by a Robin boundary condition $(1.3)_2$ (Wylock *et al.* 2012) with

$$g(\mathbf{x}) := -\frac{\gamma}{C_h} a(\mathbf{x}). \tag{4.1}$$

The parameter C_h is the Cahn number λ/L and $\gamma = 2\sqrt{2}\phi_e/3\sigma_{\mathrm{lg}}$, where σ_{lg} denotes the liquid–gas surface tension and ϕ_e the local equilibrium limiting values of F. It is straightforward to extend (4.1) to several wetting properties $a_1, a_2, \ldots, a_N$ for a positive $N \in \mathbb{N}$ such that

$$g(\mathbf{x}) := -\frac{\gamma}{C_h} \sum_{i=1}^{N} a_i(\mathbf{x}) \chi_{\partial\Omega_w^i}(\mathbf{x}) \in H^{3/2}(\partial\Omega_w). \tag{4.2}$$

For notational brevity, we will work with $N = 2$ in subsequent sections.

In §5, we briefly relate the results obtained in this paper to the results from Alberti & DeSimone (2005), where a formula for the effective contact angle is derived based on Γ-convergence and geometric measure theory.

(*a*) *Channel with heterogeneous wetting properties*

We assume that $\Omega := [0, L] \times [0, 1]^{d-1} \subset \mathbb{R}^d$ is an arbitrary straight channel of length L with walls $\partial\Omega_w$ having different wetting properties. We assume that these wetting properties repeat periodically along the channel walls. We denote the left entrance by Γ^{l} and the right exit by Γ^{r}, such that $\partial\Omega = \Gamma^{\mathrm{l}} \cup \partial\Omega_w \cup \Gamma^{\mathrm{r}}$. In particular, we define

$$\Omega^\epsilon := \left\{ \bigcup_{z\in\mathbb{Z}} \mathbf{e}_\epsilon (Y + z\mathbf{e}_1) \right\} \cap \Omega \quad \text{and} \quad \partial\Omega_w^\epsilon := \left\{ \bigcup_{z\in\mathbb{Z}} \mathbf{e}_\epsilon (Y + z\mathbf{e}_1) \right\} \cap \partial\Omega_w, \tag{4.3}$$

where $\mathbf{e}_\epsilon = \epsilon\mathbf{e}_1 + \mathbf{e}_2 + \cdots + \mathbf{e}_d$, $\mathbf{e}_i$ for $i = 1, 2, \ldots, d$ is the canonical basis of $\mathbb{R}^d$, and for the definition of Y, we refer to figure 2.

To derive an effective phase-field model for highly heterogeneous walls, we account for different surface properties on the walls $\partial\Omega_w^\epsilon$, see (4.3), by the following multi-scale formulation:

$$\left.\begin{aligned}
\partial_t(-\Delta)^{-1} w_\epsilon &= \operatorname{div}(\hat{\mathrm{M}}\nabla(\lambda^2 w_\epsilon - \phi_\epsilon + \phi_\epsilon^3)) \quad \text{in } \Omega_T^\epsilon,\\
-\Delta\phi_\epsilon &= w_\epsilon \quad \text{in } \Omega_T^\epsilon,\\
\mathbf{n}\cdot\mathbf{J}_\epsilon &= J_l \quad \text{on } \Gamma_T^{\mathrm{l}} := \Gamma^{\mathrm{l}} \times]0, T[,\\
\mathbf{n}\cdot\mathbf{J}_\epsilon &= 0 \quad \text{on } \Gamma_T^{\mathrm{r}} := \Gamma^{\mathrm{r}} \times]0, T[,\\
\nabla_n\phi_\epsilon &= -\epsilon g\left(\frac{\mathbf{x}}{\epsilon}\right) \quad \text{on } \partial\Omega_w^\epsilon \times]0, T[\\
\text{and} \qquad \phi_\epsilon(\mathbf{x}, 0) &= \psi(\mathbf{x}) \quad \text{in } \Omega,
\end{aligned}\right\} \tag{4.4}$$

where $\mathbf{J}_\epsilon$ is defined as the flux $\nabla(\lambda^2 w_\epsilon - \phi_\epsilon + \phi_\epsilon^3)$, and a_1 and a_2 are constants.

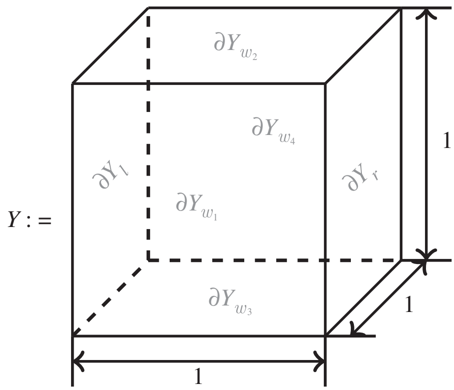

Figure 2. Reference channel $Y := [0,1]^d$ defined by channel entry ∂Y_l, channel exit ∂Y_r and wall $\partial Y_w := \bigcup_{i=1}^4 \partial Y_{w_i}$ where $\partial Y_{w_i} := \partial Y^1_{w_i} \cup \partial Y^2_{w_i}$ with two different wetting properties $\partial Y^1_{w_i}$ and $\partial Y^2_{w_i}$. We point out that Y is only scaled in $y_1 = x_1/\epsilon$ direction and keeps y_2 and y_3 fixed.

For the homogenization of heterogeneous boundary conditions such as $(4.4)_5$, we refer to Allaire *et al.* (1996). Problem (4.4) is introduced because it is *a priori* not clear whether oscillations on the solid/void interface, i.e. on the walls $\partial\Omega^\epsilon_w$, also influence the bulk. We also need to properly define the periodic microscale $x_1/\epsilon =: y_1$. We assume that the heterogeneities defined on the wall $\partial\Omega^\epsilon_w$ are periodic in the x_1-direction with period defined via a reference cell as in figure 2. Our averaging process consists of the usual limit $\epsilon \to 0$. Hence, we cover the channel Ω by reference cells Y, e.g. as in figure 2, which are only scaled by ϵ in the x_1-direction. We further need the following.

Hypothesis 4.1. *We assume that the boundary $\partial\Omega_w$ contains finitely many flat pieces with conormal not proportional to any $\mathbf{z} \in \mathbb{Z}^d$.*

If the hypothesis 4.1 is violated, then the homogenization limit does not converge towards a unique upscaled problem (Bensoussans *et al.* 1978).

Corollary 4.2 (Heterogeneous walls). *We make the same assumptions as in theorem 3.3, except that we do not require an isotropic mobility $\hat{\mathrm{M}}$. We additionally suppose that (4.1) holds and that $J_l, g \in H^{3/2}(\partial\Omega)$ in (4.4).*

Then, the microscopic wall description (4.4) becomes the following upscaled system after averaging over the microscale:

$$\left.\begin{aligned} \partial_t\phi_0 &= \mathrm{div}(\hat{\mathrm{M}}\nabla(-\phi_0 + \phi_0^3 - \lambda^2\Delta\phi_0)) \quad \text{in } \Omega_T,\\ \nabla_n\phi_0 &= J_l \quad \text{on } \partial\Omega^l_T,\\ \nabla_n\phi_0 &= 0 \quad \text{on } \partial\Omega^r_T,\\ \nabla_n\phi_0 &= g_0 \quad \text{on } \partial\Omega_w\times]0,T[\\ \text{and} \quad \phi(\boldsymbol{x},0) &= \psi(\boldsymbol{x}) \quad \text{in } \Omega, \end{aligned}\right\} \tag{4.5}$$

where $g_0 := -(\gamma/C_h)(1/|Y|)\int_Y (a_1\chi_{\partial Y^1_w}(\mathbf{y}) + a_2\chi_{\partial Y^2_w}(\mathbf{y}))\mathrm{d}\mathbf{y}$, *where the constants a_1 and a_2 characterize the material's wetting properties.*

(b) *Wetting dynamics in porous media and imbibition*

As in equation (1.5), we define the porous medium by the pore space Ω^ϵ and the solid material B^ϵ as a periodic covering by a single reference cell $Y := [0, \ell_1] \times [0, \ell_2] \times \cdots \times [0, \ell_d]$, which defines the characteristic pore geometry (figure 1).

We denote by $\partial Y_w^1 := \bigcup_{i=1}^N \partial Y_{w_i}^1$ the pore surface. The subsets $\partial Y_{w_i}^1$ belong to surfaces with different wetting properties. Correspondingly, the walls $\partial\Omega_{w_i}^\epsilon$ are defined via $\partial Y_{w_i}^1$ of the covering of Ω by Y (figure 2). Depending on applications, different boundary conditions than $(4.6)_4$ below for wetting can be imposed.

These definitions allow us to reformulate (1.3) by the following microscopic porous media problem:

$$\left.\begin{aligned} &\partial_t\phi_\epsilon = \operatorname{div}(\hat{\mathrm{M}}\nabla(-\lambda^2\Delta\phi_\epsilon + f(\phi_\epsilon))) \quad \text{in } \Omega_T^\epsilon,\\ &\mathbf{n}\cdot\mathbf{J}_\epsilon = J_l \quad \text{on } \Gamma_T^{\mathrm{l}},\\ &\mathbf{n}\cdot\mathbf{J}_\epsilon = 0 \quad \text{on } \Gamma_T^{\mathrm{r}}\\ \text{and}\quad &\nabla_n\phi_\epsilon = -\epsilon\frac{\gamma}{C_h}\left(a_1(\mathbf{x})\chi_{\partial\Omega_{w_1}^\epsilon}\left(\frac{\mathbf{x}}{\epsilon}\right) + a_2(\mathbf{x})\chi_{\partial\Omega_{w_2}^\epsilon}\left(\frac{\mathbf{x}}{\epsilon}\right)\right) \quad \text{on } \partial\Omega_w^\epsilon\times]0,T[,\end{aligned}\right\} \tag{4.6}$$

where $a_1(\mathbf{x})$ and $a_2(\mathbf{x})$ appear periodically with period ϵY and vary macroscopically in $\mathbf{x}\in\Omega^\epsilon$. We complement (4.6) with arbitrary initial conditions $\phi_\epsilon(\mathbf{x},0) = \psi(\mathbf{x}) \in H_E^2(\Omega)$.

We focus here on a porous medium with walls showing only two different wetting properties, i.e. $N = 2$. An extension to arbitrary $0 < N < \infty$ is straightforward. We explained the scaling by ϵ of the wetting boundary condition $(4.6)_4$ already in §4*a*.

Corollary 4.3 (Wetting in porous media). *We make the same assumptions as in theorem 3.3.*

Then, the microscopic porous media formulation (4.6) has the following leading order asymptotic equation on the macroscale:

$$\left.\begin{aligned} \theta_1\frac{\partial\phi_0}{\partial t} &= \operatorname{div}\left(\left[\theta_1 f'(\phi_0)\hat{\mathrm{M}} - \left(2\frac{f(\phi_0)}{\phi_0} - f'(\phi_0)\right)\hat{\mathrm{M}}_v\right]\nabla\phi_0\right)\\ &\quad - f'(\phi_0)\operatorname{div}(\hat{\mathrm{M}}_v\nabla\phi_0) + \frac{\lambda^2}{\theta_1}\operatorname{div}(\hat{\mathrm{M}}_w\nabla(\operatorname{div}(\hat{\mathrm{D}}\nabla\phi_0) - \tilde{g}_0)) \quad \textit{in } \Omega_T,\\ \mathbf{n}\cdot\mathbf{J} &= J_l \quad \textit{on } \Gamma_T^l,\\ \mathbf{n}\cdot\mathbf{J} &= 0 \quad \textit{on } \Gamma_T^r,\\ \nabla_n\phi_0 &= \mathbf{n}\cdot\nabla\phi_0 = \nabla_n\Delta\phi_0 = 0 \quad \textit{on } \partial\Omega_w\times]0,T[\\ \textit{and}\quad \phi_0(\mathbf{x},0) &= \psi(\mathbf{x}) \quad \textit{in } \Omega,\end{aligned}\right\} \tag{4.7}$$

where $\theta_1 := |Y^1|/|Y|$ is the porosity, $\mathbf{J}$ the flux corresponding to $(4.7)_1$, and the porous media correction tensors $\hat{\mathrm{D}} := \{\mathrm{d}_{ik}\}_{1\le i,k\le d}$, $\hat{\mathrm{M}}_v = \{\mathrm{m}_{ik}^v\}_{1\le i,k\le d}$ and

$\hat{\mathrm{M}}_{\mathrm{w}} = \{\mathrm{m}^w_{ik}(\mathbf{x})\}_{1\le i,k\le d}$ *are defined in (3.4). The function* $\tilde{g}_0$ *defines the upscaled wetting boundary condition,*

$$\tilde{g}_0(\mathbf{x}) := -\frac{\gamma}{C_h}\int_{\partial Y^1_w}(a_1(\mathbf{x})\chi_{\partial Y^1_{w_1}}(\mathbf{y}) + a_2(\mathbf{x})\chi_{\partial Y^1_{w_2}}(\mathbf{y}))\mathrm{d}o(\mathbf{y}). \tag{4.8}$$

5. Conclusion

We have examined the problem of upscaling the Cahn–Hilliard equation for perforated/strongly heterogeneous domains. An effective macroscopic Cahn–Hilliard equation by homogenization for such domains is derived rigorously for the first time. It is often the case that averaging strategies such as volume averages and Marle's method are applied. However, such approaches are rather heuristic and it is not clear how to choose the size of reference volume for the averaging (§1*a*). The proof of the main result obtained here is valid for free energies F defined by polynomials up to fourth-order satisfying assumption 3.2. Such polynomial free energies include generically applied double-well potentials that phenomenologically represent a large class of free energies modelling two-phase problems (e.g. the free energy of mixing (1.4)) and that mimic the Lennard-Jones potential via the LMP theory (Presutti 2009). However, they do not appear as a mean field limit of an atomistic model. Moreover, the upscaling process also provides naturally the basic algorithmic framework and analytical tools for other choices of free energies F.

The new effective Cahn–Hilliard formulation introduces an efficient and low-dimensional numerical alternative over its microscopic counterpart (1.6) and serves as a promising alternative for multi-phase problems (§1*a*). It also provides systematically effective transport coefficients like diffusion and mobility (or permeability) tensors. We further apply the new effective Cahn–Hilliard equation to wetting problems in porous media and straight channels. It turns out that the new formulation allows for a feasible computation of effective contact angles in channels with strongly heterogeneous walls, for instance. Interestingly, we recover rigorously the same equation that was suggested in the studies of Ala-Nissila *et al.* (2004) and Dubé *et al.* (1999) for imbibition but based on physical arguments, suggesting that the new equation is consistent with known physical laws.

It should also be mentioned that corollary 4.3 allows for a formal extension towards random porous media or random wetting properties where $a_1(\mathbf{x})$ and $a_2(\mathbf{x})$ are spatially homogeneous and stationary ergodic random variables, for instance. In the case of random media, one can introduce appropriate random variables such as a random porosity θ_1 or random wall fractions $\theta_{w_1} := |\partial Y^1_{w_1}|/|\partial Y^1_w|$ and $\theta_{w_2} := 1-\theta_1$. Herewith, we can redefine g_0 in (4.8) by

$$\alpha(\mathbf{x}) := -\frac{\gamma}{C_h}(a_1\theta_{w_1}(\mathbf{x}) + a_2\theta_{w_2}(\mathbf{x})), \tag{5.1}$$

where $\theta_{w_i}(\mathbf{x})$ for $i=1,2$ are homogeneous random fields characterizing the wall fractions and the periodicity assumption can be replaced by a stationary ergodic setting (Bensoussans *et al.* 1978). Equation (5.1) motivates that homogenization theory allows us to reliably introduce and consistently define the phenomenological variable α appearing in the equation for imbibition in

Ala-Nissila *et al.* (2004) and Dubé *et al.* (1999). In fact, we obtain rigorously that this variable α is connected with the wetting boundary condition g in (1.6). However, we remark that the earlier-mentioned extensions are merely formal and require careful analytical considerations in specific applications of interest.

The effective model (4.5) allows us to determine the averaged contact angle via g_0 in (4.5) or (4.8). We can determine via $\gamma := 2\sqrt{2}\phi_e/3\sigma_{lg}$ the parameter $a_{eff} = g_0 C_h/\gamma$, and ϕ_e denotes the local equilibrium limiting values of the standard phenomenological double-well potential F. By defining $\phi_e = +1$ as the liquid phase and $\phi_e = -1$ as the gaseous phase, one imposes with $a_{eff} > 0$ hydrophilic and with $a_{eff} < 0$ hydrophobic wetting conditions. After setting $A = \sqrt{2}\gamma a_{eff}$, the effective equilibrium contact angle immediately follows by

$$\cos\theta_e = \tfrac{1}{2}[(1+A)^{3/2} - (1-A)^{3/2}]. \tag{5.2}$$

We believe that herewith we can propose a convenient and feasible alternative to Alberti & DeSimone (2005) with (5.2) for the computation of effective contact angles. Formula (4.8), allows us to analytically compute the effective macroscopic contact angle θ_e in contrast to the not easily accessible formulae in Alberti & DeSimone (2005). The difference between their and our result relies on the fact that they work with the interfacial energy

$$E := \sigma_{SL}|\Sigma_{SL}| + \sigma_{SV}|\Sigma_{SV}| + \sigma_{LV}|\Sigma_{LV}| + \text{a.t.}, \tag{5.3}$$

where σ_{AB} denotes the surface tension between phases A and B, Σ_{AB} the interface between A and B ($|\Sigma_{AB}|$ its measure), for $A, B \in \{\mathrm{S}, \mathrm{L}, \mathrm{V}\}$. The letters S, L and V stand for the solid, liquid and vapour phases, respectively. In contrast, we base our considerations on the Cahn–Hilliard model (4.4) and hence provide an approximate effective contact angle due to a diffuse interface approximation. Hence, it might be interesting to study the sharp interface limit in this context. Moreover, Alberti and DeSimone connect nicely their generally valid homogenized formulas with the classical results from Wenzel (1936) and Cassie & Baxter (1944). In fact, they show that the Wenzel and Cassie–Baxter laws represent upper bounds for the effective contact angle formula derived in Alberti & DeSimone (2005).

There are of course open questions and future perspectives. A characterization of the effective macroscopic Cahn–Hilliard equation by error estimates as exemplified in different contexts by Bensoussans *et al.* (1978) and Schmuck (2012) is of great interest. Analytically, the convergence of the microscopic (periodic) formulation to the effective macroscopic Cahn–Hilliard problem is of great relevance. In applications, it is very interesting to extend the porous media formulation to fluid flow. It is well known that such an extension is rather involved because additional physical phenomena such as diffusion–dispersion effects arise (e.g. Taylor–Aris dispersion). It is still not entirely clear how one can reliably account for such phenomena.

Nevertheless, even without fluid flow, the new equations enable us to gain insights into interfacial dynamics in porous media, for instance. Two- or three-dimensional numerical results of wetting phenomena in porous media would allow us to track the phase interface of an arbitrary three-phase composite, i.e. the porous medium and arbitrary two phases in pore space. This information is of great interest for the design of synthetic porous media, membranes and generally micro-fluidic devices. But the new formulation also provides an interesting alternative for simulating oil recovery from natural porous media.

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Appendix A. Proof of theorem 3.3

We define the microscale $\mathbf{x}/\epsilon =: \mathbf{y} \in Y$ such that after setting

$$\left.\begin{aligned}
&\mathcal{A}_0 = -\sum_{i,j=1}^{d} \frac{\partial}{\partial y_i}\left(\delta_{ij}\frac{\partial}{\partial y_j}\right), \quad \mathcal{B}_0 = -\sum_{i,j=1}^{d} \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial}{\partial y_j}\right),\\
&\mathcal{A}_1 = -\sum_{i,j=1}^{d}\left[\frac{\partial}{\partial x_i}\left(\delta_{ij}\frac{\partial}{\partial y_j}\right) + \frac{\partial}{\partial y_i}\left(\delta_{ij}\frac{\partial}{\partial x_j}\right)\right],\\
&\mathcal{B}_1 = -\sum_{i,j=1}^{d}\left[\frac{\partial}{\partial x_i}\left(\mathrm{m}_{ij}\frac{\partial}{\partial y_j}\right) + \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial}{\partial x_j}\right)\right],\\
&\mathcal{A}_2 = -\sum_{i,j=1}^{d} \frac{\partial}{\partial x_j}\left(\delta_{ij}\frac{\partial}{\partial x_j}\right) \text{ and } \mathcal{B}_2 = -\sum_{i,j=1}^{d} \frac{\partial}{\partial x_j}\left(\mathrm{m}_{ij}\frac{\partial}{\partial x_j}\right),
\end{aligned}\right\} \tag{A 1}$$

$\mathcal{A}_\epsilon := \epsilon^{-2}\mathcal{A}_0 + \epsilon^{-1}\mathcal{A}_1 + \mathcal{A}_2$ and $\mathcal{B}_\epsilon := \epsilon^{-2}\mathcal{B}_0 + \epsilon^{-1}\mathcal{B}_1 + \mathcal{B}_2$, the Laplace operators Δ and $\mathrm{div}(\hat{\mathrm{M}}\nabla)$ become $\Delta u^\epsilon(\mathbf{x}) = \mathcal{A}_\epsilon u(\mathbf{x},\mathbf{y})$ and $\mathrm{div}(\hat{\mathrm{M}}\nabla)u^\epsilon(\mathbf{x}) = \mathcal{B}_\epsilon u(\mathbf{x},\mathbf{y})$, respectively, where $u^\epsilon(\mathbf{x}) := u(\mathbf{x},\mathbf{y})$. Inserting for $u \in \{w, \phi\}$ the formal asymptotic expansions $u^\epsilon \approx u_0(\mathbf{x},\mathbf{y},t) + \epsilon u_1(\mathbf{x},\mathbf{y},t) + \epsilon^2 u_2(\mathbf{x},\mathbf{y},t)$ into (2.4) and using (A 1) provides a sequence of three solvable perturbation problems, at $\mathcal{O}(\epsilon^{-2})$, $\mathcal{O}(\epsilon^{-1})$ and $\mathcal{O}(\epsilon^0)$, after equating terms of equal powers in ϵ. For simplicity, we only give the last one here

$$\mathcal{O}(\epsilon^0): \left\{\begin{aligned}
&\mathcal{B}_0 w_2 = -\lambda^2(\mathcal{B}_2 w_0 + \mathcal{B}_1 w_1)\\
&\quad -\mathcal{B}_0\left[\tfrac{1}{2}f''(\phi_0)\phi_1^2 + f'(\phi_0)\phi_2\right]\\
&\quad -\mathcal{B}_1\left[f(\phi_0)\tfrac{\phi_1}{\phi_0}\right] - \mathcal{B}_2 f(\phi_0) - \partial_t(-\Delta)^{-1}w_0 \quad \text{in } Y^1,\\
&\quad \text{no flux b.c.},\\
&\quad w_2 \text{ is } Y^1\text{-periodic},\\
&\mathcal{A}_0 v_2 = -\mathcal{A}_2 v_0 - \mathcal{A}_1 v_1 + w_0 \quad \text{in } Y^1,\\
&\quad \nabla_n v_2 = g_\epsilon \quad \text{on } \partial Y_w^1,\\
&\quad \phi_2 \text{ is } Y^1\text{-periodic},
\end{aligned}\right\} \tag{A 2}$$

where in (A 2) the following relation is applied:

$$\tfrac{1}{2}f''(\phi_0)\phi_1^2 + f'(\phi_0)\phi_2 = a_1\phi_2 + a_2(2\phi_2\phi_0 + \phi_1^2) + 3a_3(\phi_2\phi_0^2 + \phi_0\phi_1^2). \tag{A 3}$$

The first problems at $\mathcal{O}(\epsilon^{-2})$ are classical in elliptic homogenization theory and immediately imply that the leading order approximations w_0 and v_0 are independent of the microscale $\mathbf{y}$. This fact and the linear structure of the problems arising at $\mathcal{O}(\epsilon^{-1})$ suggest the following ansatz for w_1 and ϕ_1, i.e.

$$w_1(\mathbf{x},\mathbf{y},t) = -\sum_{k=1}^{d} \xi_w^k(\mathbf{y}) \frac{\partial w_0}{\partial x_k}(\mathbf{x},t) \quad \text{and} \quad \phi_1(\mathbf{x},\mathbf{y},t) = -\sum_{k=1}^{d} \xi_v^k(\mathbf{y}) \frac{\partial \phi_0}{\partial x_k}(\mathbf{x},t) = v_1. \tag{A 4}$$

Inserting (A 4) into the $\mathcal{O}(\epsilon^{-1})$ problems provides equations for the correctors ξ_w^k and ξ_v^k. The resulting equation for ξ_v^k is again standard in elliptic homogenization theory and can be immediately written for $1 \le k \le d$ as

$$\xi_\phi : \left\{\begin{array}{ll} -\sum_{i,j=1}^{d} \dfrac{\partial}{\partial y_i}\left(\delta_{ik} - \delta_{ij}\dfrac{\partial \xi_v^k}{\partial y_j}\right) - \operatorname{div}(\mathbf{e}_k - \nabla_y \xi_v^k) = 0 & \text{in } Y^1, \\ \mathbf{n}\cdot(\nabla \xi_v^k + \mathbf{e}_k) = 0 & \text{on } \partial Y_w^1, \\ \xi_v^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_v^k) = 0. & \end{array}\right\} \tag{A 5}$$

The reference cell problem for ξ_w is much more difficult since it depends on the solutions of (A 5). We first write the problem at $\mathcal{O}(\epsilon^{-1})$ for ξ_w^k in explicit terms,

$$\begin{aligned} \sum_{k,i,j=1}^{d} \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right)\frac{\partial w_0}{\partial x_k} &= \sum_{i,j=1}^{d} \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial w_0}{\partial x_j}\right) \\ &\quad - \frac{f(\phi_0)}{\phi_0}\sum_{k,i,j=1}^{d} \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\frac{\partial \phi_0}{\partial x_k} + \sum_{k,i,j=1}^{d} \frac{\partial}{\partial y_i}\left(f'(\phi_0)\mathrm{m}_{ij}\frac{\partial \phi_0}{\partial x_i}\right). \end{aligned} \tag{A 6}$$

At this point, a major obstacle is the dependence on ϕ_0 in problem (A 7). To alleviate this difficulty, we make use of the chemical potential defined in (3.1). In the case of thermodynamic equilibrium, the quantity μ is constant. Hence, it holds that $f'(\phi)(\partial\phi/\partial x_k) = f'(\phi)(\partial v/\partial x_k) = \lambda^2(\partial w/\partial x_k)$ for $1 \le k \le d$. If this identity is valid in each reference cell Y (i.e. locally) and the mobility tensor $\hat{\mathrm{M}}$ is isotropic, i.e. $\hat{\mathrm{M}} = \{\mathrm{m}_{ij}\}_{1\le i,j\le d} = \{\mathrm{m}\delta_{ij}\}_{1\le i,j\le d}$, then we can cancel $\partial w_0/\partial x_k$ in (A 6) and simplify to

$$\xi_w : \left\{\begin{array}{l} -\displaystyle\sum_{i,j,k=1}^{d} \frac{\partial}{\partial y_i}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right) \\ \quad = \lambda^2 \displaystyle\sum_{k,i,j=1}^{d} \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ik} - \frac{f(\phi_0)}{f'(\phi_0)\phi_0}\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right) \quad \text{in } Y^1, \\ \displaystyle\sum_{i,j,k=1}^{d} \mathrm{n}_i\left(\left(\delta_{ij}\frac{\partial \xi_w^k}{\partial y_j} - \delta_{ik}\right)\right. \\ \quad \left. - \lambda^2 \displaystyle\sum_{k,i,j=1}^{d} \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ik} - \frac{f(\phi_0)}{f'(\phi_0)\phi_0}\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\right) = 0 \quad \text{on } \partial Y_w^1, \\ \xi_w^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_w^k) = 0. \end{array}\right\} \tag{A 7}$$

One can guarantee well-posedness of the cell problem (A 7) under the assumption 3.2, which ensures that $r(s) := f(s)/(f'(s)s) \in L^2([\alpha_1, \alpha_2])$ and since $\phi_0 \in H^2_E(\Omega)$, it holds that

$$\int_\Omega r^2(\phi_0)\mathrm{d}\mathbf{x} \le |\Omega| \int_{\alpha_1}^{\alpha_2} r^2(s)\mathrm{d}s < \infty, \tag{A 8}$$

such that $\xi_w^k \in L^2(\Omega; H^1_{\mathrm{per}}(Y^1))$.

We now come to the last problem (A 2). Again, equation $(\mathrm{A}\,2)_2$ is much simpler because it is standard in elliptic homogenization theory. Well-known existence and uniqueness results (Fredholm alternative/Lax-Milgram) immediately guarantee solvability by verifying that the right-hand side in (A 2) is zero as an integral over Y^1. For $\tilde{g}_0 := -(\gamma/C_h)\int_{\partial Y^1}(a_1\chi_{\partial Y^1_{w_1}} + a_1\chi_{\partial Y^1_{w_2}})\,\mathrm{d}o(\mathbf{y})$, we obtain the following effective equation for the phase field:

$$-\sum_{i,k=1}^d \left[\sum_{j=1}^d \int_{Y^1}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\mathrm{d}\mathbf{y}\right]\frac{\partial^2 v_0}{\partial x_i \partial x_k} = |Y^1| w_0 + \tilde{g}_0, \tag{A 9}$$

which can be written more compactly by defining a porous media correction tensor $\hat{\mathrm{D}} := \{\mathrm{d}_{ik}\}_{1\le i,k\le d}$ by

$$|Y|\mathrm{d}_{ik} := \sum_{j=1}^d \int_{Y^1}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\mathrm{d}\mathbf{y}. \tag{A 10}$$

Equations (A 9) and (A 10) provide the final form of the upscaled equation for ϕ_0, i.e. $-\Delta_{\hat{\mathrm{D}}} v_0 := -\mathrm{div}(\hat{\mathrm{D}}\nabla v_0) = \theta_1 w_0 + \tilde{g}_0$.

The upscaled equation for w is again a result of the Fredholm alternative, i.e. a solvability criterion on equation $(\mathrm{A}\,2)_1$. This means that we require

$$\begin{aligned}\int_{Y^1}\Bigg\{&-\lambda^2(\mathcal{B}_2 w_0 + \mathcal{B}_1 w_1) - \mathcal{B}_0\left(\frac{1}{2}f''(\phi_0)\phi_1^2 + f'(\phi_0)\phi_2\right)\\ &- \mathcal{B}_1\left[f(\phi_0)\frac{\phi_1}{\phi_0}\right] - \mathcal{B}_2 f(\phi_0) - \partial_t(-\Delta)^{-1}w_0\Bigg\}\mathrm{d}\mathbf{y} = 0.\end{aligned} \tag{A 11}$$

Let us start with the terms that are easily averaged over the reference cell Y. The first two terms in (A 11) can be rewritten as

$$\begin{aligned}\int_{Y^1} -(\mathcal{B}_2 w_0 + \mathcal{B}_1 w_1)\,\mathrm{d}\mathbf{y} &= -\sum_{i,k=1}^d\left[\sum_{j=1}^d\int_{Y^1}\left(\mathrm{m}_{ik} - \mathrm{m}_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right)\mathrm{d}\mathbf{y}\right]\frac{\partial^2 w_0}{\partial x_i\partial x_k}\\ &= -\mathrm{div}(\hat{\mathrm{M}}_w\nabla w_0),\end{aligned} \tag{A 12}$$

where the effective tensor $\hat{\mathrm{M}}_w = \{\mathrm{m}^w_{ik}\}_{1\le i,k\le d}$ is defined by

$$\mathrm{m}^w_{ik} := \frac{1}{|Y|}\sum_{j=1}^d\int_{Y^1}\left(\mathrm{m}_{ik} - \mathrm{m}_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right)\mathrm{d}\mathbf{y}. \tag{A 13}$$

The next terms in (A 11) become

$$-\mathcal{B}_1\left[f(\phi_0)\frac{\phi_1}{\phi_0}\right]-\mathcal{B}_2 f(\phi_0)=\sum_{k,i,j=1}^{d}\left\{-\frac{\partial}{\partial x_i}\left(\left[\mathrm{m}_{ij}\frac{f(\phi_0)}{\phi_0}\frac{\partial \xi_v^k}{\partial y_j}\right]\frac{\partial \phi_0}{\partial x_k}\right)\right.$$
$$\left.+\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{f(\phi_0)}{\phi_0}\frac{\partial \phi_1}{\partial x_j}\right)+\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\phi_1\frac{\partial(f(\phi_0)/\phi_0)}{\partial x_j}\right)\right\}$$
$$+\sum_{k,i,j=1}^{d}\frac{\partial}{\partial x_i}\left(\mathrm{m}_{ij}f'(\phi_0)\frac{\partial \phi_0}{\partial x_j}\right), \tag{A 14}$$

and a subsequent integration of the right-hand side of (A 14) over the reference cell Y gives

$$\sum_{i,k=1}^{d}\frac{\partial}{\partial x_i}\left(\left[\sum_{j=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ik}f'(\phi_0)-\mathrm{m}_{ij}\frac{f(\phi_0)}{\phi_0}\frac{\partial \xi_v^k}{\partial y_j}\right)\mathrm{d}\mathbf{y}\right]\frac{\partial \phi_0}{\partial x_j}\right)$$
$$-\sum_{k,j=1}^{d}\left[\sum_{i=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_i}\right)\mathrm{d}\mathbf{y}\right]\frac{f(\phi_0)}{\phi_0}\frac{\partial^2 \phi_0}{\partial x_k \partial x_j}$$
$$-\sum_{k,j=1}^{d}\left[\sum_{i=1}^{d}\int_{Y^1}\left(\frac{\partial \xi_v^k}{\partial y_i}\mathrm{m}_{ij}\right)\mathrm{d}\mathbf{y}\right]\frac{\partial(f(\phi_0/\phi_0)}{\partial x_j}\frac{\partial \phi_0}{\partial x_k}, \tag{A 15}$$

where the last two terms further simplify to

$$-\sum_{k,j=1}^{d}\frac{\partial}{\partial x_j}\left(\frac{f(\phi_0)}{\phi_0}\left[\sum_{i=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_i}\right)\mathrm{d}\mathbf{y}\right]\frac{\partial \phi_0}{\partial x_k}\right). \tag{A 16}$$

With (A 16), we can finally write (A 14) in the following compact way:

$$\frac{1}{|Y|}\int_{Y^1}\left(-\mathcal{B}_1\left[f(\phi_0)\frac{\phi_1}{\phi_0}\right]-\mathcal{B}_2 f(\phi_0)\right)\mathrm{d}\mathbf{y}$$
$$=\sum_{i,k=1}^{d}\frac{\partial}{\partial x_i}\left(\left[\frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ik}f'(\phi_0)-2\,\mathrm{m}_{ij}\frac{f(\phi_0)}{\phi_0}\frac{\partial \xi_v^k}{\partial y_j}\right)\mathrm{d}\mathbf{y}\right]\frac{\partial \phi_0}{\partial x_j}\right) \tag{A 17}$$
$$=\mathrm{div}\left(\left[\theta_1 f'(\phi_0)\hat{\mathrm{M}}-2\frac{f(\phi_0)}{\phi_0}\hat{\mathrm{M}}_v\right]\nabla\phi_0\right),$$

where the tensor $\hat{\mathrm{M}}_v=\{\mathrm{m}_{ij}^v\}_{1\le i,k\le d}$ is defined by

$$\mathrm{m}_{ik}^v:=\frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\mathrm{d}\mathbf{y}. \tag{A 18}$$

It remains to elucidate the last term in (A 11). Using $(\mathrm{A}\,2)_2$, then we have

$$
\begin{aligned}
&-\mathcal{B}_0\left[\frac{1}{2}f''(\phi_0)\phi_1^2+f'(\phi_0)\phi_2\right]\\
&\quad=\sum_{i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\phi_1\frac{\partial\phi_1}{\partial y_j}\right)f''(\phi_0)+\sum_{i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial\phi_2}{\partial y_j}\right)f'(\phi_0)\\
&\quad=\sum_{i,j=1}^{d}-\left[\frac{\partial}{\partial y_i}(\mathrm{m}_{ij}\phi_1\frac{\partial\xi_v^k}{\partial y_j})\right]f''(\phi_0)\frac{\partial\phi_0}{\partial x_k}+\mathrm{m}\left(\mathcal{A}_2\phi_0+\mathcal{A}_1\phi_1-w_0\right).
\end{aligned}
\tag{A 19}
$$

If we assume an isotropic mobility matrix $\hat{\mathrm{M}}$, i.e. $\hat{\mathrm{M}}=\{\mathrm{m}\delta_{ij}\}_{1\le i,j\le d}$, and use (A 5) in the term with the summation, then the following simplification of its summands can be made:

$$
\begin{aligned}
\left[\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\phi_1\frac{\partial\xi_v^k}{\partial y_j}\right)\right]f''(\phi_0)\frac{\partial\phi_0}{\partial x_k}&=\left[\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ik}\phi_1\right)\right]\frac{\partial f'(\phi_0)}{\partial x_k}=-\left[\mathrm{m}_{ik}\frac{\partial\xi_v^l}{\partial y_i}\right]\frac{\partial\phi_0}{\partial x_l}\frac{\partial f'(\phi_0)}{\partial x_k}\\
&=-\frac{\partial}{\partial x_k}\left(f'(\phi_0)\left[\mathrm{m}_{ik}\frac{\partial\xi_v^l}{\partial y_i}\right]\frac{\partial\phi_0}{\partial x_l}\right)\\
&\quad+f'(\phi_0)\frac{\partial}{\partial x_k}\left(\left[\mathrm{m}_{ik}\frac{\partial\xi_v^l}{\partial y_i}\right]\frac{\partial\phi_0}{\partial x_l}\right).
\end{aligned}
\tag{A 20}
$$

The last term in (A 19) vanishes by the Fredholm alternative guaranteeing solvability of $(\mathrm{A}\,2)_2$. Hence, (A 19) admits after integrating over Y the following compact form:

$$
\begin{aligned}
\frac{1}{|Y|}\int_{Y^1}-\mathcal{B}_0\left[\frac{1}{2}f''(\phi_0)\phi_1^2+f'(\phi_0)\phi_2\right]\mathrm{d}\mathbf{y}&=\mathrm{div}\left(f'(\phi_0)\hat{\mathrm{M}}_v\nabla\phi_0\right)\\
&\quad-f'(\phi_0)\,\mathrm{div}\left(\hat{\mathrm{M}}_v\nabla\phi_0\right),
\end{aligned}
\tag{A 21}
$$

which then sets (A 19) to zero. These considerations finally lead to the following effective equation for ϕ_0:

$$
\begin{aligned}
\theta_1\frac{\partial\phi_0}{\partial t}&=\mathrm{div}\left(\left[\theta_1 f'(\phi_0)\hat{\mathrm{M}}-\left(2\frac{f(\phi_0)}{\phi_0}-f'(\phi_0)\right)\hat{\mathrm{M}}_v\right]\nabla\phi_0\right)\\
&\quad-f'(\phi_0)\,\mathrm{div}(\hat{\mathrm{M}}_v\nabla\phi_0)+\frac{\lambda^2}{\theta_1}\mathrm{div}(\hat{\mathrm{M}}_w\nabla(\mathrm{div}(\hat{\mathrm{D}}\nabla\phi_0)-\tilde{g}_0)).
\end{aligned}
\tag{A 22}
$$

The solvability of (A 22) follows along with the arguments in Novick-Cohen (1990) since we at least assume that $f\in C^2_{\mathrm{Lip}}(I)$ where $I\subset\mathbb{R}$ is a bounded interval. In fact, one only needs to prove a local Lipschitz continuity of the first two terms on the right-hand side of (A 22).

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