

1           **RATE OF CONVERGENCE OF GENERAL PHASE FIELD**  
2           **EQUATIONS IN STRONGLY HETEROGENEOUS MEDIA**  
3           **TOWARDS THEIR HOMOGENIZED LIMIT\***

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5           **Abstract.** Over the last few decades, phase-field equations have found increasing applicability  
6 in a wide range of mathematical-scientific fields (e.g. geometric PDEs and mean curvature flow,  
7 materials science for the study of phase transitions) but also engineering ones (e.g. as a computational  
8 tool in chemical engineering for interfacial flow studies). Here, we focus on phase-field equations  
9 in strongly heterogeneous materials with perforations such as porous media. To the best of our  
10 knowledge, we provide the first derivation of error estimates for fourth order, homogenized, and  
11 nonlinear evolution equations. Our fourth order problem induces a slightly lower convergence rate,  
12 i.e.,  $\epsilon^{1/4}$ , where  $\epsilon$  denotes the material's specific heterogeneity, than established for second-order  
13 elliptic problems (e.g. [61]) for the error between the effective macroscopic solution of the (new)  
14 upscaled formulation and the solution of the microscopic phase field problem. We hope that our  
15 study will motivate new modelling, analytic, and computational perspectives for interfacial transport  
16 and phase transformations in strongly heterogeneous environments.

17           **Key words.** upscaling, porous media, phase field, free energy, homogenization

18           **AMS subject classifications.** 68Q25, 68R10, 68U05

19           **1. Introduction.** We consider the well-accepted Cahn-Hilliard/diffuse-interface  
20 formulation [9, 57] for studying the evolution of interfaces between different phases.  
21 Its broad applicability together with increasing computational power have enabled  
22 its use to new and increasingly complex scientific and engineering problems such  
23 as the computation of transport equations in porous media [42] which represents a  
24 numerically very demanding, high-dimensional multiscale problem [26]. The purpose  
25 of the present work is to rigorously and systematically provide a reliable effective  
26 macroscopic description of how multiple phases invade strongly heterogeneous media,  
27 such as porous materials for instance.

28           The cornerstone of phase-field models is the abstract energy density

29 (1)                           
$$e(\phi) := \frac{1}{\lambda} F(\phi) + \frac{\lambda}{2} |\nabla\phi|^2 ,$$

30 where  $\phi := \frac{c_\beta}{c_\alpha + c_\beta}$  is a reduced order parameter representing the fraction of species  
31 of type  $\beta$  in a binary solution containing species  $\alpha$  and  $\beta$  with number densities  
32  $c_\alpha$  and  $c_\beta$ , respectively. The gradient term  $\lambda/2 |\nabla\phi|^2$  penalizes the interfacial area  
33 between these phases, and  $F$  is defined as the general (Helmholtz) free energy density  
34  $F(\phi) := U - TS$ , where  $U$  is the internal energy,  $T$  is the temperature and  $S$  is the  
35 entropy. The parameter  $\lambda > 0$  is proportional to the interfacial width and leads to  
36 the appearance of smooth interface.

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37 Important examples of this formulation include the regular solution theory which  
 38 has been applied successfully in a wide spectrum of scientific and technological con-  
 39 texts such as ionic melts [23], water sorption in porous solids [5], and micellization  
 40 in binary surfactant mixtures [25]. The key quantity in this theory is the so-called  
 41 regular solution energy density (also known as the Flory-Huggins energy density [18])  
 42  $F(\phi) := R(\phi) - TS_I(\phi)$ , where  $S_I(\phi) := -k_B [\phi \ln \phi - (1 - \phi) \ln (1 - \phi)]$  is the en-  
 43 tropy of mixing for ideal solutions and the regular solution term  $R(\phi) := z\omega\phi(1 - \phi)$   
 44 accounts for the interaction energy between different species. The variable  $z$  is the  
 45 coordination number defining the number of bonds of  $\beta$  with neighbouring species.  
 46  $\omega := \epsilon_{\alpha\alpha} + \epsilon_{\beta\beta} - 2\epsilon_{\alpha\beta}$  is the interaction energy parameter accounting for the minima  
 47  $\epsilon_{\alpha\alpha}$ ,  $\epsilon_{\beta\beta}$ , and  $\epsilon_{\alpha\beta}$  of interaction potentials which define attractive and repulsive forces  
 48 between the species  $\alpha$  and  $\beta$ .

49 Wetting phenomena, often studied using classical sharp-interface approximations,  
 50 e.g. [43, 45, 44, 58], also enjoy a wide-spread use of phase-field modeling [41, 60,  
 51 59, 52, 53] even in the presence of complexities such as an electric field (so called  
 52 electrowetting, e.g. [14, 34]). The reason for this is that classical sharp-interface  
 53 models consider the fluid-fluid interface to be a sharp surface of zero thickness where  
 54 quantities such as the fluid density are, in general, discontinuous, which leads to  
 55 singularity formation for interfacial problems with topological transitions, e.g. the  
 56 notorious contact line singularity [22] often cured with phenomenological approaches  
 57 such as slip models. The phase-field/diffuse-interface approach relaxes the assumption  
 58 of a sharp interface in line with the physics of the problem and in agreement with  
 59 developments and applications in the field of statistical mechanics of liquids and in  
 60 molecular simulations, with quantities varying smoothly but rapidly, and considers  
 61 the interface to have a non-zero thickness, thus allowing a “natural” regularisation  
 62 for singularities in interfacial problems with topological transitions.

63 Other applications include transport in electrochemical systems e.g. consisting of  
 64 an electrolyte and an electrode [20], or immiscible flows [28, 37] under a polynomial  
 65 free energy in the form of the classical double-well potential, i.e.,  $W(\phi) := \frac{1}{4}(1 - \phi^2)^2$   
 66 are relevant applications. Phase-field energy functionals are also of interest in image  
 67 processing such as inpainting, see e.g. [7].

68 Our formal derivation of upscaled phase-field equations is valid for general free  
 69 energies but the subsequent rigorous derivation of error estimates is based on free  
 70 energies of the following form.

71 **Polynomial Class (PC):** *Admissible free energy densities  $F$  in (1) are polyno-*  
 72 *mials of order  $2r$ , i.e.,*

$$73 \quad (2) \quad F(u) = \sum_{i=2}^{2r} b_i u^i, \quad b_i = a_{i-1}, \quad 2 \leq i \leq 2r,$$

74 *with  $f(u) = F'(u)$  vanishing at  $u = 0$ , that is,*

$$75 \quad (3) \quad f(u) = \sum_{i=1}^{2r-1} a_i u^i, \quad r \in \mathbb{N}, \quad r \geq 2,$$

76 *where the leading coefficient of both  $F$  and  $f$  is positive, i.e.,  $a_{2r-1} = 2rb_{2r} > 0$ .*

77 Temam [56] established well-posedness of the Cahn-Hilliard equation for free en-  
 78 ergies of class (PC). In computations, one often replaces the regular solution energy  
 79 density, composed of  $R$  and  $S_I$  defined above, by the polynomial double-well potential  
 80  $W(\phi)$ .

81 In difference to [51], we provide here an upscaling strategy that is valid for gen-  
 82 eral homogeneous free energy densities by making use of a Taylor expansion of the  
 83 free energy density at the effective upscaled solution. This serves also as a general  
 84 methodology for the homogenization of nonlinear problems. Moreover, to the best of  
 85 our knowledge, we present here for the first time, error estimates between the solution  
 86 of the microscopic phase-field equations solved in a periodic porous medium and the  
 87 solution of the correspondingly homogenized/upscaled equations by Theorem 1 be-  
 88 low. In the remaining part of this section, we introduce the basic equations describing  
 89 interfacial dynamics in a homogeneous environment and subsequently in a periodic  
 90 porous medium.

**(a) Homogeneous domains  $\Omega$ .** In the Ginzburg-Landau/Cahn-Hilliard for-  
 mulation, the total energy is defined by  $E(\phi) := \int_{\Omega} e(\phi) d\mathbf{x}$  with density (1) on a  
 bounded domain  $\Omega \subset \mathbb{R}^d$  with smooth boundary  $\partial\Omega$  and  $1 \leq d \leq 3$  denotes the spa-  
 tial dimension. It is well accepted that thermodynamic equilibrium can be achieved  
 by minimizing the energy  $E$ , frequently supplemented by a wetting boundary contri-  
 bution  $\int_{\partial\Omega} g(\mathbf{x}) d\mathbf{x}$  for  $g(\mathbf{x}) \in H^{3/2}(\partial\Omega)$ . The wetting property of pore walls can be  
 characterised by

$$g(\mathbf{x}) = -\frac{\gamma}{C_h} a(\mathbf{x}),$$

91 where  $C_h$  is the Cahn number  $\frac{\lambda}{L}$ ,  $L$  the macroscopic length scale, and  $\gamma = \frac{2\sqrt{2}\phi_e}{3\sigma_{lg}}$ ,  $\sigma_{lg}$   
 92 is the liquid-gas surface tension, and  $\phi_e$  is the local equilibrium limiting value of  $F$ , see  
 93 [46]. For simplicity, we set subsequently  $g = 0$  and hence assume walls with neutral  
 94 wetting characteristics, i.e., walls inducing a contact angle of 90 degrees. A widely  
 95 used minimization over time forms the  $H^{-1}$ -gradient flow with respect to  $E(\phi)$ , i.e.,

$$96 \quad (4) \quad (\text{Homogeneous case}) \quad \begin{cases} \frac{\partial}{\partial t} \phi = \operatorname{div} \left( \hat{M} \nabla \left( \frac{1}{\lambda} f(\phi) - \lambda \Delta \phi \right) \right) & \text{in } \Omega_T, \\ \nabla_n \phi := \mathbf{n} \cdot \nabla \phi = g(\mathbf{x}) & \text{on } \partial\Omega_T, \\ \nabla_n \Delta \phi = 0 & \text{on } \partial\Omega_T, \end{cases}$$

97 where  $\Omega_T := \Omega \times ]0, T[$ ,  $\partial\Omega_T := \partial\Omega \times ]0, T[$ ,  $\phi$  satisfies the initial condition  $\phi(\mathbf{x}, 0) =$   
 98  $\psi(\mathbf{x})$ , and  $\hat{M} = \{m_{ij}\}_{1 \leq i, j \leq d}$  denotes a symmetric and positive definite mobility ten-  
 99 sor. Throughout the article we write  $]a, b[$  for open intervals with  $a, b \in \mathbb{R}$  and  $a < b$ .  
 100 The gradient flow (4) is weighted by the mobility tensor  $\hat{M}$ , and is referred to as the  
 101 Cahn-Hilliard equation. This equation is a model prototype for interfacial dynamics,  
 102 e.g. [17], and phase transformation, e.g. [9], under homogeneous Neumann boundary  
 103 conditions, i.e.,  $g = 0$ , and free energy densities  $F$ .

104 We recall that the integrated energy density (1) dissipates along solutions of (4),  
 105 that means,  $E(\phi(\cdot, t)) \leq E(\phi(\cdot, 0)) =: E_0$ . This follows immediately after differenti-  
 106 ating  $E(\phi)$  with respect to time and using (4) for  $g = 0$ .

107 There is also an interesting connection between the Cahn-Hilliard/phase-field  
 108 equation and the free-boundary value problem known as the Mullins-Sekerka prob-  
 109 lem [32] or the two-phase Hele-Shaw problem [21]. The Hele-Shaw problem plays a  
 110 crucial role for deriving more regular solutions of the Cahn-Hilliard equation (4), see  
 111 [2]. Inspired by the formal derivation by Pego [40], it was rigorously verified later on  
 112 in [2, 54] that the chemical potential

$$113 \quad (5) \quad \mu(\phi) := -\lambda \Delta \phi + \frac{1}{\lambda} f(\phi),$$

114 satisfies for an evolving interfacial front  $\Gamma_t$  with initial condition  $\Gamma_{00}$  in the limit  $\lambda \rightarrow 0$

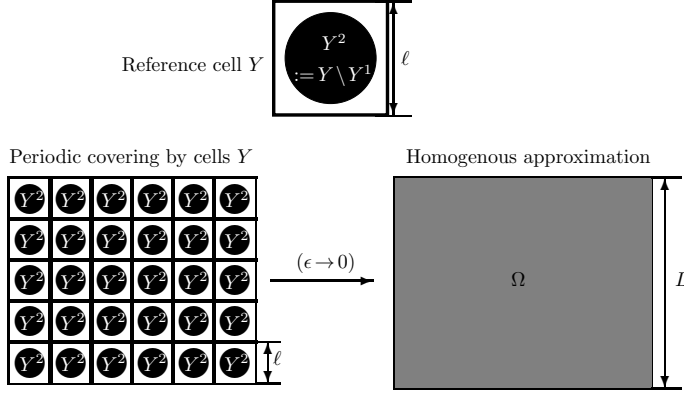


FIG. 1. **Left:** Strongly heterogeneous/perforated material as a periodic covering of reference cells  $Y := [0, \ell]^d$ . **Top, middle:** Definition of the reference cell  $Y = Y^1 \cup Y^2$  with  $\ell = 1$ . **Right:** The “homogenization limit”  $\epsilon := \frac{\ell}{L} \rightarrow 0$  scales the perforated domain such that perforations become invisible on the macroscale.

115 for  $t \in [0, T]$  the following

$$116 \quad (6) \quad \text{Hele-Shaw/Mullins-Sekerka problem:} \quad \begin{cases} \Delta \mu = 0 & \text{in } \Omega \setminus \Gamma_t, \\ \mathbf{n} \cdot \nabla \mu = 0 & \text{on } \partial \Omega, \\ \mu = \sigma \kappa & \text{on } \Gamma_t, \\ v = \frac{1}{2} [\mathbf{n} \cdot \nabla \mu]_{\Gamma_t} & \text{on } \Gamma_t, \\ \Gamma_0 = \Gamma_{00} & \text{if } t = 0, \end{cases}$$

117 where  $\sigma = \int_{-1}^1 \left( \frac{1}{2} \int_0^s f(r) dr \right)^{1/2} ds$  is the interfacial tension,  $\kappa$  the mean curvature,  
 118  $v$  the normal velocity of the interface  $\Gamma_t$ ,  $\mathbf{n}$  the unit outward normal to either  $\partial \Omega$   
 119 or  $\Gamma_t$ , and  $[\mathbf{n} \cdot \nabla \mu]_{\Gamma_t} := \mathbf{n} \cdot \nabla \mu^+ - \mathbf{n} \cdot \nabla \mu^-$  where  $\mu^+ := \mu|_{\Omega_t^+}$  and  $\mu^- := \mu|_{\Omega_t^-}$   
 120 and  $\Omega_t^+$  and  $\Omega_t^-$  denote the exterior and interior of  $\Gamma_t$  in  $\Omega$ . Herewith, we also have  
 121  $\phi \rightarrow \pm 1$  in  $\Omega_t^\pm$  for all  $t \in [0, T]$  as  $\lambda \rightarrow 0$ . Finally, the derivation of convergence  
 122 rates (Theorem 1 below) requires higher regularity of solutions of the Cahn-Hilliard  
 123 equation (Assumption C below) than available in [2, 16], which require the existence  
 124 of global in time solutions of the sharp interface limit (6).

125 **(b) Heterogeneous/perforated domains  $\Omega^\epsilon$ .** Our main study concentrates  
 126 on (1) in perforated domains  $\Omega^\epsilon \subset \mathbb{R}^d$  instead of a homogeneous domain  $\Omega \subset \mathbb{R}^d$ .  
 127 The dimensionless variable  $\epsilon > 0$  defines the heterogeneity  $\epsilon = \frac{\ell}{L}$  where  $\ell$  represents  
 128 the characteristic pore size and  $L$  is the macroscopic length of the porous medium,  
 129 see Figure 1. Hence, the porous medium is defined by a reference pore/cell  $Y :=$   
 130  $[0, \ell_1] \times [0, \ell_2] \times \dots \times [0, \ell_d]$ . For simplicity, we set  $\ell_1 = \ell_2 = \dots = \ell_d = 1$ . The pore  
 131 and the solid phase of the medium are denoted by  $\Omega^\epsilon$  and  $B^\epsilon$ , respectively. These  
 132 sets are defined by,

$$133 \quad (7) \quad \Omega^\epsilon := \bigcup_{\mathbf{z} \in \mathbb{Z}^d} \epsilon(Y^1 + \mathbf{z}) \cap \Omega, \quad B^\epsilon := \bigcup_{\mathbf{z} \in \mathbb{Z}^d} \epsilon(Y^2 + \mathbf{z}) \cap \Omega = \Omega \setminus \Omega^\epsilon,$$

134 where the subsets  $Y^1, Y^2 \subset Y$  are such that  $\Omega^\epsilon$  is a connected set. More precisely,  $Y^1$   
 135 stands for the pore phase (e.g. liquid or gas phase in wetting problems), see Figure  
 136 1. Additionally, we define the macroscopic pore walls by  $I_\Omega^\epsilon := \partial \Omega^\epsilon \cap \partial B^\epsilon$  and the

137 microscopic pore walls by  $I_Y := \partial Y^1 \cap \partial Y^2$ . Herewith, we can reformulate (4) for  
 138  $g = 0$  by the following microscopic porous media problem

$$139 \quad (8) \quad (\text{Micro porous case}) \quad \begin{cases} \partial_t \phi_\epsilon = \operatorname{div} \left( \hat{\mathbb{M}} \nabla \left( -\lambda \Delta \phi_\epsilon + \frac{1}{\lambda} f(\phi_\epsilon) \right) \right) & \text{in } \Omega_T^\epsilon, \\ \nabla_n \phi_\epsilon := \mathbf{n} \cdot \nabla \phi_\epsilon = 0 & \text{on } \partial \Omega_T^\epsilon, \\ \nabla_n \Delta \phi_\epsilon = 0 & \text{on } \partial \Omega_T^\epsilon, \\ \phi_\epsilon(\mathbf{x}, 0) = \psi(\mathbf{x}) & \text{on } \Omega^\epsilon. \end{cases}$$

140 Our main objective is the derivation of error estimates for the difference between  
 141 the upscaled/homogenized solution  $\phi_0$  of (17) and the microscopic solution  $\phi_\epsilon$  of  
 142 (8) in order to have a *qualitative and quantitative measure for the validity* of the  
 143 homogenized phase field formulation (17) (Theorem 1) obtained by passing to the  
 144 limit  $\epsilon \rightarrow 0$  in (8). This result will also provide a rigorous basis for the formal  
 145 upscaling in [50]. The homogenized equation stated in Theorem 1 below allows for  
 146 new analytical considerations such as a sharp interface study of the novel upscaled  
 147 equation or establishing more regular solutions of Cahn-Hilliard/phase field equations  
 148 as well as for new avenues in modelling. It ultimately leads to convenient, low-  
 149 dimensional computational schemes which can be solved by well-known numerical  
 150 methods developed for homogeneous domains.

151 In Section 2, we present basic notations and mathematical assumptions. The  
 152 main results are summarized in Section 3 and subsequently justified in Sections 4 and  
 153 5. Conclusions and suggestions for further work are given in Section 6.

**2. Mathematical preliminaries and notation.** We recall the splitting formu-  
 lation of the Cahn-Hilliard equation from [51] which builds the basis for our subsequent  
 homogenization analysis. To this end, we set

$$H_E^2(\Omega) := \left\{ \phi \in H^k(\Omega) \mid \nabla_n \phi = 0 \text{ and } \bar{\phi} := \frac{1}{|\Omega|} \int_\Omega \phi \, d\mathbf{x} = 0, k \geq 2 \right\}$$

and identify  $\phi = (-\Delta)^{-1} w$  in the  $H_E^2(\Omega)$ -sense, this means, we have for all  $\varphi \in H_E^2(\Omega)$   
 that

$$(-\Delta \phi, \varphi) = (-\Delta(-\Delta)^{-1} w, \varphi) = (w, \varphi),$$

154 where  $(\cdot, \cdot)$  denotes the standard  $L^2$ -scalar product. Herewith we can rewrite (8) (for  
 155 simplicity stated here for  $\Omega \subset \mathbb{R}^d$  instead of  $\Omega^\epsilon$ ) for all  $\varphi \in H_E^2(\Omega)$  as

$$156 \quad \begin{aligned} (\partial_t(-\Delta)^{-1} w, \varphi) - \left( \lambda \operatorname{div} \left( \hat{\mathbb{M}} \nabla w \right), \varphi \right) &= \left( \operatorname{div} \left( \frac{\hat{\mathbb{M}}}{\lambda} \nabla f(\phi) \right), \varphi \right), \\ (\nabla \phi, \nabla \varphi) &= (w, \varphi), \end{aligned}$$

157 which reads in the classical sense

$$158 \quad (9) \quad (\text{Splitting}) \quad \begin{cases} \partial_t(-\Delta)^{-1} w - \lambda \operatorname{div} \left( \hat{\mathbb{M}} \nabla w \right) = \operatorname{div} \left( \frac{\hat{\mathbb{M}}}{\lambda} \nabla f(\phi) \right) & \text{in } \Omega_T, \\ \nabla_n w = -\nabla_n \Delta \phi = 0 & \text{on } \partial \Omega_T, \\ -\Delta \phi = w & \text{in } \Omega_T, \\ \nabla_n \phi = 0 & \text{on } \partial \Omega_T, \\ \phi(\mathbf{x}, 0) = \psi(\mathbf{x}) & \text{in } \Omega. \end{cases}$$

159 In [35], the existence of a local solution  $\phi \in H_E^2(\Omega)$  to equation (8) has been verified  
 160 for  $f \in C_{Lip}^2(\mathbb{R})$  and hence also to (9). Furthermore, Novick-Cohen [35] states neces-  
 161 sary conditions for global existence while a proof based on Galerkin approximations

162 and a priori estimates can be found in [56, Theorem 4.2, p. 155]. The advantage of  
 163 (9) is that it allows to base our upscaling approach on well-known results from elliptic/  
 164 parabolic homogenization theory [6, 11, 24, 30, 39, 62]. The splitting (9) slightly  
 165 differs from the strategy of substituting the chemical potential, which is often applied  
 166 for computational purposes, see [4], and which seems also more appropriate for other  
 167 homogenization strategies such as periodic unfolding [12] or two-scale convergence  
 168 [3, 33] for instance.

169 Next, we briefly summarize what, to the best of our knowledge, we believe to be  
 170 the best available regularity results (Lemma 1 below) for the Cahn-Hilliard equation  
 171 [2, 16]. These results depend on two assumptions:

172 **Assumption A:**

173 **(A1)**  $F \in C^4(\mathbb{R})$  satisfies  $F(\pm 1) = 0$  and  $F > 0$  elsewhere.

174 **(A2)**  $f(u) = F'(u)$  satisfies for some finite  $\alpha > 2$  and positive constants  $k_i > 0$ ,  
 175  $i = 0, \dots, 3$ ,

$$176 \quad (10) \quad k_0 |u|^{\alpha-2} - k_1 \leq f'(u) \leq k_2 |u|^{\alpha-2} + k_3.$$

177 **(A3)** There exist constants  $0 < a_1 \leq 1$ ,  $a_2 > 0$ ,  $a_3 > 0$  and  $a_4 > 0$  such that for  
 178  $b \in \mathbb{R}$

$$179 \quad (11) \quad \begin{aligned} (f(a) - f(b), a - b) &\geq a_1 (f'(a)(a - b), a - b) - a_2 |a - b|^{2+a_3} \quad \forall |a| \leq 2a_4, \\ aF''(a) &\geq 0 \quad \forall |a| \geq a_4. \end{aligned}$$

180 It is straightforward to check that the classical double-well potential  $F(x) = (x^2 -$   
 181  $1)^2/4$  satisfies Assumption A. The following characterization of the initial condition  
 182  $\psi$  is also required for more regular solutions as derived in [2, 16] and stated in Lemma  
 183 1 below. We will frequently write  $\|u\|$  for the  $L^2$ -norm of a function  $u$ .

184 **Assumption B:** There exist uniform constants  $m_0, \sigma_j > 0$ ,  $j = 1, 2, 3$  such that

$$185 \quad \text{(B1)} \quad -1 < m_0 := \frac{1}{|\Omega|} \int_{\Omega} \psi(\mathbf{x}) \, d\mathbf{x} < 1,$$

$$186 \quad \text{(B2)} \quad \mathcal{E}_{\lambda}(\psi) := \frac{\lambda}{2} \|\nabla \psi\|^2 + \frac{1}{\lambda} \|F(\psi)\|_{L^1} \leq C\lambda^{-2\sigma_1},$$

$$187 \quad \text{(B3)} \quad \|\omega^{\lambda}\|_{H^l} := \|\lambda \Delta \psi + \frac{1}{\lambda} F(\psi)\|_{H^l} \leq C\lambda^{-\sigma_2+l}, \quad l = 0, 1,$$

188 where  $|\Omega|$  is the Lebesgue measure of  $\Omega$ .

189 Herewith, the following regularity result has been derived for homogeneous do-  
 190 mains  $\Omega$  in [2, 16].

191 **LEMMA 1. (Regularity)** *Let  $f$  and  $\psi$  satisfy the Assumption A and B, respec-*  
 192 *tively. Moreover, we suppose that the Hele-Shaw/Mullins-Sekerka problem (6) has a*  
 193 *global in time classical solution. Then, the solution  $\phi$  of the Cahn-Hilliard equation*  
 194 *(4) satisfies the estimates*

$$195 \quad (12) \quad \begin{cases} \|\phi\|_{L^{\infty}(\Omega_T)} \leq C, \\ \int_0^{\infty} \|\nabla \Delta \phi\|^2 \, dt \leq C(\lambda), \\ \|\Delta^2 \phi\|_{L^{\infty}([0, \infty[; L^2(\Omega))} \leq C\lambda^{-C}, \end{cases}$$

196 for all  $\lambda \in ]0, \kappa[$  and a family of smooth initial data  $\{\psi^{\lambda}\}_{0 < \lambda \leq 1}$  where  $\kappa$  and  $C$  are  
 197 constants. Estimate (12)<sub>3</sub> holds for  $C > 0$  large enough, if  $\lim_{s \rightarrow 0^+} \|\nabla \partial_t \phi(s)\| \leq$   
 198  $C\lambda^{-\kappa}$ .

199 **REMARK 1.** (Hele-Shaw) *Existence and uniqueness of classical solutions for the*  
 200 *so-called single phase Hele-Shaw problem in bounded domains in  $\mathbb{R}^d$  can be found for*  
 201 *instance in [15, 31].*  $\diamond$

202 We refer the interested reader to Refs. [2, 16] for a proof. Since we need slightly  
 203 stronger regularity results than stated in Lemma 1 for the proof of error estimates  
 204 (Theorem 1), we introduce the following well-accepted (see for instance [11])

205 **Assumption C:** *For smooth data, i.e.,  $\phi_0(\mathbf{x}, 0), \phi_\epsilon(\mathbf{x}, 0) \in C^\infty(\Omega^\epsilon)$ ,  $f \in C^\infty(\mathbb{R})$ ,*  
 206 *and for  $\Omega^\epsilon$  with Lipschitz boundary  $\partial\Omega^\epsilon$  and hence the interface  $I_\Omega^\epsilon$  is Lipschitz too,*  
 207 *then the solutions  $\phi_0$  of equation (17) and  $\phi_\epsilon$  the solution of the microscopic equation*  
 208 *(8) satisfy*

$$209 \quad (13) \quad \phi_0, \phi_\epsilon \in C^1(0, T; W^{k, \infty}(\Omega^\epsilon)) \quad \text{for a } k \geq 4.$$

210 *Moreover, the correctors  $\xi_\phi^k$  and  $\xi_w^k$ , which solve the cell problems (19), satisfy*

$$211 \quad (14) \quad \xi_\phi^k, \xi_w^k \in W^{1, \infty}(Y^1) \quad \text{for all } 1 \leq k \leq d.$$

212 Let  $T_\epsilon$  denote the extension operator, which extends the solutions  $\phi^\epsilon$  and  $w^\epsilon$  of (9)  
 213 defined on the perforated domain  $\Omega^\epsilon$  to the homogeneous domain  $\Omega$ . For convenience  
 214 we denote these extensions by  $\phi^\epsilon$  and  $w^\epsilon$  and skip the extension operator  $T_\epsilon$  most of  
 215 the time. The existence of such an operator  $T_\epsilon : W^{1, p}(\Omega^\epsilon) \rightarrow W_{loc}^{1, p}(\Omega)$  for  $\epsilon > 0$  was  
 216 established in [1] and  $T_\epsilon$  is characterized by the following properties:

$$218 \quad (15) \quad \begin{cases} \text{(T1)} & T_\epsilon u = u \quad \text{a.e. in } \Omega^\epsilon, \\ \text{(T2)} & \int_{\Omega(\epsilon k_0)} |T_\epsilon u|^p \, d\mathbf{x} \leq k_1 \int_{\Omega^\epsilon} |u|^p \, d\mathbf{x}, \\ \text{(T3)} & \int_{\Omega(\epsilon k_0)} |D(T_\epsilon u)|^p \, d\mathbf{x} \leq k_2 \int_{\Omega^\epsilon} |Du|^p \, d\mathbf{x}, \end{cases}$$

219 for constants  $k_0, k_1, k_2 > 0$ . Hence,  $T_\epsilon$  extends solutions defined on the pore space  
 220  $\Omega^\epsilon$  to the whole domain  $\Omega$ .

221 **3. Main results.** Our main result, i.e., the upscaling/homogenization of general  
 222 phase field equations (including the Cahn-Hilliard equation), is based on the following  
 223 local property of the chemical potential.

224 **DEFINITION 1.** (Local Thermodynamic Equilibrium) *Let  $\mu(\phi) = -\lambda\Delta\phi + \frac{1}{\lambda}f(\phi)$*   
 225 *be the chemical potential associated to the phase field free energy density (1). We say*  
 226 *that the upscaled chemical potential  $\mu_0(\phi_0) = -\lambda\text{div}(\tilde{D}\nabla\phi_0) + \frac{1}{\lambda}f(\phi_0) = \lambda w_0 + \frac{1}{\lambda}f(\phi_0)$*   
 227 *is in local thermodynamic equilibrium (LTE) if and only if*

$$228 \quad (16) \quad \frac{\partial\mu_0(\phi_0(\mathbf{x}))}{\partial x_k} = \begin{cases} 0 & \text{appearing in the cell problem depending on } \Omega \times Y, \\ \frac{\partial\mu_0(\phi_0)}{\partial x_k} & \text{appearing on the macroscale } \Omega \text{ (after averaging over } Y), \end{cases}$$

229 *where  $\phi_0(x)$  is the upscaled/slow variable, which is independent of the microscale*  
 230  *$\mathbf{y} \in Y$  and which solves the upscaled phase field equation (17) below.*

231 **REMARK 2.** *Definition 1 systematically accounts for the problem specific slow*  
 232 *(macroscopic) scale  $\mathbf{x} \in \Omega$  and the fast (microscopic) scale  $\mathbf{y} \in Y$ . Intuitively, Def-*  
 233 *inition 1 expresses the fact that the macroscopic variables are varying so slowly that*  
 234 *their variations are not visible on the microscale. The local thermodynamic equilibrium*  
 235 *characterization (16) is well accepted and appears in a wide range of applications, e.g.*  
 236 *[8, 13, 29, 27].*  $\diamond$

237 Definition 1 naturally appears in the upscaling of nonlinear problems and enables  
 238 two essential features: a) The upscaled equations are of the same form as the mi-  
 239 croscopic formulation; b) (16) guarantees the well-posedness of arising cell problems  
 240 which define effective transport coefficients. Recent examples in the context of ionic  
 241 transport equations are [46, 47, 49, 48]. These considerations allow us to recall the  
 242 following upscaling result from [50].

243 **Upscaling Result (UR):** (Effective macroscopic phase field equations) *Sup-*  
 244 *pose that  $\psi(\mathbf{x}) \in H_E^2(\Omega)$ . For chemical potentials  $\mu := \nabla_\phi E(\phi)$ , where  $\nabla_\phi$  denotes*  
 245 *the Fréchet derivative, being in local thermodynamic equilibrium as characterized by*  
 246 *Definition 1, the microscopic porous media formulation (8) can be effectively approx-*  
 247 *imated by the following macroscopic problem,*

$$248 \quad (17) \quad \begin{cases} \theta_1 \frac{\partial \phi_0}{\partial t} = \operatorname{div} \left( \hat{M}_\phi / \lambda \nabla f(\phi_0) \right) + \frac{\lambda}{\theta_1} \operatorname{div} \left( \hat{M}_w \nabla \left( \operatorname{div} \left( \hat{D} \nabla \phi_0 \right) \right) \right) & \text{in } \Omega_T, \\ \nabla_n \phi_0 = \mathbf{n} \cdot \nabla \phi_0 = 0 & \text{on } \partial \Omega_T, \\ \nabla_n \Delta \phi_0 = 0 & \text{on } \partial \Omega_T, \\ \phi_0(\mathbf{x}, 0) = \psi(\mathbf{x}) & \text{in } \Omega, \end{cases}$$

249 where  $\theta_1 := \frac{|Y^1|}{|Y|}$  is the porosity and the porous media correction tensors  $\hat{D} :=$   
 250  $\{\mathbf{d}_{ik}\}_{1 \leq i, k \leq d}$ ,  $\hat{M}_\phi = \{\mathbf{m}_{ik}^\phi\}_{1 \leq i, k \leq d}$  and  $\hat{M}_w = \{\mathbf{m}_{ik}^w\}_{1 \leq i, k \leq d}$  are defined by

$$251 \quad (18) \quad \begin{cases} \mathbf{d}_{ik} & := \frac{1}{|Y^1|} \sum_{j=1}^d \int_{Y^1} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) dy, \\ \mathbf{m}_{ik}^\phi & := \frac{1}{|Y^1|} \sum_{j=1}^d \int_{Y^1} \left( m_{ik} - m_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) dy, \\ \mathbf{m}_{ik}^w(\mathbf{x}) & := \frac{1}{|Y^1|} \sum_{j=1}^d \int_{Y^1} \left( m_{ik} - m_{ij} \frac{\partial \xi_w^k}{\partial y_j} \right) dy, \end{cases}$$

252 where  $m_{ij}$  are elements of the mobility tensor. The corrector functions  $\xi_\phi^k \in H_{per}^1(Y^1)$   
 253 and  $\xi_w^k \in L^2(\Omega; H_{per}^1(Y^1))$  for  $1 \leq k \leq d$  solve in the distributional sense the following  
 254 reference cell problems

$$255 \quad (19) \quad \begin{cases} \xi_w^k : \begin{cases} - \sum_{i,j,k=1}^d \frac{\partial}{\partial y_i} \left( m_{ik} - m_{ij} \frac{\partial \xi_w^k}{\partial y_j} \right) \\ \quad = - \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i} \left( m_{ik} - m_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) & \text{in } Y^1, \\ \sum_{i,j,k=1}^d \mathbf{n}_i \left( m_{ij} \frac{\partial \xi_w^k}{\partial y_j} - m_{ik} \right) \\ \quad + \left( m_{ik} - m_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) = 0 & \text{on } I_Y := \partial Y^1 \cap \partial Y^2, \\ \xi_w^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_w^k) = 0, \end{cases} \\ \xi_\phi^k : \begin{cases} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) = 0 & \text{in } Y^1, \\ \sum_{i,j=1}^d \mathbf{n}_i \left( \delta_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} - \delta_{ik} \right) = 0 & \text{on } I_Y, \\ \xi_\phi^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_\phi^k) = 0, \end{cases} \end{cases}$$

256 where  $\delta_{ij}$  is the Kronecker delta function and  $\mathbf{n}_i$  denotes the  $i$ -th component of the  
 257 outward normal vector  $\mathbf{n}$ .



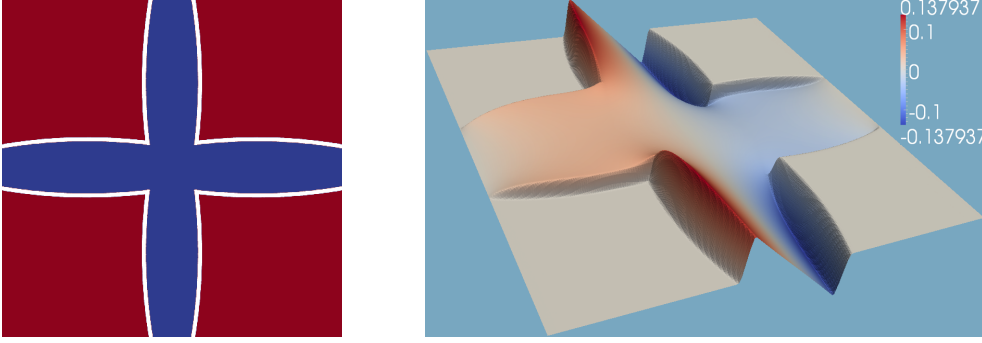


FIG. 2. **Left:** Pore geometry (shamrock) defined on reference cell (pore phase=blue, solid phase = red). **Right:** Corrector  $\xi_\phi^1$  solving the cell problem (19)<sub>2</sub> for  $Y^1$  representing the pore phase (blue color in the left picture).

258 **REMARK 3.** *i)* For an isotropic mobility, i.e.,  $\hat{M} := m\hat{I}$  where  $\hat{I}$  is the identity  
 259 matrix, it follows that  $\xi_w^k = \xi_\phi^k$ , and hence both  $\xi_w^k$  and  $\xi_\phi^k$  solve classical elliptic cell  
 260 problems, see Figure 2.

261 *ii)* The local thermodynamic equilibrium property (Definition 1) of the macroscopic  
 262 chemical potential  $\mu_0$  enables the derivation of the well-posed cell problem (19)<sub>1</sub> for  
 263  $\xi_w^k$ .  $\diamond$

264 The next result characterizes qualitatively the homogenized phase field equations  
 265 (17) with the help of error estimates.

266 **THEOREM 1.** (Error estimates) Let  $\phi^\epsilon$  be a solution of (8), or equivalently  $\phi^\epsilon$  and  
 267  $w^\epsilon$  solve the splitting formulation (9). Suppose that Assumption C holds. More-  
 268 over, the domain boundaries  $\partial\Omega^\epsilon$  and interfaces  $I_\Omega^\epsilon := \partial\Omega^\epsilon \cap \partial B^\epsilon$  shall be Lips-  
 269 chitz<sup>1</sup>. Let  $\hat{M} = m\hat{I}$  be an isotropic mobility with  $\hat{I}$  representing the identity ma-  
 270 trix. If the free energy  $F$  is polynomial of class (PC), then the error variables  
 271  $E_\epsilon^\phi := \phi^\epsilon - (\phi_0 + \epsilon\phi_1)$ ,  $E_\epsilon^w := w^\epsilon - (w_0 + \epsilon w_1)$ , where  $w_1 := -\sum_{k=1}^d \xi_w^k(\mathbf{y}) \frac{\partial w_0}{\partial x_k}(\mathbf{x}, t)$   
 272 and  $\phi_1 := -\sum_{k=1}^d \xi_\phi^k(\mathbf{y}) \frac{\partial \phi_0}{\partial x_k}(\mathbf{x}, t)$ , satisfy for  $0 \leq t \leq T$  and  $0 < T < \infty$  the following  
 273 estimates

$$\begin{aligned}
 & \|E_\epsilon^w(\cdot, t)\|_{L^2(\Omega^\epsilon)}^2 + c(m, \lambda, \kappa) \int_0^t \|\mathcal{A}_\epsilon E_\epsilon^w(\cdot, s)\|_{L^2(\Omega^\epsilon)}^2 ds \\
 274 \quad (20) \quad & \leq \epsilon^{1/2} C(T, \Omega, m, \kappa, \lambda), \\
 & \|E_\epsilon^\phi(\cdot, t)\|_{H^1(\Omega^\epsilon)} \leq \epsilon^{1/4} C(T, \Omega, m, \kappa, \lambda),
 \end{aligned}$$

275 where  $c(m, \lambda, \kappa)$  and  $C(T, \Omega, m, \kappa, \lambda)$  are constants independent of  $\epsilon$ .

276 **REMARK 4.** We note that the proof of the above Theorem 1 does not take the  
 277 behaviour in the boundary region into account by solely applying a smooth enough  
 278 truncation. This leads for linear elliptic equations to the by now classical convergence  
 279 rate  $\epsilon^{1/2}$ , e.g. [10, 61]. However, in recent attempts [55, 38], the authors can improve  
 280 the convergence rates with the help of operator estimates with a resulting rate  $\epsilon$ . We  
 281 note, that our estimates in (20) are derived based on the classical method but due to  
 282 the fourth order operator, we end up with the slightly lower rate  $\epsilon^{1/4}$ , albeit under

<sup>1</sup>see [10] for instance

283 *the generally required strong regularity Assumption C. The strongest regularity result*  
 284 *currently available seems to be the estimates stated in Lemma 1.*

285 To the best of our knowledge, this is the first error quantification in terms of con-  
 286 vergence rates with respect to the heterogeneity  $\epsilon$  of the porous media approximation  
 287 (17) for phase field equations. The estimates (20) imply convergence of solutions  $\phi^\epsilon$   
 288 of the microscopic formulation (8) to solutions  $\phi_0$  of the upscaled problem (17) for a  
 289 vanishing heterogeneity parameter based on the regularity Assumption C.

290 **4. Formal derivation of upscaled equations.** For convenience, we first recall  
 291 here the formal derivation of the effective macroscopic phase field equation from [50].  
 292 For the micro-scale variable  $\frac{\mathbf{x}}{\epsilon} =: \mathbf{y} \in Y$  it holds that,  $\frac{\partial f_\epsilon(\mathbf{x})}{\partial x_i} = \frac{1}{\epsilon} \frac{\partial f}{\partial y_i}(\mathbf{x}, \mathbf{x}/\epsilon) +$   
 293  $\frac{\partial f}{\partial x_i}(\mathbf{x}, \mathbf{x}/\epsilon)$ , and  $\nabla f_\epsilon(\mathbf{x}) = \frac{1}{\epsilon} \nabla_y f(\mathbf{x}, \mathbf{x}/\epsilon) + \nabla_x f(\mathbf{x}, \mathbf{x}/\epsilon)$ , where  $f_\epsilon(\mathbf{x}) = f(\mathbf{x}, \mathbf{y})$  is  
 294 an arbitrary function depending on two variables  $\mathbf{x} \in \Omega$ ,  $\mathbf{y} \in Y$ . Hence, we have

$$295 \quad (21) \quad \begin{cases} \mathcal{A}_0 &= -\sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ij} \frac{\partial}{\partial y_j} \right), \\ \mathcal{A}_1 &= -\sum_{i,j=1}^d \left[ \frac{\partial}{\partial x_i} \left( \delta_{ij} \frac{\partial}{\partial y_j} \right) + \frac{\partial}{\partial y_i} \left( \delta_{ij} \frac{\partial}{\partial x_j} \right) \right], \\ \mathcal{A}_2 &= -\sum_{i,j=1}^d \frac{\partial}{\partial x_j} \left( \delta_{ij} \frac{\partial}{\partial x_j} \right), \\ \mathcal{B}_0 &= -\sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \mathbf{m}_{ij} \frac{\partial}{\partial y_j} \right), \\ \mathcal{B}_1 &= -\sum_{i,j=1}^d \left[ \frac{\partial}{\partial x_i} \left( \mathbf{m}_{ij} \frac{\partial}{\partial y_j} \right) + \frac{\partial}{\partial y_i} \left( \mathbf{m}_{ij} \frac{\partial}{\partial x_j} \right) \right], \\ \mathcal{B}_2 &= -\sum_{i,j=1}^d \frac{\partial}{\partial x_j} \left( \mathbf{m}_{ij} \frac{\partial}{\partial x_j} \right). \end{cases}$$

296 Herewith, we can define  $\mathcal{A}_\epsilon := \epsilon^{-2} \mathcal{A}_0 + \epsilon^{-1} \mathcal{A}_1 + \mathcal{A}_2$  and analogously  $\mathcal{B}_\epsilon$ . Hence,  
 297 it holds for the Laplace operator that  $-\Delta f_\epsilon(\mathbf{x}) = \mathcal{A}_\epsilon f(\mathbf{x}, \mathbf{y})$ . In order to deal with  
 298 the multiscale nature of strongly heterogeneous environments [24, 46, 49, 47], the  
 299 following, formal asymptotic expansions are used,

$$300 \quad (22) \quad \zeta^\epsilon \approx \zeta_0(\mathbf{x}, \mathbf{y}, t) + \epsilon \zeta_1(\mathbf{x}, \mathbf{y}, t) + \epsilon^2 \zeta_2(\mathbf{x}, \mathbf{y}, t), \quad \text{for } \zeta \in \{w, \phi\},$$

301 where higher order terms are neglected. Before we can insert (22) into the microscopic  
 302 formulation (9), we need to approximate the derivative of the nonlinear homogeneous  
 303 free energy  $f := F'$  by a Taylor expansion of the form

$$304 \quad (23) \quad f(\phi^\epsilon) \approx f(\phi_0) + f'(\phi_0)(\phi^\epsilon - \phi_0) + \mathcal{O}((\phi^\epsilon - \phi_0)^2),$$

305 where  $\phi_0$  stands for the leading order term in (22).<sup>2</sup> Using (22) and (23) in (9) with  
 306  $\nabla_n \phi = g$  and with (21), we get the following sequence of problems,

$$307 \quad (24) \quad \mathcal{O}(\epsilon^{-2}) : \begin{cases} \mathcal{B}_0 [\lambda w_0 + 1/\lambda f(\phi_0)] = 0 & \text{in } Y^1, \\ \text{no flux b.c.}, \\ w_0 \text{ is } Y^1\text{-periodic}, \\ \mathcal{A}_0 \phi_0 = 0 & \text{in } Y^1, \\ \nabla_n \phi_0 = 0 & \text{on } \partial Y^1 \cap \partial Y^2, \\ \phi_0 \text{ is } Y^1\text{-periodic}, \end{cases}$$

<sup>2</sup> Here, we allow for general free energy densities in difference to the subsequent rigorous derivation of error estimates which is based on energy densities of the polynomial class (PC).

308

 $\mathcal{O}(\epsilon^{-1}) :$ 

$$\begin{aligned}
 & \left\{ \begin{array}{l} \mathcal{B}_0 [\lambda w_1 + 1/\lambda f'(\phi_0)\phi_1] = -\mathcal{B}_1 [\lambda w_0 + 1/\lambda f(\phi_0)] \quad \text{in } Y^1, \\ \text{no flux b.c.}, \\ w_1 \text{ is } Y^1\text{-periodic}, \\ \mathcal{A}_0 \phi_1 = -\mathcal{A}_1 \phi_0 \quad \text{in } Y^1, \\ \nabla_n \phi_1 = 0 \quad \text{on } \partial Y^1 \cap \partial Y^2, \\ \phi_1 \text{ is } Y^1\text{-periodic}, \end{array} \right. \quad (25)
 \end{aligned}$$

310

 $\mathcal{O}(\epsilon^0) :$ 

$$\begin{aligned}
 & \left\{ \begin{array}{l} \mathcal{B}_0 [\lambda w_2 + \frac{1}{\lambda} (\frac{1}{2} f''(\phi_0)\phi_1^2 + f'(\phi_0)\phi_2)] \\ \quad = -(\mathcal{B}_2 [\lambda w_0 + 1/\lambda f(\phi_0)] + \mathcal{B}_1 [\lambda w_1 + 1/\lambda f'(\phi_0)\phi_1]) \\ \quad \quad - \partial_t (-\Delta)^{-1} w_0 \quad \text{in } Y^1, \\ \text{no flux b.c.}, \\ w_2 \text{ is } Y^1\text{-periodic}, \\ \mathcal{A}_0 \phi_2 = -\mathcal{A}_2 \phi_0 - \mathcal{A}_1 \phi_1 + w_0 \quad \text{in } Y^1, \\ \nabla_n \phi_2 = g_\epsilon \quad \text{on } \partial Y^1 \cap \partial Y^2, \\ \phi_2 \text{ is } Y^1\text{-periodic}. \end{array} \right. \quad (26)
 \end{aligned}$$

312 Problem (24) immediately suggests, based on classical homogenization theory [6],  
 313 that  $\phi_0$  is independent of the microscale  $\mathbf{y}$ . This and the linear structure of (25) allow  
 314 for the following ansatz for  $w_1$  and  $\phi_1$ , i.e.,

$$\begin{aligned}
 & w_1(\mathbf{x}, \mathbf{y}, t) = - \sum_{k=1}^d \xi_w^k(\mathbf{y}) \frac{\partial w_0}{\partial x_k}(\mathbf{x}, t), \quad \phi_1(\mathbf{x}, \mathbf{y}, t) = - \sum_{k=1}^d \xi_\phi^k(\mathbf{y}) \frac{\partial \phi_0}{\partial x_k}(\mathbf{x}, t). \quad (27)
 \end{aligned}$$

316 Plugging (27) into (25)<sub>2</sub> gives an equation for  $\xi_w^k$  and  $\xi_\phi^k$ . The resulting equation  
 317 for  $\xi_\phi^k$  can be immediately written for  $1 \leq k \leq d$  as,

$$\begin{aligned}
 & \xi_\phi^k : \left\{ \begin{array}{l} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) = \\ \quad = -\text{div} \left( \mathbf{e}_k - \nabla_y \xi_\phi^k \right) = 0 \quad \text{in } Y^1, \\ \mathbf{n} \cdot \left( \nabla \xi_\phi^k + \mathbf{e}_k \right) = 0 \quad \text{on } \partial Y^1 \cap \partial Y^2, \\ \xi_\phi^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_\phi^k) = 0. \end{array} \right. \quad (28)
 \end{aligned}$$

319 To study (25)<sub>1</sub>, we first rewrite  $\mathcal{B}_0 [f'(\phi_0)\phi_1]$  and  $\mathcal{B}_1 f(\phi_0)$  as follows

$$\begin{aligned}
 & \mathcal{B}_0 [f'(\phi_0)\phi_1] = - \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i} \left( m_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \frac{\partial f(\phi_0)}{\partial x_k} \right), \\
 & \mathcal{B}_1 f(\phi_0) = - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( m_{ij} \frac{\partial f(\phi_0)}{\partial x_j} \right). \quad (29)
 \end{aligned}$$

321 Rewriting  $w_1$  and  $w_0$  in the same way and using (27) leads then to

$$\begin{aligned}
322 \quad (30) \quad & -\lambda \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i} \left( m_{ij} \left( \frac{\partial x_k}{\partial x_j} - \frac{\partial \xi_w^k}{\partial y_j} \right) \frac{\partial w_0}{\partial x_k} \right) \\
& = 1/\lambda \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i} \left( m_{ij} \left( \frac{\partial x_k}{\partial x_j} - \frac{\partial \xi_\phi^k}{\partial y_j} \right) \frac{\partial f(\phi_0)}{\partial x_k} \right),
\end{aligned}$$

323 in  $Y^1$ . Next, due to local thermodynamic equilibrium property of the upscaled chem-  
324 ical potential  $\mu_0(\phi_0)$  as defined in Definition 1, we have on the level of the reference  
325 cell  $Y$ ,

$$326 \quad (31) \quad \frac{\partial \mu_0}{\partial x_i} = \frac{\partial}{\partial x_i} \left( f(\phi_0)/\lambda - \lambda \operatorname{div}(\hat{D}\nabla\phi_0) \right) = \frac{\partial}{\partial x_i} (f(\phi_0)/\lambda + \lambda w_0) = 0.$$

327 Entering with (31) into (30) finally gives the reference cell problem for  $\xi_w^k$ ,  $1 \leq k \leq d$   
328 for given  $\xi_\phi^k$

$$329 \quad (32) \quad \begin{cases} -\sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( m_{ik} - m_{ij} \frac{\partial \xi_w^k}{\partial y_j} \right) \\ \quad = -\sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( m_{ik} - m_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) & \text{in } Y^1, \\ \sum_{i,j=1}^d n_i \left( \left( m_{ij} \frac{\partial \xi_w^k}{\partial y_j} - m_{ik} \right) + \left( m_{ik} - m_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) \right) = 0 & \text{on } \partial Y^1 \cap \partial Y^2, \\ \xi_w^k(\mathbf{y}) \text{ is } Y\text{-periodic and } \mathcal{M}_{Y^1}(\xi_w^k) = 0, \end{cases}$$

Finally, we consider the last problem (26). Standard existence and unique-  
ness results (Fredholm alternative/Lax-Milgram) guarantee solvability after validat-  
ing that the right hand side in (26) is zero as an integral over  $Y^1$ . This means,  
 $-\sum_{i,j=1}^d \int_{Y^1} \frac{\partial}{\partial x_i} \left( \delta_{ij} \left( \frac{\partial \phi_1}{\partial y_j} + \frac{\partial \phi_0}{\partial x_j} \right) \right) d\mathbf{y} - \tilde{g}_0 = |Y^1| w_0$ , where

$$\tilde{g}_0 := -\frac{\gamma}{C_h} \int_{\partial Y^1} \left( a_1 \chi_{\partial Y_{w_1}^1} + a_2 \chi_{\partial Y_{w_2}^1} \right) d\mathbf{y},$$

330 which leads to

$$331 \quad (33) \quad -\sum_{i,k=1}^d \left[ \sum_{j=1}^d \int_{Y^1} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) d\mathbf{y} \right] \frac{\partial^2 \phi_0}{\partial x_i \partial x_k} = |Y^1| w_0 + \tilde{g}_0.$$

332 The inhomogeneous Neumann boundary condition  $\tilde{g}_0$  accounts for pore walls  $\partial Y_{w_1}^1 \cup$   
333  $\partial Y_{w_2}^1 = \partial Y^1$  showing two specific wetting properties characterised by the parameters  
334  $a_1$  and  $a_2$  specifying the walls  $\partial Y_{w_1}^1$  and  $\partial Y_{w_2}^1$ , respectively. The upscaling result  
335 (17) is stated for neutral wetting characteristics of the pore walls, i.e.,  $\tilde{g} = 0$ . (33)  
336 suggests to define a porous media correction tensor  $\hat{D} := \{d_{ik}\}_{1 \leq i,k \leq d}$  by

$$337 \quad (34) \quad |Y| d_{ik} := \sum_{j=1}^d \int_{Y^1} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) d\mathbf{y}.$$

338 Equations (33) and (34) represent the upscaled equation for  $\phi_0$ , i.e.,  $-\Delta_{\hat{D}}\phi_0 :=$   
339  $-\operatorname{div}(\hat{D}\nabla\phi_0) = \theta_1 w_0 + \frac{1}{|Y^1|} \tilde{g}_0$ .

340 The upscaled equation for  $w$  is again a result of the Fredholm alternative, i.e., a  
 341 solvability criterion on equation (26)<sub>1</sub>. We require,

$$342 \quad (35) \quad \int_{Y^1} \left\{ -\lambda(\mathcal{B}_2 w_0 + \mathcal{B}_1 w_1) - \frac{1}{\lambda} \mathcal{B}_1 [f'(\phi_0) \phi_1] - \frac{1}{\lambda} \mathcal{B}_2 f(\phi_0) - \partial_t \mathcal{A}_2^{-1} w_0 \right\} d\mathbf{y} = 0.$$

343 The first two terms in (35) can be rewritten by,

$$344 \quad (36) \quad \int_{Y^1} -(\mathcal{B}_2 w_0 + \mathcal{B}_1 w_1) d\mathbf{y} = \sum_{i,k=1}^d \left[ \sum_{j=1}^d \int_{Y^1} \left( m_{ik} - m_{ij} \frac{\partial \xi_w^k}{\partial y_j} \right) d\mathbf{y} \right] \frac{\partial^2 w_0}{\partial x_i \partial x_k} \\ = \operatorname{div} \left( \hat{M}_w \nabla w_0 \right),$$

where the effective tensor  $\hat{M}_w = \{m_{ik}^w\}_{1 \leq i,k \leq d}$  is defined by

$$m_{ik}^w := \frac{1}{|Y|} \sum_{j=1}^d \int_{Y^1} \left( m_{ik} - m_{ij} \frac{\partial \xi_w^k}{\partial y_j} \right) d\mathbf{y}.$$

345 The third term in (35) becomes

$$346 \quad (37) \quad -\mathcal{B}_1 [f'(\phi_0) \phi_1] = \\ - \sum_{i,j=1}^d \left[ \frac{\partial}{\partial x_i} \left( m_{ij} f'(\phi_0) \sum_{k=1}^d \frac{\partial \xi_\phi^k}{\partial y_j} \frac{\partial \phi_0}{\partial x_k} \right) + \frac{\partial}{\partial y_i} \left( m_{ij} f'(\phi_0) \sum_{k=1}^d \xi_\phi^k \frac{\partial^2 \phi_0}{\partial x_k \partial x_j} \right) \right],$$

where the last term in (37) disappears after integrating by parts. The first term on the right-hand side of (37) can be rewritten with the help of the chain rule  $\frac{\partial^2 f(\phi_0)}{\partial x_k \partial x_j} = f''(\phi_0) \frac{\partial \phi_0}{\partial x_k} \frac{\partial \phi_0}{\partial x_j} + f'(\phi_0) \frac{\partial^2 \phi_0}{\partial x_k \partial x_j}$ , as follows

$$-\mathcal{B}_1 [f'(\phi_0) \phi_1] = - \sum_{i,j=1}^d m_{ij} \sum_{k=1}^d \frac{\partial \xi_\phi^k}{\partial y_j} \frac{\partial^2 f(\phi_0)}{\partial x_k \partial x_i},$$

to which we add the term  $-\mathcal{B}_2 f(\phi_0)$ . Herewith, we define a tensor  $\hat{M}_\phi = \{m_{ij}^\phi\}_{1 \leq i,k \leq d}$  by

$$m_{ik}^\phi := \frac{1}{|Y|} \sum_{j=1}^d \int_{Y^1} \left( m_{ik} - m_{ij} \frac{\partial \xi_\phi^k}{\partial y_j} \right) d\mathbf{y},$$

347 which allows us to write

$$348 \quad (38) \quad \int_{Y^1} \left( -\mathcal{B}_1 [f'(\phi_0) \phi_1] - \mathcal{B}_2 f(\phi_0) \right) d\mathbf{y} = \operatorname{div} \left( \hat{M}_\phi \nabla f(\phi_0) \right).$$

These considerations together with the identity

$$\partial_t \mathcal{A}_2^{-1} w_0 = \partial_t \mathcal{A}_2^{-1} (\mathcal{A}_2 \phi_0 + \mathcal{A}_1 \phi_1) = \partial_t \phi_0 + \partial_t \mathcal{A}_2^{-1} \mathcal{A}_1 \phi_1,$$

349 where the last term subsequently disappears due to  $Y$ -periodicity, finally lead after  
 350 integration over the microscale  $Y$  to the following effective equation for  $\phi_0$ , i.e.,

$$351 \quad (39) \quad \theta_1 \frac{\partial \phi_0}{\partial t} = \operatorname{div} \left( \hat{M}_\phi / \lambda \nabla f(\phi_0) \right) + \frac{\lambda}{\theta_1} \operatorname{div} \left( \hat{M}_w \nabla \left( \operatorname{div} \left( \hat{D} \nabla \phi_0 \right) - \tilde{g}_0 \right) \right).$$

352 The solvability of (39) follows along with the arguments in [35] via a local Lipschitz  
 353 argument, or via a Galerkin approximation and a priori estimates as developed in [56,  
 354 Theorem 4.2, p. 155].

355 **5. Proof of Theorem 1.** For the derivation of the error estimates (20), we  
 356 work with the splitting formulation introduced in [51] and summarized in (9). We  
 357 extend the derivation of error estimates for second order problems [11, Theorem 6.3,  
 358 Section 6.2 & Section 7.2] and [46] to the fourth order phase field problems studied  
 359 here. Hence, we compare the solution of the microscopic porous media formulation  
 360 (8) with the solution of the effective upscaled porous media formulation (17). As in  
 361 [11, 46], we introduce the error variables

$$\begin{aligned}
 \mathbf{E}_\epsilon^w &:= w^\epsilon - (w_0 + \epsilon w_1), \\
 \mathbf{E}_\epsilon^\phi &:= \phi^\epsilon - (\phi_0 + \epsilon \phi_1), \\
 \mathbf{E}_\epsilon^f &:= f(\phi^\epsilon) - (f(\phi_0) + f'(\phi_0)(\mathbf{E}_\epsilon^\phi + \epsilon \phi_1)),
 \end{aligned}
 \tag{40}$$

363 here extended by the error function  $\mathbf{E}_\epsilon^f$ . The first goal is to determine the variables  
 364  $\mathbf{F}_\epsilon^\iota$  and  $\mathbf{G}_\epsilon^\iota$  which allow us to write the equations for the errors  $\mathbf{E}_\epsilon^\iota$  for  $\iota \in \{w, \phi\}$  as  
 365 follows

$$\left\{ \begin{array}{ll}
 \frac{\partial(-\Delta)^{-1}\mathbf{E}_\epsilon^w}{\partial t} = \mathcal{B}_\epsilon \left[ -\lambda \mathbf{E}_\epsilon^w + \frac{1}{\lambda} \mathbf{E}_\epsilon^f(\phi^\epsilon, \phi_0, \phi_1) \right] + \mathbf{R}_\epsilon^\phi + \epsilon \mathbf{F}_\epsilon^w & \text{in } \Omega^\epsilon \times ]0, T[, \\
 \nabla_n \mathbf{E}_\epsilon^w = \epsilon \mathbf{G}_\epsilon^w & \text{on } \partial\Omega^\epsilon \times ]0, T[, \\
 \mathcal{A}_\epsilon \mathbf{E}_\epsilon^\phi = \mathbf{E}_\epsilon^w + \epsilon \mathbf{F}_\epsilon^\phi & \text{in } \Omega^\epsilon \times ]0, T[, \\
 \nabla_n \mathbf{E}_\epsilon^\phi = \epsilon \mathbf{G}_\epsilon^\phi & \text{on } \partial\Omega^\epsilon \times ]0, T[.
 \end{array} \right.
 \tag{41}$$

367 With the definitions (21) we can rewrite the first term on the right-hand side in (41)<sub>1</sub>  
 368 and the term on the left-hand side in (41)<sub>3</sub> as follows

$$\begin{aligned}
 \mathcal{B}_\epsilon \left[ -\lambda \mathbf{E}_\epsilon^w + \frac{1}{\lambda} \mathbf{E}_\epsilon^f(\phi^\epsilon, \phi_0, \phi_1) \right] &= \{ \epsilon^{-2} \mathcal{B}_0 + \epsilon^{-1} \mathcal{B}_1 + \mathcal{B}_2 \} \left[ -\lambda \mathbf{E}_\epsilon^w \right. \\
 &\quad \left. + \frac{1}{\lambda} \mathbf{E}_\epsilon^f(\phi^\epsilon, \phi_0, \phi_1) \right], \\
 \mathcal{A}_\epsilon \mathbf{E}_\epsilon^\phi &= \{ \epsilon^{-2} \mathcal{A}_0 + \epsilon^{-1} \mathcal{A}_1 + \mathcal{A}_2 \} \mathbf{E}_\epsilon^\phi.
 \end{aligned}
 \tag{42}$$

370 The relations (21) and (42) together with the sequence of problems (24), (25), and  
 371 (26) define the terms  $\mathbf{R}_\epsilon^\phi$ ,  $\mathbf{F}_\epsilon^w$  and  $\mathbf{F}_\epsilon^\phi$  by

$$\begin{aligned}
 \mathbf{R}_\epsilon^\phi &:= -m\Delta \left( \frac{1}{\lambda} f'(\phi_0) \mathbf{E}_\epsilon^\phi \right), \\
 \mathbf{F}_\epsilon^w &:= \mathcal{B}_2 \left( \lambda w_1 - \frac{1}{\lambda} f'(\phi_0) \phi_1 \right) + \frac{\partial}{\partial t} (-\Delta)^{-1} w_1, \\
 \mathbf{F}_\epsilon^\phi &:= -(\mathcal{A}_2 \phi_1 + w_1),
 \end{aligned}
 \tag{43}$$

373 since  $\mathcal{B}_\epsilon = -m\Delta$ . The definitions in (43) are a consequence of the two identities

$$\begin{aligned}
 \left\{ \frac{\partial}{\partial t} (-\Delta)^{-1} w^\epsilon + \mathcal{B}_\epsilon \left( \lambda w_\epsilon - \frac{1}{\lambda} f(\phi_\epsilon) \right) \right\} &= \left\{ \frac{\partial}{\partial t} (-\Delta)^{-1} w_0 + \mathcal{B}_2 \left( \lambda w_0 - \frac{1}{\lambda} f(\phi_0) \right) \right. \\
 &\quad \left. + \mathcal{B}_1 \left( \lambda w_1 - \frac{1}{\lambda} f'(\phi_0) \phi_1 \right) \right\} + \mathbf{R}_\epsilon^\phi + \epsilon \mathbf{F}_\epsilon^w, \\
 \{ \mathcal{A}_\epsilon \mathbf{E}_\epsilon^\phi - \mathbf{E}_\epsilon^w \} &= \epsilon \mathbf{F}_\epsilon^\phi,
 \end{aligned}
 \tag{44}$$

375 where the terms in the braces vanish due to the microscopic and homogenized equa-  
 376 tions and these terms represent the first and the second term in the error equation  
 377 (41)<sub>1</sub> and (41)<sub>3</sub>. The inhomogeneities in the boundary conditions in (41) satisfy

$$378 \quad \begin{aligned} (45) \quad \mathbf{G}_\epsilon^w &:= -\nabla_n w_1 = \nabla_n \sum_{k=1}^d \xi_w^k \frac{\partial w_0}{\partial x_k}, \quad \text{and} \\ \mathbf{G}_\epsilon^\phi &:= -\nabla_n \phi_1 = \nabla_n \sum_{k=1}^d \xi_\phi^k \frac{\partial \phi_0}{\partial x_k}, \end{aligned}$$

379 since the boundary conditions imply  $\nabla_n(\iota^\epsilon - \iota_0) = 0$  for  $\iota \in \{w, \phi\}$ . Under the given  
 380 regularity (Assumption C) of boundaries and interfaces, i.e.,  $\partial\Omega \in C^\infty$  as well as  
 381  $I_Y \in C^\infty$ , we obtain that  $\xi_\phi^k, \xi_w^k \in W^{1,\infty}$  by classical regularity theory for elliptic  
 382 problems [19]. We note that the above regularity requirements on  $\partial\Omega$  and  $I_Y$  are not  
 383 necessarily sharp but this question is beyond the scope of this work. Hence, elliptic  
 384 theory allows us also to estimate (41)<sub>3</sub> by

$$385 \quad \begin{aligned} (46) \quad \|\mathbf{E}_\epsilon^\phi\|_{H^1(\Omega^\epsilon)} &\leq C \left( \|\mathbf{E}_\epsilon^w\|_{L^2(\Omega^\epsilon)} + \epsilon \|\mathbf{F}_\epsilon^\phi\|_{L^2(\Omega^\epsilon)} + \epsilon \|\mathbf{G}_\epsilon^\phi\|_{H^{-1/2}(\partial\Omega^\epsilon)} \right) \\ &\leq C \|\mathbf{E}_\epsilon^w\|_{L^2(\Omega^\epsilon)} + \epsilon C \left( 1 + \epsilon^{-1/2} \right), \end{aligned}$$

386 where we subsequently justify the uniform boundedness of  $\mathbf{F}_\epsilon^\phi$  in  $L^2(\Omega^\epsilon)$  and the  
 387  $\epsilon$ -dependent bound on  $\mathbf{G}_\epsilon^\phi \in H^{1/2}(\partial\Omega^\epsilon)$ .

388 Next, we derive bounds for the terms on the right-hand side, i.e., (43). Thanks  
 389 to Assumption C, it holds that

$$390 \quad \begin{aligned} (47) \quad \|\mathbf{F}_\epsilon^\phi\|_{L^2(\Omega^\epsilon)} &\leq C \sum_{i,k,l=1}^d \left\| \frac{\partial^3 \phi_0}{\partial x_i \partial x_k \partial x_l} \right\|_{L^\infty(\Omega^\epsilon)} \left\| \delta_{ik} \xi_\phi^k \left( \frac{\cdot}{\epsilon} \right) \right\|_{L^2(\Omega^\epsilon)} + \|w_1\|_{L^2(\Omega^\epsilon)} \leq C, \end{aligned}$$

391 for a constant  $C > 0$  independent of  $\epsilon$ . Analogously, we obtain the bound

$$392 \quad \begin{aligned} (48) \quad \|\mathbf{F}_\epsilon^w\|_{L^2(\Omega^\epsilon)} &\leq C \sum_{i,k,l=1}^d \left\| \frac{\partial^3 w_0}{\partial x_i \partial x_k \partial x_l} \right\|_{L^\infty(\Omega^\epsilon)} \left\| \delta_{ik} \xi_w^k \left( \frac{\cdot}{\epsilon} \right) \right\|_{L^2(\Omega^\epsilon)} + \frac{1}{\lambda} \|\mathcal{B}_2 f'(\phi_0) \phi_1\| \\ &\quad + \left\| \frac{\partial}{\partial t} (-\Delta)^{-1} w_1 \right\|_{L^2(\Omega^\epsilon)} \leq C. \end{aligned}$$

393 We show the basic steps to bound the second last term in (48). To this end, we first  
 394 note that  $\mathcal{B}_2[f'(\phi_0)\phi_1] = -m\Delta_x[f'(\phi_0)(\xi_\phi \cdot \nabla_x)\phi_0]$  from which we can identify the  
 395 three most challenging terms to estimate:

$$396 \quad (49) \quad \begin{cases} -\Delta_x f'(\phi_0)(\xi_\phi \cdot \nabla_x)\phi_0, \\ -f'(\phi_0)(\xi_\phi \cdot \nabla_x)\Delta_x \phi_0, \\ -f'(\phi_0)(\Delta_x \xi_\phi \cdot \nabla_x)\phi_0, \end{cases}$$

397 where  $\xi_\phi$  is the vector consisting of the corrector elements  $\xi_\phi^k$  defined in (28). In  
 398 order to bound the terms containing  $\phi_0$  we use Assumption C. The factor  $f'(\phi_0)$  and

399 associated derivatives in (49) can be bounded by the fact that  $f(s)$  is a polynomial  
400 of order  $2p - 1$  with characterization (PC), i.e.,

$$401 \quad (50) \quad \begin{cases} |f'(s)| & \leq c \left(1 + |s|^{2p-2}\right), \\ |f''(s)| & \leq c \left(1 + |s|^{2p-3}\right), \\ |f'''(s)| & \leq c \left(1 + |s|^{2p-4}\right). \end{cases}$$

402 We also note that  $-\Delta_x \xi_\phi^k = -1/\epsilon^2 \Delta_y \xi_\phi^k = 0$  in view of the cell/corrector problem for  
403  $\xi_\phi^k$ ,  $1 \leq k \leq d$ .

404 Finally, the remaining term  $R_\epsilon^\phi$  first decomposes in view of Assumption C as  
405 follows,

$$406 \quad (51) \quad \begin{aligned} |R_\epsilon^\phi| &= \left| \frac{m}{\lambda} (\operatorname{div} (f'(\phi_0) \nabla E_\epsilon^\phi) + \operatorname{div} (f''(\phi_0) \nabla \phi_0 E_\epsilon^\phi)) \right| \\ &\leq |f''(\phi_0) \nabla \phi_0 \nabla E_\epsilon^\phi| + |f'(\phi_0) \Delta E_\epsilon^\phi| \\ &\quad + |f'''(\phi_0) |\nabla \phi_0|^2 E_\epsilon^\phi| + |f''(\phi_0) \Delta \phi_0 E_\epsilon^\phi| \end{aligned}$$

407 and hence

$$408 \quad (52) \quad \begin{aligned} \int_{\Omega^\epsilon} |R_\epsilon^\phi| \, d\mathbf{x} &\leq \|f''(\cdot)\|_{L^\infty(I_\phi)} \|\nabla \phi_0\|_{L^\infty(\Omega^\epsilon)} \|\nabla E_\epsilon^\phi\|_{L^2(\Omega^\epsilon)} \\ &\quad + \|f'(\cdot)\|_{L^\infty(I_\phi)} \|\Delta E_\epsilon^\phi\|_{L^2(\Omega^\epsilon)} \\ &\quad + \|f'''(\cdot)\|_{L^\infty(I_\phi)} \|\nabla \phi_0\|_{L^\infty(I_\phi)}^2 \|E_\epsilon^\phi\|_{L^2(\Omega^\epsilon)} \\ &\quad + \|f''(\cdot)\|_{L^\infty(I_\phi)} \|\Delta \phi_0\|_{L^\infty(I_\phi)} \|E_\epsilon^\phi\|_{L^2(\Omega^\epsilon)} \\ &\leq C \left( \epsilon^{1/2} + \|E_\epsilon^w\|_{L^2(\Omega^\epsilon)} \right), \end{aligned}$$

409 where  $\|\Delta E_\epsilon^\phi\| \leq \|E_\epsilon^w\| + \epsilon \|F_\epsilon^\phi\|$  thanks to (41)<sub>3</sub> and  $I_\phi := ]\underline{\phi}, \overline{\phi}[$  is the interval defined  
410 by the smallest real root  $\underline{\phi}$  and  $\overline{\phi}$  the largest real root of the polynomial free energy  
411  $F$  characterized by (2).

412 In order to control the boundary contributions (45), we apply a standard argument  
413 [6, 11] based on a cut-off function  $\chi^\epsilon$  which is defined as follows,

$$414 \quad (53) \quad \begin{cases} \chi^\epsilon \in \mathcal{D}(\Omega^\epsilon), \\ \chi^\epsilon = 1 & \text{if } \operatorname{dist}(x, \partial\Omega^\epsilon) \leq \epsilon, \\ \chi^\epsilon = 0 & \text{if } \operatorname{dist}(x, \partial\Omega^\epsilon) \geq 2\epsilon, \\ \|\nabla \chi^\epsilon\|_{L^\infty(\Omega^\epsilon)} \leq \frac{C}{\epsilon}. \end{cases}$$

415 We first look at  $G_\epsilon^\phi$ . For  $\eta_\epsilon^\phi := \chi^\epsilon G_\epsilon^\phi$ , we show that  $\eta_\epsilon^\phi \in H^1(\Omega^\epsilon)$  and

$$416 \quad (54) \quad \|\eta_\epsilon^\phi\|_{H^1(U^\epsilon)} \leq C \epsilon^{-1/2},$$

417 where  $U^\epsilon$  is the support of  $\eta_\epsilon^\phi$  and forms a neighbourhood of  $\partial\Omega^\epsilon$  of thickness  $2\epsilon$ . The  
418 regularity properties of  $\xi_w^k$ ,  $\xi_\phi^k$  and  $\chi^\epsilon$  allow us to control  $\eta_\epsilon^\phi$  as follows

$$419 \quad (55) \quad \|\eta_\epsilon^\phi\|_{H^1(U^\epsilon)} \leq C \left( \frac{1}{\epsilon} \|\phi_0\|_{H^1(U^\epsilon)} + 1 \right),$$



420 where  $C$  is independent of  $\epsilon$ . Next, we use the result ([36, Lemma 5.1, p.7]), that is,  
 421  $\|\phi_0\|_{H^1(U^\epsilon)} \leq \epsilon^{1/2} C \|\nabla \phi_0\|_{H^1(\Omega^\epsilon)}$ , for a  $C$  independent of  $\epsilon$ . Herewith, we established  
 422 (54). Using the trace theorem and the fact that  $\eta_\epsilon^\phi = G_\epsilon^\phi$  on  $\partial\Omega^\epsilon$  allow us to obtain  
 423 the estimate

$$424 \quad (56) \quad \|\mathbf{G}_\epsilon^\phi\|_{H^{1/2}(\partial\Omega^\epsilon)} = \|\eta_\epsilon^\phi\|_{H^{1/2}(\partial\Omega^\epsilon)} \leq C \|\eta_\epsilon^\phi\|_{H^1(\Omega^\epsilon)} = C \|\eta_\epsilon^\phi\|_{H^1(U^\epsilon)},$$

425 which provides with (54) the bound

$$426 \quad (57) \quad \|\mathbf{G}_\epsilon^\phi\|_{H^{1/2}(\partial\Omega^\epsilon)} \leq C\epsilon^{-1/2}.$$

427 Applying the same arguments to  $\mathbf{G}_\epsilon^w$  immediately leads to the corresponding bound

$$428 \quad (58) \quad \|\mathbf{G}_\epsilon^w\|_{H^{1/2}(\partial\Omega^\epsilon)} \leq C\epsilon^{-1/2}.$$

429 Next, we estimate (41)<sub>1</sub>. Testing (41)<sub>1</sub> with  $-\Delta \mathbf{E}_\epsilon^w = \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w$  provides

$$430 \quad (59) \quad \begin{cases} \left( \partial_t (-\Delta)^{-1} \mathbf{E}_\epsilon^w, -\Delta \mathbf{E}_\epsilon^w \right) &= (\partial_t \mathbf{E}_\epsilon^w, \mathbf{E}_\epsilon^w) + [BT1] - [BT2], \\ -\lambda (\mathcal{B}_\epsilon \mathbf{E}_\epsilon^w, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w) &= -\lambda m (\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w) = -\lambda m \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\|^2, \\ (\mathcal{B}_\epsilon \mathbf{E}_\epsilon^f, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w) &= m \left( \mathcal{A}_\epsilon \left\{ f(\phi^\epsilon) - f(\phi_0) - \epsilon f'(\phi_0)(\mathbf{E}_\epsilon^\phi + \epsilon \phi_1) \right\}, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w \right), \\ \epsilon (\mathbf{R}_\epsilon^\phi, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w) &\leq C(\kappa) \left( \epsilon + \|\mathbf{E}_\epsilon^w\|_{L^2(\Omega^\epsilon)}^2 \right) + \kappa/2 \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\|^2 \\ \epsilon (\mathbf{F}_\epsilon^w, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w) &\leq \epsilon C(\kappa) \|\mathbf{F}_\epsilon^w\|^2 + \kappa/2 \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\|^2, \end{cases}$$

431 where we used (52) and the boundary terms [BT1] and [BT2] are bounded as follows

$$432 \quad (60) \quad \begin{aligned} |[BT1]| &:= \left| \int_{\partial\Omega^\epsilon} \partial_t (-\Delta)^{-1} \nabla_n \mathbf{E}_\epsilon^w \mathbf{E}_\epsilon^w \, d\sigma \right| = \left| \int_{\partial\Omega^\epsilon} \partial_t (-\Delta)^{-1} \epsilon \mathbf{G}_\epsilon^w \mathbf{E}_\epsilon^w \, d\sigma \right| \\ &\leq \epsilon C \|\partial_t (-\Delta)^{-1} \mathbf{G}_\epsilon^w\|_{W^{l-3,2}(\Omega^\epsilon)} \|\mathbf{E}_\epsilon^w\|_{H^1(\Omega^\epsilon)} \leq \epsilon^{1/2} C \quad \text{for } l \geq 4, \\ |[BT2]| &:= \left| \int_{\partial\Omega^\epsilon} \partial_t (-\Delta)^{-1} \mathbf{E}_\epsilon^w \nabla_n \mathbf{E}_\epsilon^w \, d\sigma \right| = \left| \int_{\partial\Omega^\epsilon} \partial_t (-\Delta)^{-1} \mathbf{E}_\epsilon^w \epsilon \mathbf{G}_\epsilon^w \, d\sigma \right| \leq \epsilon^{1/2} C. \end{aligned}$$

433 In (60)<sub>1</sub>, we used Assumption C to assure in terms of regularity that  $\phi_0 = (-\Delta)^{-1} w_0 \in$   
 434  $C^1(0, T; W^{l,\infty}(\Omega^\epsilon))$  and hence the final bound is a consequence of the trace theorem  
 435 and (58). The same argument holds for (60)<sub>2</sub>.

436 All this together then leads to the estimate

$$437 \quad (61) \quad \begin{aligned} &\frac{1}{2} \frac{d}{dt} \|\mathbf{E}_\epsilon^w\|^2 + (m\lambda - \kappa) \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\|^2 \\ &\leq C(m, \kappa) \left( |(\mathcal{A}_\epsilon [f(\phi^\epsilon) - f(\phi_0)], \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w)| \right. \\ &\quad \left. + |(\mathcal{A}_\epsilon [f'(\phi_0)(\mathbf{E}_\epsilon^\phi + \epsilon \phi_1)], \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w)| \right) \\ &\quad + C(\kappa) \left( \epsilon + \|\mathbf{E}_\epsilon^w\|_{L^2(\Omega^\epsilon)}^2 \right) + \epsilon \|\mathbf{F}_\epsilon^w\|^2 + \epsilon^{1/2} C, \end{aligned}$$

438 where the last summand reflects the boundary terms. In order to control the terms  
 439 on the right-hand side in (61), we make use of the fact that  $f(s)$  is a polynomial and

440 satisfies (50). The first term in (61) satisfies the following inequality

$$\begin{aligned}
& |(\mathcal{A}_\epsilon [f(\phi^\epsilon) - f(\phi_0)], \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w)| \leq C \left( \left| \left( \{f''(\phi^\epsilon) - f''(\phi_0)\} |\nabla \phi^\epsilon|^2, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w \right) \right| \right. \\
441 \quad (62) \quad & + |(f''(\phi_0) \nabla(\phi^\epsilon + \phi_0) \nabla(\phi^\epsilon - \phi_0), \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w)| \\
& \left. + |(\{f'(\phi^\epsilon) - f'(\phi_0)\} \Delta \phi^\epsilon, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w)| + |(f'(\phi_0) \Delta(\phi^\epsilon - \phi_0), \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w)| \right).
\end{aligned}$$

442 Before we proceed, we estimate the terms on the right-hand side in (62):

443 *1st term in (62):* We first note that with the remainder term in Taylor series we  
444 obtain

$$\begin{aligned}
& |f''(\phi^\epsilon) - f''(\phi_0)| \leq \sup_{\theta \in I_\phi} f'''(\theta) |\phi^\epsilon - \phi_0| \leq \|f'''(\cdot)\|_{L^\infty(I_\phi)} |\phi^\epsilon - \phi_0| \\
445 \quad (63) \quad & \leq \|f'''(\cdot)\|_{L^\infty(I_\phi)} (|\mathbf{E}_\epsilon^\phi| + \epsilon |\phi_1|) \\
& \leq \|f'''(\cdot)\|_{L^\infty(I_\phi)} (|\mathbf{E}_\epsilon^\phi| + \epsilon |(\boldsymbol{\xi}_\phi \cdot \nabla_x) \phi_0|) \\
& \leq \|f'''(\cdot)\|_{L^\infty(I_\phi)} (|\mathbf{E}_\epsilon^\phi| + \epsilon C),
\end{aligned}$$

446 where  $I_\phi := ]\underline{\phi}, \overline{\phi}[$  is the interval defined by the smallest real root  $\underline{\phi}$  and  $\overline{\phi}$  the largest  
447 real root of the polynomial free energy  $F$  characterized by (2). We used Assumption  
448 C in (63). Herewith, we can estimate the first term (e.g. in  $d = 3$ ) as follows

$$\begin{aligned}
& \left| \left( \{f''(\phi^\epsilon) - f''(\phi_0)\} |\nabla \phi^\epsilon|^2, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w \right) \right| \\
& \leq C \|f'''(\cdot)\|_{L^\infty(I_\phi)} (|\mathbf{E}_\epsilon^\phi|_{L^6} + \epsilon) \|\nabla \phi^\epsilon\|_{L^6}^2 \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\| \\
449 \quad (64) \quad & \leq C \|f'''(\cdot)\|_{L^\infty(I_\phi)} (|\mathbf{E}_\epsilon^\phi|_{H^1} + \epsilon) \|\nabla \phi^\epsilon\|_{H^1}^2 \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\| \\
& \leq C(\kappa) (|\mathbf{E}_\epsilon^\phi|_{H^1}^2 + \epsilon^2) + \kappa \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\|^2 \\
& \leq C(\kappa) \left( \|\mathbf{E}_\epsilon^w\|^2 + \epsilon^2 (2 + \epsilon^{1/2})^2 \right) + \kappa \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\|^2.
\end{aligned}$$

450

451 *2nd term in (62):* With Sobolev inequalities, e.g. Fridrichs' inequality in the perforated domain case [10], and the identity  $\phi^\epsilon - \phi_0 = \mathbf{E}_\epsilon^\phi + \epsilon \phi_1$  we obtain the following  
452 estimate  
453

$$\begin{aligned}
& |(f''(\phi_0) \nabla(\phi^\epsilon + \phi_0) \nabla(\phi^\epsilon - \phi_0), \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w)| \leq C(T) \left( \|\nabla \phi^\epsilon\|_{L^6} \right. \\
454 \quad (65) \quad & \left. + \|\nabla \phi_0\|_{L^6} \right) \left( \|\nabla \mathbf{E}_\epsilon^\phi\|_{L^3} + \epsilon \|\nabla \phi_1\|_{L^3} \right) \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\| \\
& \leq C(T, \kappa) \left( \|\mathbf{E}_\epsilon^w\|^2 + \epsilon^2 \right) + \kappa \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\|^2,
\end{aligned}$$

455 where we again used Assumption C and classical regularity results from the elliptic  
456 PDE theory.

457 *3rd term in (62):* Following the same ideas as for the *1st term* estimated in (64), we  
458 immediately get the bound

$$\begin{aligned}
& |(\{f'(\phi^\epsilon) - f'(\phi_0)\} \Delta \phi^\epsilon, \mathcal{A}_\epsilon \mathbf{E}_\epsilon^w)| \\
459 \quad (66) \quad & \leq C(\Omega, T, \kappa) \left( \|\mathbf{E}_\epsilon^w\|^2 + \epsilon^2 \right) + \kappa \|\mathcal{A}_\epsilon \mathbf{E}_\epsilon^w\|^2.
\end{aligned}$$

460

 461 *4th term in (62):* The last term can finally be controlled as follows

$$\begin{aligned}
 & |(f'(\phi_0)\Delta(\phi^\epsilon - \phi_0), \mathcal{A}_\epsilon E_\epsilon^w)| \\
 462 \quad (67) \quad & \leq C(\Omega, T) \left( \|\Delta E_\epsilon^\phi\| + \epsilon \|\Delta \phi_1\| \right) \|\mathcal{A}_\epsilon E_\epsilon^w\| \\
 & \leq C(\Omega, T, \kappa) \left( \left( \|E_\epsilon^w\|^2 + \epsilon^2 \|F_\epsilon^\phi\|^2 \right) + \epsilon^2 \right) + \kappa \|\mathcal{A}_\epsilon E_\epsilon^w\|^2,
 \end{aligned}$$

 463 where we again used Assumption C and classical regularity results from the theory of  
 464 elliptic PDEs.

 465 Back to controlling (61), it leaves to derive a bound on the second term on the  
 466 right-hand side, i.e.,  $|\mathcal{A}_\epsilon[f'(\phi_0)(E_\epsilon^\phi + \epsilon\phi_1)], \mathcal{A}_\epsilon E_\epsilon^w|$ . We have

$$\begin{aligned}
 467 \quad (68) \quad & |\mathcal{A}_\epsilon[f'(\phi_0)(E_\epsilon^\phi + \epsilon\phi_1)], \mathcal{A}_\epsilon E_\epsilon^w| \leq C \left( \epsilon + \|E_\epsilon^\phi\|_{L^2(\Omega^\epsilon)} + \|\nabla E_\epsilon^\phi\|_{L^2(\Omega^\epsilon)} + \|E_\epsilon^w\|_{L^2(\Omega^\epsilon)} \right) \\
 & \leq C \left( \epsilon + \|E_\epsilon^w\|_{L^2(\Omega^\epsilon)} \right),
 \end{aligned}$$

468 where we used the facts that

$$\begin{aligned}
 469 \quad (69) \quad & \mathcal{A}_\epsilon[f'(\phi_0)(E_\epsilon^\phi + \epsilon\phi_1)] = -\Delta[f'(\phi_0)(E_\epsilon^\phi + \epsilon\phi_1)] \\
 & = -f'''(\phi_0)|\nabla\phi_0|^2(E_\epsilon^\phi + \epsilon\phi_1) - f''(\phi_0)\Delta\phi_0(E_\epsilon^\phi + \epsilon\phi_1) \\
 & \quad - f''(\phi_0)\nabla\phi_0\nabla(E_\epsilon^\phi + \epsilon\phi_1) - f'(\phi_0)\Delta(E_\epsilon^\phi + \epsilon\phi_1),
 \end{aligned}$$

 470 Assumption C, and error equation (41)<sub>3</sub>.

471 Hence, with the previously derived bounds (62) and (68) we obtain,

$$\begin{aligned}
 472 \quad (70) \quad & \frac{d}{dt} \|E_\epsilon^w\|^2 + 2(m\lambda - \kappa) \|\mathcal{A}_\epsilon E_\epsilon^w\|^2 \\
 & \leq C(m, \kappa, \lambda, \Omega, T) \left( \|E_\epsilon^w\|^2 + A(\epsilon) \right) + 8\kappa \|\mathcal{A}_\epsilon E_\epsilon^w\|^2,
 \end{aligned}$$

 473 where  $A(\epsilon) := (\epsilon^2(2 + \epsilon^{1/2})^2 + \epsilon^2 + \epsilon + \epsilon^{1/2})$ . A consideration of  $\frac{d}{dt} (\exp(-Ct) \|E_\epsilon^w\|)$   
 474 leads after some rewriting to the following bound,

$$475 \quad (71) \quad \|E_\epsilon^w(\cdot, T)\|^2 \leq \exp(CT) CA(\epsilon),$$

 476 which guarantees the control of (61). Herewith, we are also in the position to derive  
 477 a bound on  $\|\mathcal{A}_\epsilon E_\epsilon^w\|^2$  after integrating (70) over time, that means,

$$\begin{aligned}
 478 \quad (72) \quad & \|E_\epsilon^w\|^2(t) + 2(m\lambda - n\kappa) \int_0^t \|\mathcal{A}_\epsilon E_\epsilon^w\|^2(s) ds \\
 & \leq C(\exp(Ct)) A(\epsilon)t,
 \end{aligned}$$

 479 for  $n \in \mathbb{N}$  finite. □

 480 **6. Conclusions.** Based on a microscopic porous media formulation (8), we de-  
 481 rived upscaled/ homogenized phase-field equations for general free energy densities.  
 482 We gave a rigorous justification of this new effective macroscopic equations for a class  
 483 of polynomial free energies which include the widely used double-well potential. The

484 porous materials considered here can be represented by a periodic covering of a single  
 485 reference cell  $Y$  which accounts for the pore geometry. It is well-known that transport  
 486 as well as fluid flow in porous media lead to high-dimensional computational problems,  
 487 since the mesh size needs to be much smaller than the heterogeneity  $\epsilon := \frac{\ell}{L}$ , the ratio  
 488 of the characteristic length scale of the pores  $\ell$  over the size of macroscopic porous  
 489 medium  $L$ . We rigorously derived qualitative error estimates for the approximation  
 490 error between the solution of the effective macroscopic problem (17) and the solution  
 491 of the fully resolved microscopic equation (8). We also recovered the classical error  
 492 behavior from homogenization of elliptic problems based on a truncation not resolving  
 493 boundary effects in the context of fourth order phase field problems.

494 This error quantification is of fundamental interest in applications as it provides  
 495 guidance on the applicability of the new effective macroscopic phase-field formulation  
 496 in dependence of the heterogeneity  $\epsilon > 0$  defined by the heterogeneous material under  
 497 consideration. Our dimensionally reduced phase field formulation can also be seen as  
 498 the precursor to an effective and systematic computational strategy where microscopic  
 499 properties such as the geometry and wall characteristics (e.g. wetting properties) of a  
 500 reference pore enter the macroscopic description in an effective manner, thus avoiding  
 501 a full numerical resolution of the finer details of the porous structure.

502 There are a number of interesting mathematical-physical questions related to the  
 503 analysis presented here. For instance: (i) The error estimates still require rather high  
 504 regularity assumptions (Assumption C) for which Lemma 1 seems to provide currently  
 505 the best available estimates; (ii) Moreover, the error behavior in time in (20) seems  
 506 not optimal; (iii) And a more physically motivated question is: “What is the influence  
 507 of the pore or material geometry on phase transformations in heterogeneous media  
 508 such as composites and porous materials and does the effective formulation capture  
 509 such geometry dependent phenomena?”

510 Finally, we believe that, due to the popularity and the wide range of applicability  
 511 of phase-field equations, the new effective macroscopic formulation, could ultimately  
 512 serve as a promising computational tool in material-chemical- physical sciences and  
 513 engineering. In particular, the effective phase-field formulation (17) could form the  
 514 basis for a promising new direction for modelling multiphase flow in porous media  
 515 without making use of Darcy’s law.

516 We shall examine these and related questions in future studies.

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519

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