UPSCALED PHASE FIELD MODELS FOR INTERFACIAL DYNAMICS IN STRONGLY HETEROGENEOUS/PERFORATED DOMAINS *

M. SCHMUCK †, M. PRADAS ‡, G. A. PAVLIOTIS §, AND S. KALLIADASIS ¶

Abstract. This article is devoted to the derivation of a new effective macroscopic Cahn-Hilliard equation whose free energy can be represented by 4-th order polynomials. To the best knowledge of the authors, this seems to be the first attempt of upscalinging the Cahn-Hilliard equation from microscopically perforated domains. The new homogenized equation enjoys a broad range of application since its additional feature of reliably accounting for confined geometries brings new perspectives for modeling and numerics in science and engineering. At the end, we apply the achieved result to wetting in porous media and to a single channel with strongly heterogeneous walls.

Key words. Phase field models, wetting, multi-scale, homogenization, Cahn-Hillard, porous media

Subject classifications.

1. Introduction

Consider the abstract energy density

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

where the gradient term $\lambda^2 |\nabla \phi|^2$ penalizes the interfacial area between phases ϕ emerging from a homogeneous free energy F defined as the polynom

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

The definition of the energy $E(\phi) := \int_\Omega e(\phi)\, dx$ with density (1.2) depends on the problem of interest. In general, the number of local minima of F is equivalent to the number of possible phases separated by a diffuse interface whose spatial extension is minimized by the gradient term.

The classical idea of equilibrium phase field modeling consists in minimizing the free energy f over a domain $\Omega \subset \mathbb{R}^d$ of interest. $0 \le d \le 3$ denotes the spatial dimension. We assume that Ω is bounded and denote its boundary by $\partial\Omega$. It is well accepted that thermodynamic equilibrium can be achieved by minimizing the free energy (1.1) with respect to its gradient flow, that means,

$$\begin{cases} \frac{\partial}{\partial t}\phi = \operatorname{div}\left(\hat{\mathrm{M}} \nabla \left(f(\phi) - \lambda^2 \Delta \phi\right)\right) & \text{in } \Omega_T := \Omega \times]0,T[, \\ \nabla_n \phi := \mathbf{n} \cdot \nabla \phi = g(\mathbf{x}) & \text{on } \partial\Omega_T := \partial\Omega \times]0,T[, \\ \nabla_n \Delta \phi = 0 & \text{on } \partial\Omega_T, \\ \phi(\mathbf{x},0) = \phi_0(\mathbf{x}) & \text{on } \Omega, \end{cases} \tag{1.3}$$

---

*

†Chemical Engineering and Mathematics, Imperial College, UK, South Kensington Campus, London, (mschmuck@imperial.ac.uk),

‡Chemical Engineering, Imperial College, UK, South Kensington Campus, London, (m.pradas@imperial.ac.uk),

§Mathematics, Imperial College, UK, South Kensington Campus, London, (g.pavliotis@imperial.ac.uk),

¶Chemical Engineering, Imperial College, UK, South Kensington Campus, London, (s.kalliadasis@imperial.ac.uk).

where g and ϕ_0 represent suitable boundary and initial conditions, respectively. The equation (1.3) is the gradient flow with respect to the H^{-1}-norm and referred to as the Cahn-Hilliard equation. It was motivated in [13] that the gradient system (1.3) corresponds to the free energy (1.1) if $f(s)$ is a double well potential. Recent rigorous analysis suggests that the minimization of a free energy is well defined in the context of the Wasserstein distance [15]. But a practical/numerical realization for such an approach still addresses many open questions [16]. However, it is well known that the free energy (1.1) dissipates, that means,

$$E(\phi(\cdot,t)) \leq E(\phi(\cdot,0)) =: E_0\,, \tag{1.4}$$

which immediately follows after differentiating (1.1) with respect to time and using (1.3). This is also the main motivation why the gradient flow (1.3) is a formally reasonable (despite not necessarily optimal) formulation to approximate thermodynamic equilibrium.

The phase field equation (1.3) goes back to Cahn-Hilliard [9] where they successfully suggest a free energy formulation for nonuniform systems. Since then, this formalism became a fundamental modeling tool in science and engineering. Cahn-Hilliard or more generally phase field energy functionals are for example applied in image processing such as inpainting, see [7]. By modifying the energy functional one can even employ such a formulation to denoising, edge detection, and motion estimation in image sequence processing [21]. A mathematical model for electrowetting is analyzed in [12]. This kind of wetting phenomena are of great interest in technological applications for the development of microfluidic devices. But already pure wetting phenomena without electric forces are not completely understood and impose interesting questions like the appearance of hysteresis [26]. In [17] a phase-field model is proposed to describe the dynamics of vesicles such as spinodal decompostion, coarsening, budding, and fission. However, next to a Cahn-Hilliard equation on a surface also Allen-Cahn type of equations are employed therein. In [8], a relation between mean curvature and the standard Cahn-Hilliard equation, i.e., where the free energy F is chosen as the double well potential, is exploited to analyze it with the help of the Willmore flow. Due to the large amount of literature available, we restrict ourselves to the above selection in order to emphasize the versatility of phase-field (Cahn-Hilliard) formulations by its emergence from "simple" energies of the form (1.1).

This long history of the Cahn-Hilliard equation and its seemingly unlimited range of application are a major motivation for the first homogenization result derived here in the context of perforated or strongly heterogeneous domains. That is, we study the energy density (1.1) with respect to a perforated domain Ω^ϵ instead of a homogeneous Ω. The parameter $\epsilon > 0$ represents the size of the perforations/heterogeneities. These heterogeneities are defined by a reference cell Y in unit length which represents a single pore in a porous medium for instance. A well accepted approximation is then the periodic covering of the macroscopic porous medium by such a single reference cell ϵY.

We are not aware of any previous work which upscales the Cahn-Hilliard equation in such a setup. Based on the energy density (1.1) we derive the following effective

macroscopic Cahn-Hilliard equation

$$\begin{aligned}\theta_1\frac{\partial}{\partial t}\phi_0 = \operatorname{div}\Big(\Big[\theta_1 f'(\phi_0)\hat{\mathrm{M}} - \Big(2\frac{f(\phi_0)}{\phi_0} - f'(\phi_0)\Big)\hat{\mathrm{M}}_v\Big]\nabla\phi_0\Big) \\ - f'(\phi_0)\operatorname{div}\Big(\hat{\mathrm{M}}_v\nabla\phi_0\Big) + \frac{\lambda^2}{\theta_1}\operatorname{div}\Big(\hat{\mathrm{M}}_w\nabla\Big(\operatorname{div}\Big(\hat{\mathrm{D}}\nabla\phi_0\Big)\Big)\Big),\end{aligned} \tag{1.5}$$

which accounts for periodic microscopic heterogeneities via the correction tensors $\hat{\mathrm{D}}$, $\hat{\mathrm{M}}_v$, and $\hat{\mathrm{M}}_w$ in a systematic way. The parameter θ_1 is the porosity representing the volume fraction $\frac{|\Omega^\epsilon|}{|\Omega|}$ between the region where the phase field variable exists and its topological complement.

The polynom f, defined in (1.2), encloses a set of free energies which allow for the same steps in the rigorous homogenization process leading to the main Theorem 3.2. This theorem states the new effective macroscopic Cahn-Hilliard equation that reliably accounts for strongly perforated domains. It is straightforward to adapt the steps in the upscaling process for higher polynomial degrees in (1.2). Since this article is the first derivation of this kind by the best knowledge of the authors, it provides the basic, algorithmic framework and analytical tools for other choices of f.

So far, homogenization has only been applied to Allen-Cahn (L^2-gradient flow of $E(\phi)$) and Ginzburg-Landau type of equations [5, 6]. These equations are of second order and hence allow for a direct application of parabolic homogenization theory. We also refer the reader to [24] for a physical discussion between the related diffuse interface approximations such as Allen-Cahn, Cahn-Hilliard, and viscous Cahn-Hilliard. An interesting article that derives effective wetting properties with the help of homogenization theory is [2]. In contrast to the considerations here, this article does not rely on the Cahn-Hilliard energy formulation but rather on a interfacial energy alone analyzed with the help of geometric measure theory and gamma convergence, see Section 4.1 for more details.

Finally, we give two direct applications of the effective description (1.5) in the context of wetting. In Corollary 4.4 we present a macroscopic description of wetting dynamics in porous or highly heterogeneous structures. Hereweith, we support a heuristically suggested interface model for imbibition [1, 11]. The basic idea is a slight modification of the free energy (1.1) by an additional term g modeling absorption of one phase (e.g. liquid) or wetting properties of the medium. That means, (1.1) is extended towards,

$$E(\phi) = \frac{\alpha}{2}\phi^2(1-\frac{\beta}{2\alpha}\phi^2) + \lambda^2|\nabla\phi|^2 - g(\mathbf{x})\phi(\mathbf{x},t)\,. \tag{1.6}$$

We remark that depending on the function g, the homogeneous free energy F defined as the potential

$$W(\phi,g) := \frac{\alpha}{2}\phi^2(1-\frac{\beta}{2}\phi^2) - g(\mathbf{x})\phi(\mathbf{x},t)\,,$$

might not have a double-well form anymore. The gradient flow corresponding to (1.6) then reads,

$$\frac{\partial}{\partial t}\phi = \operatorname{div}\Big(\hat{\mathrm{M}}\nabla\big(-\phi+\phi^3-\lambda^2\Delta\phi-g\big)\Big) \quad \text{in } \Omega_T\,. \tag{1.7}$$

The variable g is a random variable, if one considers random media as the authors in [1, 11]. We rigorously recover such a function g after averaging the phase field model (1.3) over a porous medium. It turns out that g contains the upscaled information from the wetting boundary condition $(1.3)_2$. That means, problem (1.3) satisfies asymptotically, i.e., in the limiit $\epsilon \to$ for scaled reference cells ϵY, the following porous media approximation,

$$\begin{aligned}\theta_1 \frac{\partial}{\partial t}\phi_0 = \operatorname{div}\left(\left[\theta_1 f'(\phi_0)\hat{\mathrm{M}} - \left(2\frac{f(\phi_0)}{\phi_0} - f'(\phi_0)\right)\hat{\mathrm{M}}_v\right]\nabla\phi_0\right) \\ - f'(v_0)\operatorname{div}\left(\hat{\mathrm{M}}_v\nabla\phi_0\right) + \frac{\lambda^2}{\theta_1}\operatorname{div}\left(\hat{\mathrm{M}}_w\nabla\left(\operatorname{div}\left(\hat{\mathrm{D}}\nabla\phi_0\right) - g_0\right)\right),\end{aligned} \tag{1.8}$$

where $g_0(\mathbf{x}) := -\frac{\gamma}{C_h}\frac{1}{|Y|}\int_{\partial Y_w^1}\left(a_1\chi_{\partial Y_{w_1}^1}(\mathbf{y}) + a_2\chi_{\partial Y_{w_2}^1}(\mathbf{y})\right)ds(\mathbf{y})$ and the effective mobility tensors $\hat{\mathrm{M}}_\phi, \hat{\mathrm{M}}$, and $\hat{\mathrm{D}}$ are reliably defined by the multi-scale approach applied. The function g_0 is the homogenized wetting boundary condition which accounts for pore surfaces with different wetting properties. The upscaled equation (1.8) shows qualitative agreement with [1, 11]. Moreover, we give a brief generalization towards random porous media at the end and motivate more rigorous considerations.

Let us remark that an extension similar to (1.6) is also suggested for the purpose of pattern formation in non-equilibrium systems in [14]. The only difference is that g is chosen as a diffusive field that linearly responds to changes in ϕ. The purpose of introducing the field g is to extend a Landau-Ginzburg model for second order phase transitions to situations far from equilibrium. The resulting partial differential equations are coupled reaction diffusion systems with numerous applications in physical, chemical and biological sciences.

We introduce two relevant formulations of the Cahn-Hilliard equation in Section 2. The main theorem, which states the new macroscopic Cahn-Hilliard equation, follows in Section 3 and is derived in the last Section Section 5. In Section 4, we apply this new result to wetting problems.

2. Two reformulations of the Cahn-Hilliard equation: Zero mass and splitting In this section we present two equivalent formulations of the Cahn-Hilliard equation. The first aims to achieve solvability in the context of parabolic equations with Lipschitz inhomogeneities and is referred to as the "zero mass formulation". The second, referred to as "splitting formulation", decouples the Cahn-Hilliard equation into two second order problems which allow for a feasible upscaling by the multiple-scale method.

2.1. Zero mass: For solvability In [18], Novick-Cohen achieves well-posedness of the Cahn-Hilliard problem (1.3) rewritten by the following zero mass formulation

$$\textbf{(Zero mass)} \quad \begin{cases} \partial_t v = \operatorname{div}\left(\hat{\mathrm{M}}\nabla\left(bv + h(v) - \lambda^2\Delta v\right)\right) & \text{in } \Omega_T := \Omega\times]0,T[, \\ \nabla_n v = \mathbf{n}\cdot\nabla\Delta v = 0 & \text{on } \partial\Omega_T := \partial\Omega\times]0,T[, \\ v(\mathbf{x},0) = v_0(\mathbf{x}) = \phi_0(\mathbf{x}) - \overline{\phi}, \end{cases} \tag{2.1}$$

where $v(\mathbf{x},t):=\phi(\mathbf{x},t)-\overline{\phi}$, $b:=f'(\phi)$, $h(v):=f(\overline{\phi}+v)-bv$, and by mass conservation of (1.3) we define

$$\frac{1}{|\Omega|}\int_\Omega \phi\, d\mathbf{x}:=\frac{1}{|\Omega|}\int_\Omega \phi_0\, d\mathbf{x}=:\overline{\phi}. \tag{2.2}$$

These definitions imply $bv+h(v)=f(\overline{\phi}+v)$. For $k\geq 0$, we introduce the space

$$H^k_E(\Omega)=\left\{\phi\in H^k(\Omega)\,\middle|\,\nabla_n\phi=0 \text{ and } \overline{\phi}=0\right\}. \tag{2.3}$$

Novick-Cohen verifies in [18] existence of solutions $v\in H^2_E(\Omega)$ of problem (2.1) for $f(\phi)\in C^2_{Lip}(\mathbb{R})$ with $|f(s)|\to\infty$ as $s\to\pm\infty$ and $v(\mathbf{x},0)\in H^2_E(\Omega)$.

[19, 18]

2.2. Splitting: For homogenization The existence result summarized in the previous section enables us to give the following weak formulation of problem (1.3). There exists for all $\varphi\in H^2_E(\Omega)$ a weak solution $v\in H^2_E(\Omega)$ solving the equation

$$\frac{d}{dt}(v,\varphi)+\lambda^2\left(\Delta v,\mathrm{div}\left(\hat{\mathrm{M}}\nabla\varphi\right)\right)=\left(\mathrm{div}\left(\hat{\mathrm{M}}\nabla f(\phi)\right),\varphi\right), \tag{2.4}$$

where we recall that $\phi=\overline{\phi}+v$. The second term motivates to introduce a new variable w defined by the equation

$$\begin{aligned}(-\Delta v,\psi)&=(w,\psi) && \text{for all } \psi\in H^2_E(\Omega),\\ \nabla_n v&=0 && \text{on } \partial\Omega.\end{aligned} \tag{2.5}$$

Equation (2.5) allows also to define the inverse operator $(-\Delta)^{-1}$ by identifying

$$v=(-\Delta)^{-1}w, \tag{2.6}$$

in the $H^2_E(\Omega)$-sense. Since $\psi\in H^2_E(\Omega)$, we can choose test functions $\psi=(-\Delta)^{-1}\xi\in H^2_E(\Omega)$ in (2.5) such that

$$(v,\xi)=\left(-\Delta v,(-\Delta)^{-1}\xi\right)=\left(w,(-\Delta)^{-1}\xi\right)=\left((-\Delta)^{-1}w,\xi\right)\quad\text{for all } \xi\in L^2_E(\Omega), \tag{2.7}$$

where $L^2_E(\Omega):=H^0_E(\Omega)$. Via (2.7) and (2.6) it follows that v is *a.e.* equal to $(-\Delta)^{-1}w$.

With solvability of equation (2.4) and identity (2.7) we are able to introduce the following problem

$$\textbf{(Splitting)}\quad\begin{cases}\partial_t(-\Delta)^{-1}w-\lambda^2\mathrm{div}\left(\hat{\mathrm{M}}\nabla w\right)=\mathrm{div}\left(\hat{\mathrm{M}}\nabla f(\phi)\right) & \text{in } \Omega,\\ \nabla_n w=-\nabla_n\Delta v=0 & \text{on } \partial\Omega_T,\\ -\Delta v=w & \text{in } \Omega,\\ \nabla_n v=g(\mathbf{x}), & \text{on } \partial\Omega_T,\end{cases} \tag{2.8}$$

which is equivalent to (1.3) in the H^2_E-sense and hence for $g=0$ well-posed too [18]. The advantage of (2.8) is that it allows to base our upscaling approach on well-known results from elliptic/parabolic homogenization theory [4, 20].

3. Main results Our main interest is in problem (1.3) for perforated or strongly heterogeneous domains. It is a well accepted approximation to define such domains as the periodic covering of a single reference cell $Y := [0,\ell_1]\times[0,\ell_2]\times\cdots\times[0,\ell_d]$ which defines the characteristic pore geometry for example. Without loss of generality we set $\ell_1=\ell_2=\cdots=\ell_d=1$. The pore and the solid phase of the medium are denoted by Ω^ϵ and B^ϵ, respectively. These sets are defined by,

$$\begin{aligned}\Omega^\epsilon &:= \bigcup_{\mathbf{z}\in\mathbb{Z}^d} \epsilon\left(Y^1+\mathbf{z}\right)\cap\Omega,\\ B^\epsilon &:= \bigcup_{\mathbf{z}\in\mathbb{Z}^d} \epsilon\left(Y^2+\mathbf{z}\right)\cap\Omega = \Omega\setminus\Omega^\epsilon,\end{aligned} \tag{3.1}$$

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).

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

$$\begin{cases} \partial_t\phi_\epsilon = \operatorname{div}\left(\hat{\mathrm{M}}\nabla\left(-\lambda^2\Delta\phi_\epsilon-\phi_\epsilon+\phi_\epsilon^3\right)\right) & \text{in } \Omega^\epsilon,\\ \nabla_n\phi_\epsilon := \mathbf{n}\cdot\nabla\phi_\epsilon = 0 & \text{on } \partial\Omega_T^\epsilon,\\ \nabla_n\Delta\phi_\epsilon = 0 & \text{on } \partial\Omega_T^\epsilon,\\ \phi_\epsilon(\mathbf{x},0)=\phi_0(\mathbf{x}) & \text{on } \Omega^\epsilon. \end{cases} \tag{3.2}$$

Before we state our main result, we need the following

Definition 3.1. *We say that the phase-field ϕ is in local thermodynamic equilibrium if and only if*

$$\frac{\delta E(\phi)}{\delta\phi} = \mu(\phi) = f(\phi)-\lambda^2\Delta\phi = \text{const.}, \tag{3.3}$$

where μ stands for the chemical potential.

Assumption of local thermodynamic equilibrium can be justified on physical and mathematical grounds by the assumed separation of macroscopic and microscopic length scales and the emerging difference in the associated characteristic timescales.

Remark 3.1. *Equilibrium assumptions of the form (3.3) seem to be central for homogenization of models based on thermodynamic principles by the free energy formulations. For example, macroscopic porous media equations for ionic transport based on dilute solution theory [22, 23] require the same type of equilibrium assumptions for mathematical well-posedness.*

Theorem 3.2. (Upscaled Cahn-Hilliard equations) *Let $\hat{\mathrm{M}} = \{\mathrm{m}\delta_{ij}\}_{1\le i,j\le d}$ for $m>0$ be an isotropic mobility tensor. Moreover, we suppose that the phase-field is in local thermodynamic equilibrium, see Definition 3.1.*

Then, the microscopic porous media formulation (3.2) can be effectively approximated by the following macroscopic problem,

$$\begin{cases} \theta_1\frac{\partial\phi_0}{\partial t} = \operatorname{div}\Bigg(\left[\theta_1 f'(\phi_0)\hat{\mathrm{M}} - \left(2\frac{f(\phi_0)}{\phi_0}-f'(\phi_0)\right)\hat{\mathrm{M}}_v\right]\nabla\phi_0\Bigg)\\ \qquad -f'(\phi_0)\operatorname{div}\left(\hat{\mathrm{M}}_v\nabla\phi_0\right)+\frac{\lambda^2}{\theta_1}\operatorname{div}\left(\hat{\mathrm{M}}_w\nabla\left(\operatorname{div}\left(\hat{\mathrm{D}}\nabla\phi_0\right)\right)\right)\Bigg) & \textit{in } \Omega,\\ \nabla_n\phi_0 = \mathbf{n}\cdot\nabla\phi_0 = 0 & \textit{on } \partial\Omega,\\ \nabla_n\Delta\phi_0 = 0 & \textit{on } \partial\Omega, \end{cases} \tag{3.4}$$

where $\theta_1 := \frac{|Y^1|}{|Y|}$ *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* $\hat{\mathrm{M}}_w = \{\mathrm{m}^w_{ik}\}_{1\le i,k\le d}$ *are defined by*

$$\begin{aligned}
\mathrm{d}_{ik} &:= \frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\left(\delta_{ik}-\delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)d\mathbf{y},\\
\mathrm{m}^v_{ik} &:= \frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\mathrm{m}\left(\delta_{ik}-\delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)d\mathbf{y},\\
\mathrm{m}^w_{ik} &:= \frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\mathrm{m}\left(\delta_{ik}-\delta_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right)d\mathbf{y}.
\end{aligned} \tag{3.5}$$

The corrector functions ξ_v^k *and* ξ_w^k *for* $1\le k\le d$ *are solutions of the following reference cell problems*

$$\begin{aligned}
\xi_v^k:\quad &\begin{cases}
-\sum_{i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\delta_{ik}-\delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)=0 & \text{in } Y^1,\\
\sum_{i,j=1}^{d}\mathrm{n}_i\delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}=\mathbf{n}\cdot\nabla\xi_v^k=0 & \text{on } \partial Y_w^1,\\
\xi_v^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_v^k)=0,
\end{cases}\\
\xi_w^k:\quad &\begin{cases}
-\sum_{i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\delta_{ik}(1+\lambda^2\mathrm{m})-\delta_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right)=0 & \text{in } Y^1,\\
\mathbf{n}\cdot\left(\nabla_y\xi_w^k-\mathbf{e}_k(1+\lambda^2\mathrm{m})\right)=0 & \text{on } \partial Y_w^1,\\
\xi_w^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_w^k)=0.
\end{cases}
\end{aligned} \tag{3.6}$$

4. Applications to wetting Due to the freedom in defining the free energy $F(\phi)$ as the precursor of the phase field equation (1.3), one obtains a very general and powerful tool for arbitrary physical, mathematical and computational needs.

By choosing the homogenous free energy F as the standard double well potential

$$F(\phi)=\frac{1}{4}(\phi^2-a^2)^2, \tag{4.1}$$

we are immediately in the position to 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 $(1.3)_2$ with

$$g(\mathbf{x}) := -\frac{\gamma}{C_h}a. \tag{4.2}$$

The parameter C_h is the Cahn number ζ/L_x and $\gamma = 2\sqrt{2}\phi_e/3\sigma_{lg}$ where σ_{lg} denotes the liquid-gas surface tension. It is straightforward to extend (4.2) to more than the two wetting properties a_1 and a_2 introduced for notational brevity in subsequent sections.

At the end of Section 4.1 we briefly connect to results from [2] where a formula for the effective contact angle is derived based on gamma convergence and geometric measure theory. This result is of interest because it gives an understanding for the physically motivated formulas suggested by Wenzel [25] and Cassie and Baxter [10].

4.1. Channel with heterogeneous wetting properties We assume that $\Omega \subset \mathbb{R}^d$ is an arbitrary straight channel with walls having different wetting properties. For simplicity, we assume that these wetting properties repeat periodically along the channel walls. That means, we define

$$\begin{aligned} \Omega &:= \bigcup_{\mathbf{z}\in\mathbb{Z}_N} \epsilon(Y+z)\,, \\ \partial\Omega_w &:= \bigcup_{\mathbf{z}\in\mathbb{Z}_N} \epsilon(\partial Y_w+z)\,, \\ \partial\Omega_l &:= \epsilon(\partial Y_l+N)\,, \\ \partial\Omega_r &:= \epsilon(\partial Y_r+N-1)\,, \end{aligned} \tag{4.3}$$

where $\mathbb{Z}_N := \left\{ z\in\mathbb{Z} \,\middle|\, |z|\le N-1, z\ge -N \right\}$ and for the definition of Y see Figure 4.1.

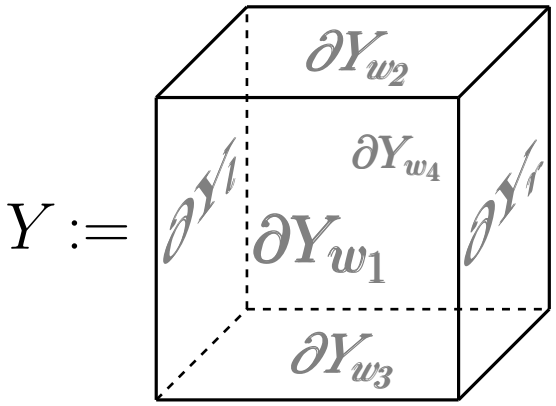

FIG. 4.1. **Reference channel** $Y := [0,1]^d$ *defined by channel entry* ∂Y_l*, channel exit* ∂Y_r*, and wall* $\partial Y_w := \bigcup_{i=1}^4 \partial Y_{w_i}$ *where* $\partial Y_{w_i} := \partial Y_{w_i}^1 \cup \partial Y_{w_i}^2$ *with two different wetting properties* $\partial Y_{w_i}^1$ *and* $\partial Y_{w_i}^2$*.*

In order to derive an effective phase-field model for highly heterogeneous walls, we account for different surface properties on the walls $\partial\Omega_w$, see (4.3), by the following multiscale formulation,

$$\begin{cases} \partial_t(-\Delta)^{-1} w_\epsilon = \operatorname{div}\left(\hat{\mathrm{M}}\nabla\left(\lambda^2 w_\epsilon - \phi_\epsilon + \phi_\epsilon^3\right)\right) & \text{in } \Omega, \\ -\Delta\phi_\epsilon = w_\epsilon & \text{in } \Omega, \\ \mathbf{n}\cdot\mathbf{J}_\epsilon = F_l & \text{on } \partial\Omega_l, \\ \mathbf{n}\cdot\mathbf{J}_\epsilon = 0 & \text{on } \partial\Omega_r, \\ \nabla_n\phi_\epsilon = -\epsilon\frac{\gamma}{C_h}\sum_{i=1}^4 \left(a_1\chi_{\partial\Omega_{w_i}^1}(x/\epsilon) + a_2\chi_{\partial\Omega_{w_i}^2}(x/\epsilon)\right) & \text{on } \partial\Omega_w, \end{cases} \tag{4.4}$$

where $\mathbf{J}_\epsilon$ is defined as the flux $\nabla\left(\lambda^2 w_\epsilon - \phi_\epsilon + \phi_\epsilon^3\right)$.

Problem (4.4) is introduced because it is *a priori* not clear whether oscillations on the solid/void interface, i.e., on the walls $\partial\Omega_w$, also influence the bulk. That means, system (4.4) motivates the intuitive application of formal asymptotic expansions,

$$\begin{aligned} \phi_\epsilon(\mathbf{x},t) &\approx \phi_0(\mathbf{x},x_1/\epsilon,t) + \epsilon\phi_1(\mathbf{x},x_1/\epsilon,t) + \epsilon^2\phi_2(\mathbf{x},x_1/\epsilon,t) + \dots, \\ w_\epsilon(\mathbf{x},t) &\approx w_0(\mathbf{x},x_1/\epsilon,t) + \epsilon w_1(\mathbf{x},x_1/\epsilon,t) + \epsilon^2 w_2(\mathbf{x},x_1/\epsilon,t) + \dots. \end{aligned} \tag{4.5}$$

We remark that (4.5) is only formal because convergence of such series is a priori not guaranteed and boundary layers are not taken into account. We also need to properly define the microscale $x_1/\epsilon =: y_1 \in Y := [0,1]$. We assume that the heterogeneities defined on the wall $\partial\Omega_w$ are periodic in x_1-direction with period $Y = [0,\ell] \cup [\ell,1]$. Our averaging process consists in the usual limit $\epsilon \to 0$ where where the period is scaled by a parameter ϵ, i.e., ϵY. Hence, we cover the walls $\partial\Omega_w$ with smaller and smaller reference cells ϵY whose number goes to ∞ as we pass to the limit $\epsilon \to 0$.

We further need the following

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

REMARK 4.1. *If the Hypothesis* **(HI)** *is violated, then the homogenization limit does not converge towards a unique upscaled problem, see [4]. From a physical point of view, such a restriction arises purely by the averaging method applied. Hence, we define* the unique limit *in the "particular case", i.e., when* **(HI)** *is violated, as we were in the "generic case".*

There exists also a technical way to prevent the particular case mentioned in Remark 4.1. Since $\partial\Omega_w$ consists of parallel walls, a simple rotation R_α allows to prevent a failure of Hypothesis **(HI)**. We can restrict ourselves to a single axial rotation around the x_3-axis for simplicity. In the three dimensional case for example such a rotation can be represented by the matrix,

$$R_\alpha := \left\{ r_\alpha^{kl} \right\}_{1 \le k,l \le d} := \begin{bmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{4.6}$$

COROLLARY 4.2. (Heterogeneous walls) *Without loss of generality we assume that* **(HI)** *holds. The microscopic wall description (4.4) becomes the following upscaled system after averaging over the microscale,*

$$\begin{cases} \partial_t \phi_0 = \operatorname{div}\left(\hat{\mathrm{M}} \nabla \left(-\phi_0 + \phi_0^3 - \lambda^2 \Delta \phi_0 \right) \right) & \text{in } \Omega, \\ \nabla_n \phi_0 = F_l & \text{on } \partial\Omega^l, \\ \nabla_n \phi_0 = 0 & \text{on } \partial\Omega^r, \\ \nabla_n \phi_0 = g_0(x) & \text{on } \partial\Omega_w, \end{cases} \tag{4.7}$$

where

$$g_0 := -\frac{\gamma}{C_h} \frac{1}{|Y|} \int_Y \left(a_1 \chi_{\partial Y_w^1}(y_1) + a_2 \chi_{\partial Y_w^2}(y_1) \right) dy_1 . \tag{4.8}$$

REMARK 4.3. *We note that the oscillations imposed by the wetting boundary conditions (4.4)$_5$ form boundary layers which we a priori neglect by Ansatz (4.5). This might be a reason why we do not recover oscillations in the bulk phase. Hence, a study of possible boundary layers is an interesting topic for future considerations.*

The effective model (4.7) allows us to determine the averaged contact angle via (4.8) as demonstrated in [26]. We can determine via $\gamma := \frac{2\sqrt{2}\phi_e}{3\sigma_{lg}}$ the parameter

$$a = \frac{g_0 C_h}{\gamma}. \tag{4.9}$$

After setting $A=\sqrt{2}\gamma a$, the effective equilibrium contact angle immediately follows by

$$\cos\theta_e = \frac{1}{2}\left[(1+A)^{3/2}-(1-A)^{3/2}\right]. \tag{4.10}$$

We believe that we are able to propose a convenient and feasible alternative to [2] with (4.10) for the computation of effective contact angles. Based on formula (4.8), we are able to analytically compute the contact angle θ_e in contrast to not easily accessible formulas in [2]. The difference between [2] and our result relies on the fact that Alberti and DeSimone work with the interfacial energy

$$E := \sigma_{SL}\,|\Sigma_{SL}| + \sigma_{SV}\,|\Sigma_{SV}| + \sigma_{LV}\,|\Sigma_{LV}| + \text{a.t.}, \tag{4.11}$$

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 $A,B\in\{S,L,V\}$. The letters S,L, and V stand for the solid, liquid, and vapor phase, 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 a sharp interface limit in this context. Moreover, Alberti and DeSimone connect nicely their generally valid homogenized formulas with the classical results from Wenzel [25] and Cassie and Baxter [10]. In fact, they show that the Wenzel and Cassie-Baxter laws represent upper bounds for the effective contact angel formula derived in [2].

4.2. Wetting dynamics in porous media and imbibition As in Section 2.2, we define the porous medium 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. Without loss of generality we set $\ell_1=\ell_2=\cdots=\ell_d=1$. The pore and the solid phase of the medium are denoted by Ω^ϵ and B^ϵ, respectively. These sets are defined by,

$$\begin{aligned}\Omega^\epsilon &:= \bigcup_{\mathbf{z}\in\mathbb{Z}^d} \epsilon\left(Y^1+\mathbf{z}\right)\cap\Omega,\\ B^\epsilon &:= \bigcup_{\mathbf{z}\in\mathbb{Z}^d} \epsilon\left(Y^2+\mathbf{z}\right)\cap\Omega = \Omega\setminus\Omega^\epsilon,\end{aligned} \tag{4.12}$$

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) and we denote by $\partial Y^1_w := \bigcup_{i=1}^N \partial Y^1_{w_i}$ the solid walls or pore surface, see Figure 4.1. The subsets $\partial Y^1_{w_i}$ belong to surfaces with different wetting properties. Correspondingly, the walls $\partial\Omega^\epsilon_{w_i}$ are defined via $\partial Y^1_{w_i}$ of the covering of Ω by Y. Depending on applications, different boundary conditions than $(4.13)_4$ below for wetting can be imposed.

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

$$\begin{cases} \partial_t\phi_\epsilon = \operatorname{div}\left(\hat{\mathrm{M}}\nabla\left(-\lambda^2\Delta\phi_\epsilon-\phi_\epsilon+\phi_\epsilon^3\right)\right) & \text{in } \Omega^\epsilon,\\ \mathbf{n}\cdot\mathbf{J}_\epsilon = F_l & \text{on } \partial\Omega_l,\\ \mathbf{n}\cdot\mathbf{J}_\epsilon = 0 & \text{on } \partial\Omega\setminus\{\partial\Omega_l\cup\partial\Omega^\epsilon_w\},\\ \nabla_n\phi_\epsilon = -\epsilon\frac{\gamma}{C_h}\left(a_1\chi_{\partial\Omega^\epsilon_{w_1}}(x/\epsilon)+a_2\chi_{\partial\Omega^\epsilon_{w_2}}(x/\epsilon)\right) & \text{on } \partial\Omega^\epsilon_w := \partial\Omega^\epsilon_{w_1}\cap\partial\Omega^\epsilon_{w_2}, \end{cases} \tag{4.13}$$

We complement (4.13) with arbitrary initial conditions

$$\phi_\epsilon(0,\mathbf{x}) = \phi_\epsilon^0(\mathbf{x}) \in H_E^2(\Omega)\,. \tag{4.14}$$

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.

COROLLARY 4.4. (Wetting in porous media) *Without loss of generality we can assume that* **(HI)** *holds. Let* $\hat{\mathrm{M}} = \{\mathrm{m}\delta_{ij}\}_{1\le i,j\le d}$ *for* $m>0$ *be an isotropic mobility tensor. Moreover, we suppose that the phase-field is in local thermodynamic equilibrium in the sense of Defintion 3.1.*

Then, the miscroscopic porous media formulation (4.13) has the following leading order asymptotic equation on the macroscale,

$$\begin{cases} \theta_1 \frac{\partial \phi_0}{\partial t} = \mathrm{div}\Big(\Big[\theta_1 f'(\phi_0)\hat{\mathrm{M}} - \Big(2\frac{f(\phi_0)}{\phi_0} - f'(\phi_0)\Big)\hat{\mathrm{M}}_v\Big]\nabla\phi_0 \Big) \\ \qquad -f'(\phi_0)\mathrm{div}\left(\hat{\mathrm{M}}_v\nabla\phi_0\right) + \frac{\lambda^2}{\theta_1}\mathrm{div}\left(\hat{\mathrm{M}}_w\nabla\left(\mathrm{div}\left(\hat{\mathrm{D}}\nabla\phi_0\right) - \tilde{g}_0\right)\right). & \text{in } \Omega, \\ \mathbf{n}\cdot\mathbf{J} = F_l & \text{on } \partial\Omega_l, \\ \nabla_n\phi_0 = \mathbf{n}\cdot\nabla\phi_0 = 0 & \text{on } \partial\Omega\setminus\partial\Omega_l, \\ \nabla_n\Delta\phi_0 = 0, \end{cases} \tag{4.15}$$

where $\theta_1 := \frac{|Y^1|}{|Y|}$ *is the porosity,* $\mathbf{J}$ *the flux corresponding to (4.15)*$_1$*, and the porous media correction tensors* $\hat{\mathrm{D}} := \{\mathrm{d}_{ik}\}_{1\le i,k\le d}$*,* $\hat{\mathrm{M}}_v = \{\mathrm{m}^v_{ik}\}_{1\le i,k\le d}$ *and* $\hat{\mathrm{M}}_w = \{\mathrm{m}^w_{ik}\}_{1\le i,k\le d}$ *are defined in (3.5). The function* $\tilde{g}_0$ *defines the upscaled wetting boundary condition*

$$\tilde{g}_0(\mathbf{x}) := -\frac{\gamma}{C_h}\int_{\partial Y_w^1}\Big(a_1\chi_{\partial Y^1_{w_1}}(\mathbf{y}) + a_2\chi_{\partial Y^1_{w_2}}(\mathbf{y})\Big)\,ds(\mathbf{y}). \tag{4.16}$$

Finally, we motivate that Theorem 4.4 immediately allows for an extension towards random porous media or random wetting properties. Up to this end, one only needs to introduce appropriate random variables such as a random porosity θ_1 or random wall fractions

$$\theta_{w_1} := \frac{\left|\partial Y^1_{w_1}\right|}{|\partial Y^1_w|} \qquad \text{and} \qquad \theta_{w_2} := \frac{\left|\partial Y^1_{w_2}\right|}{|\partial Y^1_w|}\,. \tag{4.17}$$

In fact, with the wall fractions (4.17) we can redefine g_0 in (4.16) by

$$\alpha(\mathbf{x}) := -\frac{\gamma}{C_h}\left(a_1\theta_{w_1}(\mathbf{x}) + a_2\theta_{w_2}(\mathbf{x})\right), \tag{4.18}$$

where $\theta_{w_i}(\mathbf{x})$ for $i=1,2$ denote space dependent random variables characterizing the wall fractions (4.17). It is also possible to define the parameters a_1 and a_2 as random variables for the purpose of modeling uncertainties in the material's wetting properties. Equation (4.18) demonstrates that homogenization allows to reliably introduce and consistently define the variable α suggested in [1, 11], see (1.6). However, we remark that rigorous stochastic homogenization theory restricts to homogeneous random variables and imposes additional constraints such as a stationary ergodic setting which is equivalent to the periodicity requirement in the deterministic case, see [4]. Such rigorous derivations also start with the microscopic formulation (4.13).

5. Derivation of Theorem 3.2 We define the micro-scale $\frac{\mathbf{x}}{\epsilon} =: \mathbf{y} \in Y$ such that the following multiscale properties for spatial differentiation hold,

$$\begin{aligned} \frac{\partial f_\epsilon(\mathbf{x})}{\partial x_i} &= \frac{1}{\epsilon}\frac{\partial f}{\partial y_i}(\mathbf{x},\mathbf{x}/\epsilon) + \frac{\partial f}{\partial x_i}(\mathbf{x},\mathbf{x}/\epsilon), \\ \nabla f_\epsilon(\mathbf{x}) &= \frac{1}{\epsilon}\nabla_y(\mathbf{x},\mathbf{x}/\epsilon) + \nabla_x(\mathbf{x},\mathbf{x}/\epsilon), \end{aligned} \tag{5.1}$$

where $f_\epsilon(\mathbf{x}) = f(\mathbf{x},\mathbf{y})$ is an arbitrary function depending on two variables $\mathbf{x}\in\Omega$, $\mathbf{y}\in Y$. The Laplace operators Δ and $\operatorname{div}\left(\hat{\mathrm{M}}\nabla\right)$ then behave according to (5.1) as,

$$\begin{aligned} \mathcal{A}_0 &= -\textstyle\sum_{i,j=1}^d \frac{\partial}{\partial y_i}\left(\delta_{ij}\frac{\partial}{\partial x_j}\right), & \mathcal{B}_0 &= -\textstyle\sum_{i,j=1}^d \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial}{\partial y_j}\right), \\ \mathcal{A}_1 &= -\textstyle\sum_{i,j=1}^d \left[\frac{\partial}{\partial x_i}\left(\delta_{ij}\frac{\partial}{\partial y_j}\right)\right. & \mathcal{B}_1 &= -\textstyle\sum_{i,j=1}^d \left[\frac{\partial}{\partial x_i}\left(\mathrm{m}_{ij}\frac{\partial}{\partial y_j}\right)\right. \\ &\quad \left. + \frac{\partial}{\partial y_i}\left(\delta_{ij}\frac{\partial}{\partial x_j}\right)\right], & &\quad \left. + \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial}{\partial x_j}\right)\right], \\ \mathcal{A}_2 &= -\textstyle\sum_{i,j=1}^d \frac{\partial}{\partial x_j}\left(\delta_{ij}\frac{\partial}{\partial x_j}\right), & \mathcal{B}_2 &= -\textstyle\sum_{i,j=1}^d \frac{\partial}{\partial x_j}\left(\mathrm{m}_{ij}\frac{\partial}{\partial x_j}\right), \end{aligned} \tag{5.2}$$

such that we can define $\mathcal{A}_\epsilon := \epsilon^{-2}\mathcal{A}_0 + \epsilon^{-1}\mathcal{A}_1 + \mathcal{A}_2$ and correspondingly $\mathcal{B}_\epsilon$. Hence, it holds for the Laplace operator that $\Delta f_\epsilon(\mathbf{x}) = \mathcal{A}_\epsilon f(\mathbf{x},\mathbf{y})$. We recall that $\phi = \overline{\phi} + v$ and hence $\phi^\epsilon \approx \phi_0 + \epsilon\phi_1 + \epsilon^2\phi_2 + \dots$ where

$$\phi_0 = \overline{\phi} + v_0, \qquad \phi_1 = v_1, \qquad \phi_2 = v_2, \qquad \text{and so on.} \tag{5.3}$$

Inserting the formal asymptotic expansions

$$\begin{aligned} w^\epsilon &\approx w_0(\mathbf{x},\mathbf{y},t) + \epsilon w_1(\mathbf{x},\mathbf{y},t) + \epsilon^2 w_2(\mathbf{x},\mathbf{y},t), \\ \phi^\epsilon &\approx \phi_0(\mathbf{x},\mathbf{y},t) + \epsilon\phi_1(\mathbf{x},\mathbf{y},t) + \epsilon^2\phi_2(\mathbf{x},\mathbf{y},t), \end{aligned} \tag{5.4}$$

into (2.8) and using (5.2) provides the following sequence of problems after equating terms of equal power in ϵ, that means,

$$\mathcal{O}(\epsilon^{-2}): \quad \begin{cases} \mathcal{B}_0 w_0 = \mathcal{B}_0 f(\phi_0) & \text{in } Y^1, \\ \quad \text{no flux b.c.}, & \\ \quad w_0 \text{ is } Y^1\text{-periodic}, & \\ \mathcal{A}_0 v_0 = 0 & \text{in } Y^1, \\ \quad \nabla_n v_0 = 0 & \text{on } \partial Y_w^1, \\ \quad \phi_0 \text{ is } Y^1\text{-periodic}, & \end{cases} \tag{5.5}$$

$$\mathcal{O}(\epsilon^{-1}): \quad \begin{cases} \mathcal{B}_0 w_1 = -\mathcal{B}_1 w_0 - \mathcal{B}_0\left[f(\phi_0)\frac{\phi_1}{\phi_0}\right] - \mathcal{B}_1 f(\phi_0) & \text{in } Y^1, \\ \quad \text{no flux b.c.}, & \\ \quad w_1 \text{ is } Y^1\text{-periodic}, & \\ \mathcal{A}_0 v_1 = -\mathcal{A}_1 v_0 & \text{in } Y^1, \\ \quad \nabla_n v_1 = 0 & \text{on } \partial Y_w^1, \\ \quad \phi_1 \text{ is } Y^1\text{-periodic}, & \end{cases} \tag{5.6}$$

$$\mathcal{O}(\epsilon^0)\colon\quad \begin{cases} \mathcal{B}_0 w_2 = -\lambda^2(\mathcal{B}_2 w_0 + \mathcal{B}_1 w_1) \\ \qquad\qquad -\mathcal{B}_0\left[\frac{1}{2}f''(\phi_0)\phi_1^2 + f'(\phi_0)\phi_2\right] \\ \qquad\qquad -\mathcal{B}_1\left[f(\phi_0)\frac{\phi_1}{\phi_0}\right] - \mathcal{B}_2 f(\phi_0) - \partial_t(-\Delta)^{-1}w_0 & \text{in } Y^1, \\ \quad \text{no flux b.c.}, & \\ \quad w_2 \text{ is } Y^1\text{-periodic}, & \\ \mathcal{A}_0 v_2 = -\mathcal{A}_2 v_0 - \mathcal{A}_1 v_1 + w_0 & \text{in } Y^1, \\ \quad \nabla_n v_2 = g_\epsilon & \text{on } \partial Y_w^1, \\ \quad \phi_2 \text{ is } Y^1\text{-periodic}, & \end{cases} \tag{5.7}$$

where in (5.7) the following relation is applied,

$$\frac{1}{2}f''(\phi_0)\phi_1^2 + f'(\phi_0)\phi_2 = a_1\phi_2 + a_2\left(2\phi_2\phi_0 + \phi_1^2\right) + 3a_3\left(\phi_2\phi_0^2 + \phi_0\phi_1^2\right). \tag{5.8}$$

The first problem (5.5) is of the well-known form from elliptic homogenization theory and immediately implies that the leading order approximation is independent of the microscale $\mathbf{y}$. This fact and the linear structure of (5.6) suggests the following Ansatz for w_1 and ϕ_1, i.e.,

$$\begin{aligned} w_1(\mathbf{x},\mathbf{y},t) &= -\sum_{k=1}^{d}\xi_w^k(\mathbf{y})\frac{\partial w_0}{\partial x_k}(\mathbf{x},t), \\ v_1(\mathbf{x},\mathbf{y},t) &= -\sum_{k=1}^{d}\xi_v^k(\mathbf{y})\frac{\partial v_0}{\partial x_k}(\mathbf{x},t) = -\sum_{k=1}^{d}\xi_v^k(\mathbf{y})\frac{\partial \phi_0}{\partial x_k}(\mathbf{x},t) = \phi_1(\mathbf{x},\mathbf{y},t). \end{aligned} \tag{5.9}$$

Inserting (5.9) into (5.6) 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,

$$\xi_\phi\colon\quad \begin{cases} -\sum_{i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right) = \\ \qquad = -\operatorname{div}\left(\mathbf{e}_k - \nabla_y \xi_v^k\right) = 0 & \text{in } Y^1, \\ \mathbf{n}\cdot\left(\nabla\xi_v^k + \mathbf{e}_k\right) = 0 & \text{on } \partial Y_w^1, \\ \xi_v^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_v^k) = 0. & \end{cases} \tag{5.10}$$

This reference cell problem can be solved numerically for example. In the case of straight or perturbed straight channels one can find computed results in the literature, see [3] for example.

The reference cell problem for ξ_w is much more difficult since it depends on the solutions of (5.10). We first write $(5.6)_1$ in explicit terms,

$$\begin{aligned} \sum_{k,i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right)\frac{\partial w_0}{\partial x_k} &= \sum_{i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial w_0}{\partial x_j}\right) \\ &\quad - \frac{f(\phi_0)}{\phi_0}\sum_{k,i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\frac{\partial \phi_0}{\partial x_k} \\ &\quad + \sum_{k,i,j=1}^{d}\frac{\partial}{\partial y_i}\left(f'(\phi_0)\mathrm{m}_{ij}\frac{\partial \phi_0}{\partial x_i}\right). \end{aligned} \tag{5.11}$$

At this point a major problem is the dependence on ϕ_0 in problem (5.14). In order to reduce this complexity, we need the chemical potential,

$$\frac{\delta E(v)}{\delta v} = \mu(v) = f(\phi) - \lambda^2 \Delta v. \tag{5.12}$$

In the case of thermodynamic equilibrium, the quantity μ is constant. Hence, it holds that,

$$f'(\phi)\frac{\partial \phi}{\partial x_k} = f'(\phi)\frac{\partial v}{\partial x_k} = \lambda^2 \frac{\partial w}{\partial x_k} \quad \text{for } 1 \le k \le d. \tag{5.13}$$

If identity (5.13) is valid in each reference cell Y (that means, 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 replace $\frac{\partial w_0}{\partial x_k}$ in (5.14) such that we can simplify (5.11) with $(5.6)_2$ to,

$$\begin{cases} -\sum_{i,j,k=1}^d \frac{\partial}{\partial y_i}\left(\delta_{ik} - \delta_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right) = \lambda^2 \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ik} - \frac{f(\phi_0)}{f'(\phi_0)\phi_0}\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right) & \text{in } Y^1, \\ \sum_{i,j,k=1}^d \mathrm{n}_i \Big(\Big(\delta_{ij}\frac{\partial \xi_w^k}{\partial y_j} - \delta_{ik}\Big) \\ \qquad -\lambda^2 \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i}\left(\mathrm{m}_{ik} - \frac{f(\phi_0)}{f'(\phi_0)\phi_0}\mathrm{m}_{ij}\frac{\partial \xi_v^k}{\partial y_j}\right)\Big) = 0 & \text{on } \partial Y_w^1, \\ \xi_w^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_w^k) = 0. \end{cases} \tag{5.14}$$

Via (1.2) it holds that,

$$\frac{f(s)}{f'(s)s} = \frac{F'(s)}{F''(s)s}, \tag{5.15}$$

and since we are in local thermodynamic equilibrium, ϕ_0 minimizes F and hence is a critical point of $F' = f$ such that

$$\frac{f(\phi_0)}{f'(\phi_0)\phi_0} = \frac{F'(\phi_0)}{F''(\phi_0)\phi_0} = 0. \tag{5.16}$$

Hence, (5.14) reduces for $1 \le k \le d$ to

$$\xi_w: \quad \begin{cases} -\sum_{i,j=1}^d \frac{\partial}{\partial y_i}\left(\delta_{ik}(1+\lambda^2\mathrm{m}) - \delta_{ij}\frac{\partial \xi_w^k}{\partial y_j}\right) = 0 & \text{in } Y^1, \\ \mathbf{n}\cdot\left(\nabla_y \xi_w^k - \mathbf{e}_k(1+\lambda^2\mathrm{m})\right) = 0 & \text{on } \partial Y_w^1, \\ \xi_w^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_w^k) = 0. \end{cases} \tag{5.17}$$

However, (5.17) still allows with the paramter $\lambda^2 > 0$ for a further sharp interface approximation on the level of the reference cells only. The solution of the resulting limit problem after passing $\lambda \to 0$ is equal to ξ_v^k. This becomes immediately evident if one recognizes that (5.17) and (5.10) are identical after such a limit. The thermodynamic equilibrium (5.12) is necessary to arrive at (5.17) and hence also guarantees well-posedness.

It leaves to study the last problem (5.7). Again, equation $(5.7)_2$ is much simpler because it is standard in elliptic homogenization theory. Standard existence and uniqueness results (Fredholm alternative/Lax-Milgram) immediately guarantee solvability by verifying that the right hand side in (5.7) is zero as an integral over Y^1. This means,

$$-\sum_{i,j=1}^d \int_{Y^1} \frac{\partial}{\partial x_i}\left(\delta_{ij}\left(\frac{\partial v_1}{\partial y_j} + \frac{\partial v_0}{\partial x_j}\right)\right) d\mathbf{y} - \tilde{g}_0 = \left|Y^1\right| w_0 + \tilde{g}_0, \tag{5.18}$$

where $\tilde{g}_0 := -\frac{\gamma}{C_h}\int_{\partial Y^1}\left(a_1\chi_{\partial Y^1_{w_1}} + a_1\chi_{\partial Y^1_{w_2}}\right)do(\mathbf{y})$. We obtain the following effective equation for the phase field,

$$-\sum_{i,k=1}^{d}\left[\sum_{j=1}^{d}\int_{Y^1}\left(\delta_{ik}-\delta_{ij}\frac{\partial\xi_v^k}{\partial y_j}\right)d\mathbf{y}\right]\frac{\partial^2 v_0}{\partial x_i\partial x_k} = \left|Y^1\right| w_0\,, \tag{5.19}$$

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,

$$|Y|\,\mathrm{d}_{ik} := \sum_{j=1}^{d}\int_{Y^1}\left(\delta_{ik}-\delta_{ij}\frac{\partial\xi_v^k}{\partial y_j}\right)d\mathbf{y}\,. \tag{5.20}$$

Equations (5.19) and (5.20) provide the final form of the upscaled equation for ϕ_0, i.e.,

$$-\Delta_0 v_0 := -\mathrm{div}\left(\hat{\mathrm{D}}\nabla v_0\right) = \theta_1 w_0 + \tilde{g}_0\,. \tag{5.21}$$

The upscaled equation for w is again a result of the Fredholm alternative, i.e., a solvability criterion on equation $(5.7)_1$. This means that we require,

$$\begin{aligned}\int_{Y^1}\Big\{-\lambda^2(\mathcal{B}_2 w_0+\mathcal{B}_1 w_1)-\mathcal{B}_0\left(\frac{1}{2}f''(\phi_0)\phi_1^2+f'(\phi_0)\phi_2\right)\\ -\mathcal{B}_1\left[f(\phi_0)\frac{\phi_1}{\phi_0}\right]-\mathcal{B}_2 f(\phi_0)-\partial_t(-\Delta)^{-1}w_0\Big\}d\mathbf{y}=0\,.\end{aligned} \tag{5.22}$$

Let us start with the terms that are easily averaged over the reference cell Y. The first two terms in (5.22) can be rewritten by,

$$\begin{aligned}\int_{Y^1}-(\mathcal{B}_2 w_0+\mathcal{B}_1 w_1)\,d\mathbf{y} = -\sum_{i,k=1}^{d}\left[\sum_{j=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ik}-\mathrm{m}_{ij}\frac{\partial\xi_w^k}{\partial y_j}\right)d\mathbf{y}\right]\frac{\partial^2 w_0}{\partial x_i\partial x_k}\\ = -\mathrm{div}\left(\hat{\mathrm{M}}_w\nabla w_0\right),\end{aligned} \tag{5.23}$$

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

$$\mathrm{m}^w_{ik} := \frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ik}-\mathrm{m}_{ij}\frac{\partial\xi_w^k}{\partial y_j}\right)d\mathbf{y}\,. \tag{5.24}$$

The next terms in (5.22) become

$$\begin{aligned}-\mathcal{B}_1\left[f(\phi_0)\frac{\phi_1}{\phi_0}\right]-\mathcal{B}_2 f(\phi_0) = \sum_{k,i,j=1}^{d}\Bigg\{-\frac{\partial}{\partial x_i}\left(\left[\mathrm{m}_{ij}\frac{f(\phi_0)}{\phi_0}\frac{\partial\xi_v^k}{\partial y_j}\right]\frac{\partial\phi_0}{\partial x_k}\right)\\ +\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{f(\phi_0)}{\phi_0}\frac{\partial\phi_1}{\partial x_j}\right)+\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\phi_1\frac{\partial(f(\phi_0)/\phi_0)}{\partial x_j}\right)\Bigg\}\\ +\sum_{k,i,j=1}^{d}\frac{\partial}{\partial x_i}\left(\mathrm{m}_{ij}f'(\phi_0)\frac{\partial\phi_0}{\partial x_j}\right),\end{aligned} \tag{5.25}$$

and a subsequent integration of the right hand side of (5.25) over the reference cell Y gives

$$\begin{aligned}
&\sum_{i,k=1}^{d}\frac{\partial}{\partial x_i}\left(\left[\sum_{j=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ik}f'(\phi_0)-\mathrm{m}_{ij}\frac{f(\phi_0)}{\phi_0}\frac{\partial\xi_v^k}{\partial y_j}\right)d\mathbf{y}\right]\frac{\partial\phi_0}{\partial x_j}\right)\\
&-\sum_{k,j=1}^{d}\left[\sum_{i=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ij}\frac{\partial\xi_v^k}{\partial y_i}\right)d\mathbf{y}\right]\frac{f(\phi_0)}{\phi_0}\frac{\partial^2\phi_0}{\partial x_k\partial x_j}\\
&-\sum_{k,j=1}^{d}\left[\sum_{i=1}^{d}\int_{Y^1}\left(\frac{\partial\xi_v^k}{\partial y_i}\mathrm{m}_{ij}\right)d\mathbf{y}\right]\frac{\partial(f(\phi_0/\phi_0)}{\partial x_j}\frac{\partial\phi_0}{\partial x_k},
\end{aligned}\tag{5.26}$$

where the last two terms further simplify to

$$-\sum_{k,j=1}^{d}\frac{\partial}{\partial x_j}\left(\frac{f(\phi_0)}{\phi_0}\left[\sum_{i=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ij}\frac{\partial\xi_v^k}{\partial y_i}\right)d\mathbf{y}\right]\frac{\partial\phi_0}{\partial x_k}\right).\tag{5.27}$$

With (5.27) we can finally write (5.25) in the following compact way

$$\begin{aligned}
&\frac{1}{|Y|}\int_{Y^1}\left(-\mathcal{B}_1\left[f(\phi_0)\frac{\phi_1}{\phi_0}\right]-\mathcal{B}_2f(\phi_0)\right)d\mathbf{y}\\
&=\sum_{i,k=1}^{d}\frac{\partial}{\partial x_i}\left(\left[\frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ik}f'(\phi_0)-2\mathrm{m}_{ij}\frac{f(\phi_0)}{\phi_0}\frac{\partial\xi_v^k}{\partial y_j}\right)d\mathbf{y}\right]\frac{\partial\phi_0}{\partial x_j}\right)\\
&=\operatorname{div}\left(\left[\theta_1f'(\phi_0)\hat{\mathrm{M}}-2\frac{f(\phi_0)}{\phi_0}\hat{\mathrm{M}}_v\right]\nabla\phi_0\right),
\end{aligned}\tag{5.28}$$

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

$$\mathrm{m}_{ik}^v:=\frac{1}{|Y|}\sum_{j=1}^{d}\int_{Y^1}\left(\mathrm{m}_{ij}\frac{\partial\xi_v^k}{\partial y_j}\right)d\mathbf{y}.\tag{5.29}$$

It leaves to elucidate the last term in (5.22). Using $(5.7)_2$, then we have,

$$\begin{aligned}
-\mathcal{B}_0\left[\frac{1}{2}f''(\phi_0)\phi_1^2+f'(\phi_0)\phi_2\right]&=\sum_{i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\phi_1\frac{\partial\phi_1}{\partial y_j}\right)f''(\phi_0)\\
&\quad+\sum_{i,j=1}^{d}\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial\phi_2}{\partial y_j}\right)f'(\phi_0)\\
&=\sum_{i,j=1}^{d}-\left[\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\phi_1\frac{\partial\xi_v^k}{\partial y_j}\right)\right]f''(\phi_0)\frac{\partial\phi_0}{\partial x_k}+m(\mathcal{A}_2\phi_0+\mathcal{A}_1\phi_1-w_0).
\end{aligned}\tag{5.30}$$

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 (5.10) in the term with the summation, then the following simplification of its summands

can be made,

$$\left[\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\phi_1\frac{\partial\xi_v^k}{\partial y_j}\right)\right]f''(\phi_0)\frac{\partial\phi_0}{\partial x_k}=\left[\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ik}\phi_1\right)\right]\frac{\partial f'(\phi_0)}{\partial x_k}=-\left[\mathrm{m}_{ik}\frac{\partial\xi_v^l}{\partial y_i}\right]\frac{\partial\phi_0}{\partial x_l}\frac{\partial f'(\phi_0)}{\partial x_k}$$
$$=-\frac{\partial}{\partial x_k}\left(f'(\phi_0)\left[\mathrm{m}_{ik}\frac{\partial\xi_v^l}{\partial y_i}\right]\frac{\partial\phi_0}{\partial x_l}\right)+f'(\phi_0)\frac{\partial}{\partial x_k}\left(\left[\mathrm{m}_{ik}\frac{\partial\xi_v^l}{\partial y_i}\right]\frac{\partial\phi_0}{\partial x_l}\right). \tag{5.31}$$

The last term in (5.30) vanishes by the Fredholm alternative guaranteeing solvability of $(5.7)_2$, i.e.,

$$0=m\int_{Y^1}\left(\mathcal{A}_2\phi_0+\mathcal{A}_1\phi_1-w_0\right)d\mathbf{y}=-\sum^d\frac{\partial}{\partial x_i}\left(\left|Y^1\right|\mathrm{m}_{ij}\frac{\partial\phi_0}{\partial x_j}\right)f'(\phi_0)$$
$$-\left(\sum_{i,j=1}^d\int_{Y^1}\left[\frac{\partial}{\partial x_i}\left(\mathrm{m}_{ij}\frac{\partial\phi_1}{\partial y_j}\right)+\frac{\partial}{\partial y_i}\left(\mathrm{m}_{ij}\frac{\partial\phi_1}{\partial x_j}\right)\right]d\mathbf{y}-\left|Y^1\right|w_0\right)f'(\phi_0). \tag{5.32}$$

Hence, (5.30) admits after integrating over Y the following compact form,

$$\frac{1}{|Y|}\int_{Y^1}-\mathcal{B}_0\left[\frac{1}{2}f''(\phi_0)\phi_1^2+f'(\phi_0)\phi_2\right]d\mathbf{y}=\mathrm{div}\left(f'(\phi_0)\hat{\mathrm{M}}_v\nabla\phi_0\right)$$
$$-f'(\phi_0)\mathrm{div}\left(\hat{\mathrm{M}}_v\nabla\phi_0\right), \tag{5.33}$$

which then sets (5.30) to zero. These considerations finally lead to the following effective equation for ϕ_0, i.e.,

$$\theta_1\frac{\partial\phi_0}{\partial t}=\mathrm{div}\left(\left[\theta_1f'(\phi_0)\hat{\mathrm{M}}-\left(2\frac{f(\phi_0)}{\phi_0}-f'(\phi_0)\right)\hat{\mathrm{M}}_v\right]\nabla\phi_0\right)$$
$$-f'(\phi_0)\mathrm{div}\left(\hat{\mathrm{M}}_v\nabla\phi_0\right)+\frac{\lambda^2}{\theta_1}\mathrm{div}\left(\hat{\mathrm{M}}_w\nabla\left(\mathrm{div}\left(\hat{\mathrm{D}}\nabla\phi_0\right)-\tilde{g}_0\right)\right). \tag{5.34}$$

The solvability of (5.34) follows along with the arguments in [18] since we at least assume that $f\in C^2_{Lip}(\mathbb{R})$. In fact, one only needs to prove a local Lipschitz continuity of the first two terms on the right hand side of (5.34). For further details we refer the interested reader to Section (2.1) and [18].

6. Conclusion The main result of this article is the rigorous derivation of an effective macroscopic Cahn-Hilliard equation. The proof is valid for free energies F defined by arbitrary polynomials up to 4-th order. This polynomial free energy F includes the well-known double well potential which is the basis for a large class of two-phase problems. Such a broad range of applications is possible due to its capability of modeling interfacial dynamics of two-phase composites. Moreover, the steps in the upscaling process give the basic algorithmic framework and analytical tools for other free energies F.

The new Cahn-Hilliard formulation brings an essential numerical advantage. It allows for efficient low dimensional computations of two-phase transport through porous media for example. Moreover, it provides systematically effective transport coefficients like diffusion and mobility tensors. We further apply the 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 channles with strongly heterogeneous walls for instance. An motivation that the new upscaled Cahn-Hilliard equation follows along physical laws is given by its application to imbibition [1]. We recover by mathematical homogenization the same equation which was suggested in [1] based on ad-hoc physical arguments.

There are of course open questions and future perspectives. In applications, it is very interesting to extend the porous media formulation to fluid flow. It is well known that such an extension is very involved, since additional physical phenomena like diffusion-dispersion effects arise. It is still not entirely clear how one reliably can account for such phenomena.

Even without fluid flow, the new equations enable to gain insight into interfacial dynamics in porous media for instance. Two- or three-dimensional numerical results of wetting phenomena in porous media allow to track the phase interface of an arbitrary three-phase composite, i.e. the porous medium, and arbitrary two phases in pore space. Such an 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.

REFERENCES

[1] T Ala-Nissila, Sami Majaniemi, and Ken Elder. Phase-field modeling of dynamical interface phenomena in fluids. *Lecture Notes in Physics*, 640:357–388, 2004.

[2] G. Alberti and a. DeSimone. Wetting of rough surfaces: a homogenization approach. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 461(2053):79–97, January 2005.

[3] J.-L. Auriault and Jolanta Lewandowska. Effective Diffusion Coefficient: From Homogenization to Experiment. *Transport in Porous Media*, 27(2):205–223, 1997.

[4] A. Bensoussans, J.L. L. Lions, and G. Papanicolaou. *Analysis for Periodic Structures*. North-Holland Publishing Company, North-Holland, Amsterdam, 1978.

[5] L. Berlyand and E. Khruslov. Homogenization of harmonic maps and superconducting composites. *SIAM Journal on Applied Mathematics*, 59(5):1892–1916, 1999.

[6] Leonid Berlyand, Doina Cioranescu, and Dmitry Golovaty. Homogenization of a Ginzburg-Landau functional. *Comptes Rendus Mathematique*, 340(1):87–92, 2005.

[7] Andrea L Bertozzi, Selim Esedoglu, and Alan Gillette. Inpainting of binary images using the Cahn-Hilliard equation. *IEEE transactions on image processing : a publication of the IEEE Signal Processing Society*, 16(1):285–91, January 2007.

[8] M. Burger, Sh. Chu, P. Markowich, and C.-B. Schonlieb. The Willmore functional and instabilities in the Cahn-Hilliard equation. *preprint*.

[9] John W. Cahn and John E. Hilliard. Free Energy of a Nonuniform System. I. Interfacial Free Energy. *The Journal of Chemical Physics*, 28(2):258, 1958.

[10] A. B. D. Cassie and S. Baxter. Wettability of porous surfaces. *Transactions of the Faraday Society*, 40(5):546, 1944.

[11] M. Dubé, M. Rost, K. Elder, M. Alava, S. Majaniemi, and T. Ala-Nissila. Liquid Conservation and Nonlocal Interface Dynamics in Imbibition. *Physical Review Letters*, 83(8):1628–1631, August 1999.

[12] C. Eck, M. Fontelos, G. Grün, F. Klingbeil, and O. Vantzos. On a phase-eld model for electrowetting. *Interfaces and Free Boundaries*, 11:259–290, 2009.

[13] P. C. Fife. Dynamical aspects of the Cahn-Hilliard equation. In *Barrett Lectures, University of Tennesse*, 1991.

[14] A. Hagberg and E. Meron. Domain walls in nonequilibrium systems and the emergence of persistent patterns. *Physical Review E*, 48(2):705–708, 1993.

[15] Richard Jordan, David Kinderlehrer, and Felix Otto. The Variational Formulation of the Fokker-Planck Equation. *SIAM Journal on Mathematical Analysis*, 29(1):1, 1998.

[16] D. Kinderlehrer and N.J. Walkington. Approximation of parabolic equations using the Wasserstein metric. *M2AN*, 33(4):837–852, 1999.

[17] John Lowengrub, Andreas Rätz, and Axel Voigt. Phase-field modeling of the dynamics of mul-

ticomponent vesicles: Spinodal decomposition, coarsening, budding, and fission. *Physical Review E*, 79(3):1–13, March 2009.
[18] A. Novick-Cohen. On Cahn-Hilliard type equations. *Nonlinear Analysis: Theory, Methods & Applications*, 15(9):797–814, 1990.
[19] A. Novick-Cohen and L. A. Peletier. The steady states of one dimensional Sivashinsky equations. *Applied Mathematics Letters*, 4(3):69–71, 1991.
[20] G A Pavliotis and A M Stuart. *Multiscale methods: averaging and homogenization*. 2008.
[21] T Preusser, M Droske, C S Garbe, A Telea, and M Rumpf. A Phase Field Method for Joint Denoising, Edge Detection, and Motion Estimation in Image Sequence Processing. *SIAM Journal on Applied Mathematics*, 68(3):599, 2008.
[22] M. Schmuck. A new upscaled Poisson-Nernst-Planck system for strongly oscillating potentials. *submitted*, 2011.
[23] M. Schmuck and M. Z. Bazant. Effective equations for electrochemical transport in porous media. *submitted*, 2011.
[24] J. E. Taylor and J. W. Cahn. Linking anisotropic sharp and diffuse surface motion laws via gradient flows. *Journal of Statistical Physics*, 77(1-2):183–197, October 1994.
[25] R. N. Wenzel. Resistence of solid surfaces to wetting by water. *Ind. Engng Chem.*, 28:988–994, 1936.
[26] Christophe Wylock, Marc Pradas, Benoit Haut, Pierre Colinet, and Serafim Kalliadasis. Disorder-induced hysteresis and nonlocality of contact line motion in chemically heterogeneous microchannels. *preprint*, pages 1–9, 2011.

Acknowledgement.