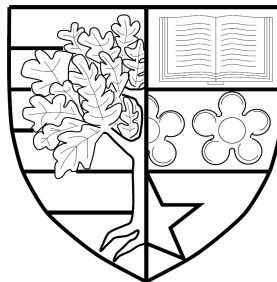


# Multiscale Modelling Analysis and Computations of Complex Heterogeneous Multiphase Systems

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# Abstract

In this thesis, we analytically and computationally investigate various aspects related to the multiphase-multicomponent interfacial processes and reactive transport in homogeneous domains and heterogeneous periodic perforated media. More precisely, we perform formal homogenization arguments to the microscopic Cahn-Hilliard type equations governed the dynamics in binary and ternary mixtures, in the presence of two or more phases. We additionally consider the coupling of the Cahn-Hilliard type species diffusion to fluid flow, a coupling which gives rise to more complex systems since a Navier-Stokes momentum balance is involved. Each particular model can be formally derived by an Energetic Variational Approach, that combines the classical idea of gradient flows for free energy minimization as a direct consequence of the second law of thermodynamics, together with the Least Action and Maximum Dissipation Principles.

Moreover, as an extension of the already established two-scale convergence approach, we investigate further a reiterated homogenization procedure over three separated scales of periodic oscillations. Finally, we examine the General Equations for Non-Equilibrium Reversible-Irreversible Coupling commonly known by the abbreviation GENERIC, an extended two-generator variational framework, which was initially developed in order to model the rheological properties of complex fluids, far from thermodynamic equilibrium.

*"What we do in life, echoes in eternity"*

MARCUS AURELIUS

To my family

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# Contents

<b>Abstract</b>	<b>1</b>
<b>Acknowledgements</b>	<b>3</b>
<b>Overview of the thesis</b>	<b>6</b>
<b>1 Introduction to Cahn-Hilliard type dynamics.</b>	<b>14</b>
1.1 <b>Free energy of a non-uniform system: the classical statement by Cahn and Hilliard.</b>	<b>15</b>
1.2 <b>Minimization of the Ginzburg-Landau/Cahn-Hilliard free energy: The Cahn-Hilliard equation.</b>	<b>20</b>
1.2.1 <b>General minimization procedure for an Euclidean function: method of gradient descent.</b>	<b>20</b>
1.2.2 <b>Extension for functionals: gradient flows.</b>	<b>21</b>
1.2.3 <b>The <math>L^2</math> and <math>H^{-1}</math> gradient flows of the Cahn-Hilliard free energy.</b>	<b>23</b>
1.2.4 <b>Physical interpretation of the Cahn-Hilliard dynamics</b>	<b>26</b>
1.2.5 <b>A review on well-posedness of the classical Cahn-Hilliard equation.</b>	<b>28</b>
<b>2 Numerical studies, porous media and homogenization.</b>	<b>34</b>
2.1 <b>Microscopic formulations, discretization and homogenization of Cahn-Hilliard type equations.</b>	<b>34</b>
2.1.1 <b>Upscaled Allen-Cahn/Cahn-Hilliard equations.</b>	<b>42</b>
2.1.2 <b>Homogenization with the help of a two-scale asymptotic expansion.</b>	<b>49</b>
2.1.3 <b>Derivation of homogenized/upscaled equations via a rigorous two-scale convergence approach.</b>	<b>54</b>
2.1.4 <b>Homogenized Allen-Cahn/Cahn-Hilliard equations, derived by a reiterated rigorous three-scale convergence approach.</b>	<b>62</b>
2.1.5 <b>Multiphase-ternary mixtures and homogenization.</b>	<b>73</b>
2.2 <b>Physical interpretation and numerical experiments for binary mixtures.</b>	<b>91</b>

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2.2.1	<b>An overview of coarsening dynamics for the Cahn-Hilliard Equation. . . . .</b>	91
2.2.2	<b>The concept of curve shortening flows and the relation to the Cahn-Hilliard dynamics. . . . .</b>	94
2.2.3	<b>Deformation dynamics of a semi-circular interface located on the left boundary. . . . .</b>	98
<b>3</b>	<b>Introduction to the GENERIC formalism and applications</b>	<b>103</b>
3.1	<b>Introductory concepts. . . . .</b>	103
3.2	<b>Metriplectic flows/GENERIC formalism. . . . .</b>	114
3.2.1	<b>Properties of GENERIC. . . . .</b>	115
3.2.2	<b>The equations of hydrodynamics via GENERIC in the macroscale. . . . .</b>	120
3.2.3	<b>Appendix . . . . .</b>	129
3.2.4	<b>GENERIC formulation for the Allen-Cahn/Cahn-Hilliard coupled with Navier-Stokes model. . . . .</b>	138
3.2.5	<b>The equations of hydrodynamics and coarse-graining . . .</b>	150
<b>4</b>	<b>Further applications of Cahn-Hilliard/Navier-Stokes couplings.</b>	<b>159</b>
4.1	<b>A Cahn-Hilliard/Navier-Stokes system for the dynamics of adsorption. . . . .</b>	159
4.1.1	<b>Derivation of the equations of motion. . . . .</b>	160
4.2	<b>The Poisson-Nerst-Planck/Navier-Stokes system. . . . .</b>	167
	<b>Bibliography</b>	<b>172</b>

# Overview of the thesis.

An increasing interest to explore and develop more complicated mathematical theories for modelling complex physical phenomena, has been shown over the centuries. The ability to perform experiments with less computational cost, using mathematical models has literally developed new fields of research, in order to understand better the complexity of nature. However, despite the growth of computer capabilities, any feasible mathematical model still requires significant simplification due to the complexity of the various natural processes. To this end, the objective of studying a mathematical model is not to recreate reality, but rather to shed some light on the governing dynamics of the process being modelled. Hence, from a purely mathematical perspective, modelling can lead to the construction of new and interesting systems of partial differential equations. Finally, as the development of new theories goes by and comes to my research, one could divide it into the following separately indicative but also interconnected sections.

## **Phase-field modelling, flow in porous media and homogenization.**

Phase-field modelling has received increasing interest for theoretical and computational investigation of physical, chemical and even experimental systems and is generally applied to multi-phase solidification dynamics in binary alloys [1] as well as fracture dynamics [2] in materials science and other physical phenomena. Strongly inspired by the work of J. W. Cahn and J. Hilliard [3], the idea of diffuse interface models is based on the study of the abstract free energy  $\mathcal{F}(c) : H^1(D) \rightarrow \mathbb{R}$ , (where  $D \subset \mathbb{R}^d$ ), of a non-uniform isotropic binary mixture, with variable composition  $c := c(\mathbf{r}, t)$ , which can be expressed in the following form

$$\mathcal{F}(c) = \int_D F_{CH}(c) \, d\mathbf{r} := \int_D f_L(c) + \frac{\lambda^2}{2} |\nabla c|^2 \, d\mathbf{r},$$

which is also known as Ginzburg-Landau free energy in the context of the theory of superconductivity [4]. It is composed of two terms, the free energy density of a solution with uniform composition  $f_L(c)$  and a gradient term which penalizes the interfacial area of width  $\lambda$ , between the two phases. In order to approach the concept of thermodynamic equilibrium which corresponds to minimum free energy, we recruit the gradient descent method, extended for a functional  $\mathcal{F}(c)$  (gradient flow) for all times  $t \in [0, T]$ :

$$\langle \partial_t c, \varphi \rangle_{L^2(D)} = \langle \nabla_c^{\mathcal{X}_i} \mathcal{F}(c), \varphi \rangle_{\mathcal{Z}(D)}, \quad \forall \varphi \in \mathcal{X}_i(D) \subseteq \mathcal{Z}(D),$$

where  $\mathcal{X}_i(D) \subseteq \mathcal{Z}(D)$  are Hilbert spaces.

Consequently, we review the classical statement of minimization of the Ginzburgh-Landau free energy  $\mathcal{F}(c)$ , via the  $L^2$ - and  $H^{-1}$ -gradient flows, which eventually leads to the Allen-Cahn and Cahn-Hilliard equations [5, 6], respectively:

$$\begin{cases} \partial_t c = -(f'_L(c) - \lambda^2 \Delta c), & \text{in } D_T := D \times (0, T), \\ \partial_t c = \Delta(f'_L(c) - \lambda^2 \Delta c), & \text{in } D_T, \end{cases}$$

supplemented with homogeneous Neumann  $\partial_n c|_{\partial D_T} = 0$ , the corresponding no-flux  $\partial_n(f'_L(c) - \lambda^2 \Delta c)|_{\partial D_T} = 0$  boundary conditions and some initial condition  $c(\mathbf{r}, 0) \in H^1(D)$ . To this end, summarising the work by C. M. Elliot, C. Garcke, A. Novick-Cohen and others [7, 8], we study existence and uniqueness of solutions of the Cahn-Hilliard equation, for both the cases of constant and degenerate mobilities. In the same context we examine the initial-boundary value problem

$$\begin{cases} \partial_t c = \operatorname{div}(\mathbb{M} \nabla \mu(c)) - \mu(c) & \text{in } D_T, \\ \partial_n c = \partial_n \mu(c) = \partial_n \Delta c = 0 & \text{on } \partial D_T, \end{cases}$$

by adapting the classical definition of the Cahn-Hilliard chemical potential  $\mu(c) := f'_L(c) - \lambda^2 \Delta c$ . The specific formalism with constant mobility  $\mathbb{M} > 0$ , was first introduced by G. Karali and M. Katsoulakis [9] as a more simplified model of a mesoscopic formulation for multiple microscopic mechanisms, in simultaneously interacting surface processes. The Cahn-Hilliard term corresponds to surface diffusion, and the Allen-Cahn to adsorption/desorption. Existence and uniqueness of solutions has been studied by G. Karali and Y. Nagase [10] for the constant mobility case and by X. Zhang and C. Liu [11], for the degenerate mobility case. The proofs follow similar lines (with the appropriate modifications) as the one for the classical Cahn-Hilliard and therefore we are not going into details on the analysis part.

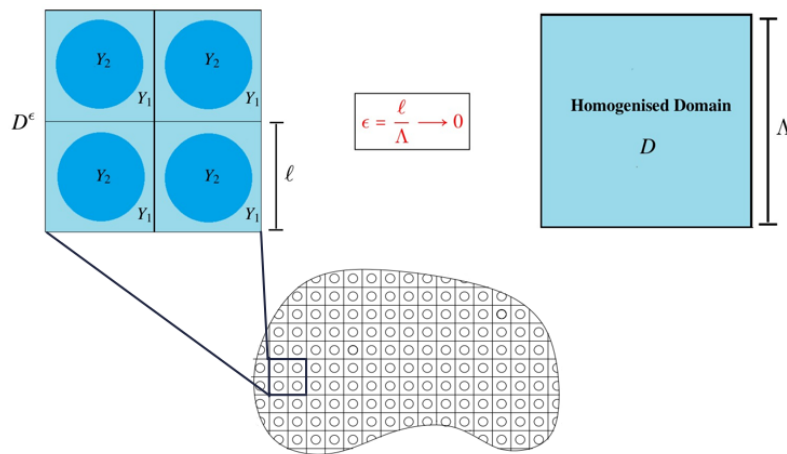


Figure 1: The idea of upscaling.

We are mainly interested in the periodic porous media setting of the problem (see Figure 1) of the Allen-Cahn/Cahn-Hilliard and on the derivation of effective/upscaled equations for this model by applying the basic principles of homogenization theory [12, 13]. We finally obtain the upscaled equations for isotropic mobility  $\mathbb{M} := m\mathbb{I}$ , via a



two-scale asymptotic expansion  $c^\varepsilon(\mathbf{r}, t) = \sum_{i=0}^{\infty} \varepsilon^i c^i(\mathbf{r}, \mathbf{y}, t)$ , with  $\mathbf{y} := \mathbf{r}/\varepsilon$ , namely:

$$p \partial_t c_0 = m \operatorname{div}(\mathbb{D} \nabla f'_L(c_0)) - \lambda^2 p^{-1} m \operatorname{div}(\mathbb{D} \nabla [\operatorname{div}(\mathbb{D} \nabla c_0)]) - p f'_L(c_0) + \lambda^2 \operatorname{div}(\mathbb{D} \nabla c_0) \text{ in } D_T,$$

where  $p := |Y_1|/|Y|$ ,  $\varepsilon := \ell/\Lambda$  denote the porosity and the heterogeneity of the periodic porous medium, respectively. The elements of the effective tensor  $\mathbb{D} := \{\mathbb{D}_{ij}\}_{1 \leq i, j \leq d}$ , can be defined by:

$$\mathbb{D}_{ik} := \frac{1}{|Y|} \int_{Y_1} \left( \delta_{ik} - \frac{\partial \xi_c^k(\mathbf{y})}{\partial y_i} \right) d\mathbf{y}, \text{ for all } i, k = 1, \dots, d.$$

The correctors  $\xi_c^k(\mathbf{y})$  are solutions of the following elliptic reference cell problem

$$\begin{cases} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_c^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi_c^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi_c^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi_c^k) = 0. \end{cases}$$

In comparison to the two-scale case we also examine the homogenization process in a domain that contains small perforations of size  $\varepsilon > 0$  periodically distributed with period  $\varepsilon$  and very small perforations of size  $\varepsilon \varepsilon_1(\varepsilon) > 0$  with periodicity  $\varepsilon \varepsilon_1(\varepsilon)$ , such that  $0 < \varepsilon_1(\varepsilon) < \varepsilon$ . To this end, we introduce one additional microscopic variable  $\mathbf{y}_1 := \mathbf{r}/\varepsilon \varepsilon_1(\varepsilon)$ , for which the homogenization procedure, following a rigorous three-scale convergence approach, yields a similar effective macroscopic equation in  $D_T$  with porosity  $p_1 := |Y_1| |Z_1| / |Y| |Z|$ :

$$p_1 \partial_t c_0 = m \operatorname{div}(\mathbb{D}_1 \nabla f'_L(c_0)) - \lambda^2 (p_1)^{-1} m \operatorname{div}(\mathbb{D}_1 \nabla [\operatorname{div}(\mathbb{D}_1 \nabla c_0)]) - p_1 f'_L(c_0) + \lambda^2 \operatorname{div}(\mathbb{D}_2 \nabla c_0) \text{ in } D_T,$$

where the elements of the effective tensor  $\mathbb{D}_1 := \{(\mathbb{D}_1)_{ij}\}_{1 \leq i, j \leq d}$  are given by

$$(\mathbb{D}_1)_{ij} := \frac{1}{|Y| |Z|} \int_{Y_1 \times Z_1} \sum_{k,l=1}^d \left( \delta_{ij} - \delta_{il} \frac{\partial \xi^j(\mathbf{y})}{\partial y_l} - \delta_{ik} \frac{\partial \xi_*^j(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1k}} + \delta_{il} \frac{\partial \xi_*^k(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1l}} \cdot \frac{\partial \xi^j(\mathbf{y})}{\partial y_k} \right) d\mathbf{y} d\mathbf{y}_1, \quad (0.0.1)$$

where each of the functions  $\xi^j(\mathbf{y}), \xi_*^k(\mathbf{y}, \mathbf{y}_1)$ ,  $j, k = 1, \dots, d$  are solutions of cell problems defined analogously as in the two-scale case.

We further extend our considerations to more than two-component mixtures in the presence of multiple phases and more precisely, we examine the dynamics in ternary alloys. The modelling of dynamic behaviour in multiphase and three-component  $c_i$ ,  $i = 1 : 3$  flows (ternary mixtures) is based on an abstract free energy functional of the form [14–16]:

$$\mathcal{F}_m(c_i, \phi_\alpha) := \int_D F(c_i, \phi_\alpha) d\mathbf{r} := \int_D f_0(c_i, \phi_\alpha, \Theta) + \left( \sum_{\alpha, \beta=1}^{N-1} \frac{1}{2} k_{\alpha\beta} \nabla \phi_\alpha \cdot \nabla \phi_\beta + \sum_{i,j=1}^2 \frac{1}{2} \lambda_{ij}^2 \nabla c_i \cdot \nabla c_j \right) d\mathbf{r},$$

where  $i = 1, 2$ , and  $\alpha = 1, \dots, N$  and we also denoted

$$\begin{aligned} f_0(c_i, \phi_\alpha, \Theta) &:= \sum_{\alpha=1}^N \phi_\alpha f_\alpha(c_i, \Theta) + \sum_{\beta \neq \alpha} W_{\alpha\beta} \phi_\alpha \phi_\beta, \\ &:= K(\Theta) \sum_{i=1}^2 \frac{1}{4} (c_i - 1)^2 c_i^2 + \sum_{\beta \neq \alpha} W_{\alpha\beta} \phi_\alpha \phi_\beta, \quad i = 1, 2, \end{aligned}$$

with  $W_{\alpha\beta} > 0$  being a mean field interaction potential between phases and the phase fraction  $\phi_\alpha$  which corresponds to each phase  $\alpha$ , varies between the values 0 and 1.

To this end, we formally derive by gradient flows the following system of Cahn-Hilliard type equations for the evolution of the two substances  $c_i$ ,  $i = 1, 2$ :

$$\left\{ \begin{array}{l} \partial_t c_i = \operatorname{div} \left( \mathbb{M}_i \sum_{j=1}^2 \hat{\mathbb{M}}_{ij}(\mathbf{c}) \nabla (\partial_{c_j} F(c_j, \phi_\alpha)) \right) \quad \text{in } D_T, \\ \partial_{c_i} F(c_i, \phi_\alpha) := \sum_{\alpha=1}^N \phi_\alpha \frac{\partial f_\alpha(c_i, \phi_\alpha)}{\partial c_i} - \sum_{j=1}^2 \lambda_{ij}^2 \Delta c_j \quad \text{in } D_T, \\ \partial_{\mathbf{n}} \mathbf{J}_i(\mathbf{c}) = \partial_{\mathbf{n}} c_i = 0 \quad \text{on } \partial D_T, \end{array} \right. \quad (0.0.2)$$

where  $\hat{\mathbb{M}}_{ij}(\mathbf{c}) := c_i(\delta_{ij} - c_j)$ ,  $i, j = 1, 2$  with  $\mathbf{c} := [c_1, c_2]$ . Independently, we consider that the evolution of the phase-field functions  $\phi_\alpha$ ,  $\alpha = 1, \dots, N$  is dictated by the Allen-Cahn dynamics, i.e.,

$$\partial_t \phi_\alpha = -k_\alpha \partial_{\phi_\alpha} F(c_i, \phi_\alpha), \quad k_\alpha > 0 \quad \text{in } D_T,$$

with  $\partial_{\mathbf{n}} \phi_\alpha = 0$  and the evolution of the potential term to be defined by

$$\partial_{\phi_\alpha} F(c_i, \phi_\alpha) := \frac{\partial f_0}{\partial \phi_\alpha} - \sum_{\beta=1}^{N-1} k_{\alpha\beta} \Delta \phi_\beta, \quad k_{\alpha\beta} > 0 \quad \text{in } D_T.$$

We subsequently obtain upscaled/homogenized equations by verifying existence of weak solutions for the same model in the porous media setting and then passing to the limit in the two-scale sense [17].

Furthermore, we provide a more concrete investigation and understanding of the Cahn-Hilliard type dynamics, with some numerical experiments with the help of Python-FEniCs library [18], illustrating some interesting results related to the concept of curve shortening flow of the interface (Mullins-Sekerka [19]) and the relation to the Cahn-Hilliard dynamics. We adapt a discrete mixed weak formulation scheme for the discretization of the Cahn-Hilliard microscopic formulation and similar approaches for the effective/homogenized approximations [20]. More precisely we define the mass matrix by  $\mathbb{G} := \{(\varphi_i, \varphi_j)\}_{1 \leq i, j \leq d}$  (where  $\{\varphi_j\}_{j=1}^J$ , linear finite element basis on  $V_h$ ), the stiffness matrix  $\mathbb{S} := \{(\nabla \varphi_i, \nabla \varphi_j)\}_{1 \leq i, j \leq d}$  and the nonlinear matrix  $\mathbb{K}(\mathbf{c}_{n+1}^{\varepsilon, l}) := \{((\mathbf{c}_{n+1}^{\varepsilon, l})^2 \varphi_i, \varphi_j)\}_{1 \leq i, j \leq d}$ . We denoted by  $\langle \nabla^k \varphi_i, \nabla^k \varphi_j \rangle$ ,  $k = 0, 1$  the usual  $L^2$ -scalar product  $\int_D \nabla^k \varphi_i \cdot \nabla^k \varphi_j \, dr$ ,  $k = 0, 1$ . In addition, we denote by  $c_{h,k}^\varepsilon := \sum_{j=1}^J c_j^n \varphi_j(\mathbf{r})$  the finite element approximation of the microscopic solution  $c^\varepsilon$  for  $t_n = n\Delta t$ . The index  $l \in N, 0 \leq l \leq L$ , denotes the iteration level in the scheme, linearised by a fixed point iteration. The scheme also consists of the  $\theta$ -method:  $\boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1} := (1-\theta)\boldsymbol{\mu}_n^\varepsilon + \theta\boldsymbol{\mu}_{n+1}^{\varepsilon, l+1}$ ,  $0 \leq \theta \leq 1$ . Therefore, the following mixed finite element scheme can be applied for mobility  $\mathbb{M} = m\mathbb{I}$ ,  $m > 0$ :

$$\left\{ \begin{array}{l} \mathbb{G} \mathbf{c}_{n+1}^{\varepsilon, l+1} + m\Delta t \mathbb{S} \boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1} = \mathbb{G} \mathbf{c}_n^\varepsilon, \\ \mathbb{G} \boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1} + \mathbb{K}(\mathbf{c}_{n+1}^{\varepsilon, l}) \mathbf{c}_{n+1}^{\varepsilon, l+1} - \frac{1}{2} \mathbb{G} \mathbf{c}_{n+1}^{\varepsilon, l+1} - \lambda^2 \mathbb{S} \mathbf{c}_{n+1}^{\varepsilon, l+1} = 0, \end{array} \right.$$

where  $(\mathbf{c}_{n+1}^{\varepsilon, l+1}, \boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1})$  with  $\boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1} := \{\mu_{j,n}^{\varepsilon, l+1}\}_{j=1}^J$  and  $\mathbf{c}^{\varepsilon, l+1} := \{c_{j,n}^{\varepsilon, l+1}\}_{j=1}^J$ , are coefficient vectors of the related finite element functions. Finally we considered in the discretization scheme, the following form of the homogeneous free energy:  $f_L(c) = (1/4)c^2(1-c)^2$ .

A (shrinking) circular equilibrium shape is asymptotically being approached by any (non)-convex closed interface (independent of its initial shape), under the curve shortening flow (Gage-Hamilton and Grayson theorems [21, 22]). To this end, we computationally validate this theorem, under the Cahn-Hilliard flow in both homogeneous domains and periodically perforated media, for sufficiently small heterogeneity. We illustrate the coarsening phenomenon, for random initial data, in both homogeneous [23, 24] and periodically perforated domains. The universal coarsening rate  $\mathcal{O}(t^{1/3})$  [25], is computationally recovered in the porous media setting [20]. In the case of critical quenching and after adding thermal noise to the microscopic porous media formulation, we observe that the influence of thermal fluctuations on the coarsening rate shows after a short, expected phase of universal coarsening, a sharp transition towards a different regime [20, 26].

Moreover, a recently derived effective macroscopic formulation [13], which takes systematically the pore geometry into account, is computationally validated. The theoretically derived convergence rate  $\mathcal{O}(\varepsilon^{1/4})$  [27] is confirmed for circular pore-walls of a periodic porous medium with heterogeneity  $\varepsilon$ . An even better convergence of  $\mathcal{O}(\varepsilon)$  holds for square shaped pore-walls. To this end, we compare numerical solutions obtained by fully resolving the microscopic pore-scale with solutions of the upscaled/homogenized porous media formulation.

### Non-equilibrium thermodynamics and the GENERIC formalism.

This part is mainly devoted to an extended variational framework (General Equations for Non-Equilibrium Reversible-Irreversible Coupling-GENERIC formalism by H. C. Öttinger and M. Grmela [28, 29]), which was initially developed to model the rheological properties of complex fluids and it was first introduced by P. J. Morisson in the context of metriplectic flows [30] (dynamical systems with both Hamiltonian [31] and dissipative parts). The specific formalism provides a full dynamic description of a set of state-space field variables  $\mathbf{z}$ , that can model various systems from a thermodynamic point of view. The variables can be chosen to be for example the composition or phase field denoted by  $c$  as earlier, the mass density  $\rho$ , the momentum density  $\mathbf{P}$ , or just the velocity  $\mathbf{v}$ , the entropy and internal energy densities and many other, depending on the requirements of each particular problem. The approach by Öttinger-Grmela suggests that, for a set of  $\{z_i\}_{i=1}^n$  state variables, the evolution equations are expressed as a generalised gradient flow combined by a reversible (energy density  $e(\mathbf{z})$  contribution) and an irreversible (entropy density  $s(\mathbf{z})$  term), as follows:

$$\partial_t z_i(\mathbf{r}) = \int_D \sum_{j=1}^m \mathbb{L}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \partial_{z_j} e(\mathbf{z}(\mathbf{r}')) d\mathbf{r}' + \int_D \sum_{j=1}^m \mathbb{M}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \partial_{z_j} s(\mathbf{z}(\mathbf{r}')) d\mathbf{r}', \text{ for } i = 1, \dots, m,$$

where the tensor  $\mathbb{L}(\mathbf{z}) = -(\mathbb{L}(\mathbf{z}))^T$  satisfies the Jacoby identity and the Leibniz rule, and the tensor  $\mathbb{M}(\mathbf{z}) = (\mathbb{M}(\mathbf{z}))^T \geq 0$  admits symmetry properties in the sense of Onsager-Casimir [32]. The evolution equations are supplemented with the complementary degeneracy

requirements for all  $i = 1, \dots, m$ :

$$\begin{cases} \int_D \sum_{j=1}^m \mathbb{M}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \partial_{z_j} e(\mathbf{z}(\mathbf{r}')) d\mathbf{r}' = 0, \\ \int_D \sum_{j=1}^m \mathbb{L}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \partial_{z_j} s(\mathbf{z}(\mathbf{r}')) d\mathbf{r}' = 0. \end{cases}$$

The requirement that the entropy gradient is in the null-space of the Poisson tensor  $\mathbb{L}$ , indicates the reversible nature of the first contribution to the dynamics, irrespective of the particular form of the Hamiltonian. In addition, the constraint that the energy gradient is in the null-space of the friction tensor  $\mathbb{M}$ , corresponds to the total energy conservation by the irreversible contribution. Moreover, Onsager reciprocal relationships [33, 34] as well as the Poisson brackets of classical mechanics, play a major role in the development of this formalism. We additionally extend our considerations to systems with possible interaction with the surroundings, where the formulation of the evolutions equations is slightly modified, including the related boundary contributions to the dynamics.

The interesting and substantially more involved part is the derivation of the macroscopic equations following the principles of GENERIC, using coarse-graining [35], which is a procedure that interconnects the different levels of description of the problem, involving the basic tools and principles of statistical mechanics, such as statistical ensemble averages, projection operator techniques and the Green-Kubo expressions for transport coefficients [36], in close connection with dynamic density functional theory [37, 38]. The idea is to consider the total energy to be expressed as an ensemble average of the microscopic Hamiltonian, defined over the volume of the phase-space  $V_{\Gamma_N}(\mathbf{z})$ , associated with a macrostate  $\mathbf{z}$ , by

$$\langle \cdot \rangle_{\mathbf{z}} := \frac{1}{V_{\Gamma_N}(\mathbf{z})} \int_{\Gamma_N} \delta(\Pi_{\mathbf{z}}(\mathbf{x}) - \mathbf{z}) d\mathbf{x} := \frac{1}{V_{\Gamma_N}(\mathbf{z})} \int_{\Gamma_N} \prod_i (\Pi_{z_i}(\mathbf{x}) - z_i) d\mathbf{x},$$

where  $\Pi_{z_i}(\mathbf{x})$ 's denote microscopic dynamical functions (corresponding to the field variables  $z_i$ ), in terms of the microstate  $\mathbf{x} = \{\mathbf{r}_i, \mathbf{p}_i\}_{i=1, \dots, N}$ . The field variables that are essential to describe each particular system, are interpreted as a combination of functions of the position  $\mathbf{r}$  and momentum of particles [39]. As an example the best choice of the state variables defined for all times, in this case of Navier-Stokes would be  $\mathbf{z} = (\rho, \mathbf{P}, u) \in \mathcal{Z}_1(D) \times \mathcal{Z}_2(D) \times \mathcal{Z}_3(D)$  and hence we can subsequently define the corresponding microscopic dynamical functions  $\Pi_{z_i}$  of  $\mathbf{P}, \rho, u$  in terms of  $r_k$  and  $\mathbf{p}_k$ , as follows:

$$\begin{cases} \Pi_{\rho}(\mathbf{z}, \mathbf{r}) = \sum_{k=1}^N m_k \delta(\mathbf{r} - \mathbf{r}_k), \Pi_{\mathbf{P}}(\mathbf{z}, \mathbf{r}) = \sum_{i=k}^N \mathbf{p}_k \delta(\mathbf{r} - \mathbf{r}_k) \text{ and} \\ \Pi_u(\mathbf{z}, \mathbf{r}) = \sum_{k=1}^N \left( \frac{m_k}{2} \mathbf{p}_k^2 + \frac{1}{2} \sum_l V(\mathbf{r}_{kl}) \right) \delta(\mathbf{r} - \mathbf{r}_k), \text{ where } \mathbf{r}_{kl} = \mathbf{r}_k - \mathbf{r}_l. \end{cases}$$

The microscopic derivation of the Navier-Stokes equations which is presented in detail as a review part in this thesis, is based on the van der Waals assumption that the molecular potential consists of a short-range hard core part and a long-range attractive tail contribution. This fact provides that in the macroscopic setting, we obtain

thermodynamically consistent behaviour predicted by the van der Waals equation of state.

Moreover, apart from the applications of GENERIC in the context of the classical and relativistic hydrodynamics [40–42], the framework was extended to the phase-field/Navier-Stokes coupling (Model H) under (or without) the influence of some external force  $g_{ex}(\mathbf{r})$  [43],

$$\begin{cases} \partial_t c + \mathbf{v} \cdot \nabla c = \gamma \Delta (f_L'(c) - \lambda^2 \Delta c), \\ \partial_t \mathbf{P} + \mathbf{v} \cdot \nabla \mathbf{P} = -\text{div} \left( P_{res} \mathbb{I} - (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) \eta(c)/2 + \lambda^2 (\nabla c \otimes \nabla c) \right) + g_{ex}, \end{cases}$$

particle adsorption systems and even more complex. Finally, recent advances involve the application of GENERIC in the context of anisotropic inelastic and viscoplastic solids [44] and thermoelastic dissipative materials [45].

### Energetic Variations and complex systems.

As a more complex example, we formally derive using an Energetic Variational Approach a Cahn-Hilliard/Navier-Stokes model for the dynamics of particle adsorption on dynamic interfaces [46], with the free energy to be defined by

$$\mathcal{F}_{ads}(\phi, c) := \int_D \mathcal{F}_{ads} \, d\mathbf{r} := \int_D F_{CH}(\phi) + F_{other}(c, \phi) \, d\mathbf{r} := \int_D F_{CH}(\phi) + m(\lambda) f_L(\phi) f_I(\phi, c) + \chi_1(\phi) f_b^{ex}(c) \, d\mathbf{r},$$

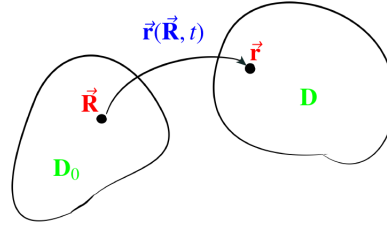
where  $f_I(\phi, c)$  denotes an interfacial free energy density whereas  $f_b^{ex}(c)$  stands for the excess in bulk grand canonical free energy density and finally  $F_{CH}(\phi) := f_L(\phi) + \lambda^2 |\nabla_{\mathbf{r}} \phi|^2 / 2$  denotes the classical Cahn-Hilliard free energy density for a nonuniform binary mixture. Although the two arguments of the free energy density, are considered to be independent parameters, the phase field order parameter  $\phi := \phi(\mathbf{r}, t) \in (-1, 1)$  is linearly connected by a certain constraint with the local volume fraction of particles  $c := c(\mathbf{r}, t) > 0$ , in the immiscible two-phase fluid. Therefore, for the minimization of  $\mathcal{F}_{ads}(\phi, c) \geq 0$  we recruit the following gradient flow formulation for  $z \in (\phi, c)$  which can be expressed in a weak form, as follows:

$$\langle \partial_t z, v \rangle_{L^2(D)} = - \langle \hat{M}_z \nabla_z^{\mathcal{X}} \mathcal{F}_{ads}(z), v \rangle_{\mathcal{Z}(D)},$$

for all  $v \in \mathcal{X} \subseteq \mathcal{Z}(D)$ . The mobility coefficient  $\hat{M}_z$  is set to be a constant  $M_z$  for  $z = \phi$  and as a function  $M(z) := z M_z$  if  $z = c$ . Moreover, the resulting evolution equations for  $c$  and  $\phi$ , coupled to fluid flow via the Least Action Principle, applied to the functional

$$\begin{aligned} \mathcal{A}(\mathbf{r}(\mathbf{R}, t)) &:= \int_{(D_0)_t} \left( \frac{1}{2} |\partial_t \mathbf{r}(\mathbf{R}, t)|^2 - f_L(\phi(\mathbf{r}(\mathbf{R}, t), t)) - \frac{\lambda^2}{2} |\nabla_{\mathbf{r}} \phi(\mathbf{r}(\mathbf{R}, t), t)|^2 \right) d\mathbf{R} \, dt \\ &\quad - \int_{(D_0)_t} m(\lambda) f_L(\phi(\mathbf{r}(\mathbf{R}, t), t)) f_I(\phi(\mathbf{r}(\mathbf{R}, t), t), c(\mathbf{r}(\mathbf{R}, t), t)) \, d\mathbf{R} \, dt \\ &\quad - \int_{(D_0)_t} \chi_1(\phi(\mathbf{r}(\mathbf{R}, t), t)) f_b^{ex}(c(\mathbf{r}(\mathbf{R}, t), t)) \, d\mathbf{R} \, dt, \end{aligned}$$

where  $\mathbf{r}(\mathbf{R}, t)$  stands for the Eulerian flow map in terms of the the Lagrangian (initial) material coordinate  $\mathbf{R}$ , from the reference volume  $D_0$  to the deformed volume over some time  $D$ .


 Figure 2: Flow map from the reference domain  $D_0$  to the current  $D$ .

The resulting coupled system of adsorption dynamics, can be expressed in the following form

$$\begin{cases} \partial_t \phi = -\mathbf{v} \cdot \nabla \phi + M_\phi \Delta \partial_\phi F_{ads}, \\ \partial_t c = -\mathbf{v} \cdot \nabla c + M_c \operatorname{div}(c \nabla \partial_c F_{ads}), \\ \partial_t \mathbf{v} = -\mathbf{v} \cdot \nabla \mathbf{v} + \Delta \mathbf{v} - \nabla P_{res} - \partial_c F_{ads} \nabla c - \partial_\phi F_{ads} \nabla \phi. \end{cases}$$

Finally, we take a step further to more applied problems and more precisely to the transport of charged particles in porous media, via the Poisson-Nerst-Planck system [47], one of the most extensively investigated models with many applications in electro-kinetic fluids, fuel cells and other energy storage systems. The full system in terms of the positive and negative charge distributions,  $c_\pm^\varepsilon := c_\pm^\varepsilon(\mathbf{r}, t)$  and the electric potential  $\phi^\varepsilon(\mathbf{r}, t)$ , reads

$$\begin{cases} \partial_t c_\pm^\varepsilon + \operatorname{div}(\mathbf{v}^\varepsilon c_\pm^\varepsilon) = \operatorname{div}(\mathbb{D}_\pm \nabla c_\pm^\varepsilon - C_e \mathbb{D}_\pm c_\pm^\varepsilon \nabla \phi^\varepsilon), \\ \rho(\partial_t \mathbf{v}^\varepsilon + \mathbf{v}^\varepsilon \cdot \nabla \mathbf{v}^\varepsilon) - \eta \Delta \mathbf{v}^\varepsilon + \nabla P_{res}^\varepsilon = (c_-^\varepsilon - c_+^\varepsilon) C_e \nabla \phi, \\ -\lambda^2 \Delta \phi^\varepsilon = C_e (c_+^\varepsilon - c_-^\varepsilon) \text{ with } \operatorname{div}(\mathbf{v}^\varepsilon) = 0, \end{cases}$$

where  $\mathbb{D}_\pm$  are diffusion constant coefficients of negative or positive ions, respectively and the constant term  $C_e := ze$  stands for the product of the valence  $z$  of ion and the charge  $e$  of one electron. We therefore provide an overview of the derivation of this system coupled with Navier-Stokes, using an energetic variational approach, including the Least Action and Maximum Dissipation Principles and provides a unique way for the derivation of the coupled dynamical systems from the total energy and dissipation functionals.

# Chapter 1

## Introduction to Cahn-Hilliard type dynamics.

Multiphase systems characterized by the coexistence of more than one phases such as liquid, gas, etc. Examples can be observed in the natural environment and in a wide range of engineering applications, such as fuel cells, batteries, etc. The investigation of fluids with complex internal microstructure gives rise to innovative flow properties. A still challenging issue is to achieve desirable properties and structure in advanced complex materials. Diffuse interface formulations have recently attracted a high level of interest, especially in the context of contact lines dynamics and particle adsorption on dynamic interfaces in the porous media context [48, 49].

The study of mixtures of two incompressible fluids, that are separated into two discrete phases (binary alloys), forms a classical model that has attracted considerable attention in the research on multiphase flows [50]. The concept of thermodynamic equilibrium, which corresponds to minimum free energy and its variational structure, allow for thermodynamic modelling of phase transitions [51, 52], in heterogeneous porous media providing many advantages for a wide range of applications in electro-kinetics such as intercalation dynamics in Lithium-Ion batteries, modelling of polyelectrolyte membrane fuel cells or magnetodynamics in ferrofluids and other [53–59]. Mathematical modelling of Lithium-Ion batteries though is not of primary interest in this particular thesis and could be considered as future work, since it follows directly from the main tools and techniques that are examined and applied in this project. Since many of those systems and the corresponding applications involve strongly heterogeneous media, we refer to these by the general term complex heterogeneous multiphase systems.

Phase-field methods, with many applications in multiphase materials science and engineering [60, 61], are based on the general theory of diffuse interfaces, which seems to have its origins to the modelling of capillarity by van der Waals [62]. Another more recent and promising extension of Cahn-Hilliard's diffuse interface concept is the phase field crystal method [63] which takes atomistic information into account for modelling crystal growth, as proposed in [64]. A major step towards the theoretical investigation of phase-field models had been taken in three papers of 1958-1959, by J. W. Cahn and

J. Hilliard [3, 65, 66], with the derivation of the free energy of a non-uniform binary mixture and the properties of spinodal decomposition and nucleation in such systems. Phase-field models for the first-order phase transition was initially studied by J. S. Langer and G. J. Fix [67, 68], followed by a similar approach for solidification, by J. B. Collins and H. Levin [69]. Finally, the minimum interface criterion and the relation to  $\Gamma$ -convergence theory in phase transitions was extensively examined by M. Gurtin, L. Modica, S. Mortola and others [70–73].

## 1.1 Free energy of a non-uniform system: the classical statement by Cahn and Hilliard.

According to the Cahn-Hilliard’s approach [3], we consider a mixture composed of two pure or fairly pure substances  $A$  and  $B$ . The system has a spatial variation in the composition  $c := c(\mathbf{r}, t) : D \times [0, T] \rightarrow \mathbb{R}$  of the  $B$  component (non-uniform system), on a bounded region  $D \subset \mathbb{R}^d$  for all times  $0 \leq t \leq T$ . Composition is interpreted either as volume fraction or mass fraction, depending on the particular system under investigation. As a consequence  $0 \leq c \leq 1$ , by definition and if we consider that  $c$  stands for the composition of the one component  $B$ , then the composition of  $A$  is given by  $1 - c$ . Alternatively, if  $c$  stands for the difference between the compositions of the two components then the assigned values to the composition are  $-1 \leq c \leq 1$ .

**Theorem 1.1.1 (Cahn-Hilliard free energy).** *The free energy  $\mathcal{F}(c) : H^1(D) \rightarrow \mathbb{R}$ , of an isotropic binary mixture of non-uniform composition which is assumed to form a cubic crystal geometry, is given by:*

$$\mathcal{F}(c) := N \int_D F(c, \nabla_{\mathbf{r}} c, \nabla_{\mathbf{r}}^2 c, \nabla_{\mathbf{r}}^3 c, \dots) \, d\mathbf{r} = N \int_D (f_L^m(c) + \frac{\lambda_N^2}{2} |\nabla_{\mathbf{r}} c|^2 + h.o.t.) \, d\mathbf{r}, \quad (1.1.1)$$

where *h.o.t.* (higher order terms) stand for the terms involving a combination of second order or higher partial derivatives of  $c$ , as can be derived from the multivariable expansion (1.1.2). In addition,  $N$  denotes the number of molecules,  $f_L^m$  stands for the free energy per molecule of a homogeneous system, and  $\lambda_N$  is a parameter which, in general, may be dependent on  $c$  and temperature, but for a regular solution is a constant.

*Proof.* The free energy density  $F$ , can be considered as a continuous function of a combination of the composition  $c$  and its spatial derivatives which are assumed to be independent variables, thus once may write  $F(\mathbf{c}) := F(c, \nabla_{\mathbf{r}} c, \nabla_{\mathbf{r}}^2 c, \dots)$ . Following the classical statement by J. W. Cahn and J. Hilliard (1958) [3] and also the review article by D. Lie et al [74], one can expand  $F$  in multivariable Taylor series about  $\mathbf{c}_L := (c, 0, 0, \dots)$  and by considering the free energy per molecule  $F(\mathbf{c}_L) := f_L^m(c)$  of a solution with uniform composition  $c$ , one obtains



$$\begin{aligned}
 F(\mathbf{c}) &= \sum_{n=0}^{\infty} \frac{1}{n!} [((\mathbf{c} - \mathbf{c}_L) \cdot \nabla_{\mathbf{c}})^n F(\mathbf{c})]_{\mathbf{c}=\mathbf{c}_L} \\
 &= f_L^m(c) + [(\nabla_{\mathbf{r}} c \partial_{\nabla_{\mathbf{r}} c} + \nabla_{\mathbf{r}}^2 c \partial_{\nabla_{\mathbf{r}}^2 c} + \nabla_{\mathbf{r}}^3 c \partial_{\nabla_{\mathbf{r}}^3 c} + \dots) F(\mathbf{c})]_{\mathbf{c}=\mathbf{c}_L} \\
 &\quad + \frac{1}{2} [(\nabla_{\mathbf{r}} c \partial_{\nabla_{\mathbf{r}} c} + \nabla_{\mathbf{r}}^2 c \partial_{\nabla_{\mathbf{r}}^2 c} + \nabla_{\mathbf{r}}^3 c \partial_{\nabla_{\mathbf{r}}^3 c} + \dots)^2 F(\mathbf{c})]_{\mathbf{c}=\mathbf{c}_L} + \dots \\
 &= f_L^m(c) + \sum_{i=1}^d \gamma_i \frac{\partial c}{\partial r_i} + \sum_{i,j=1}^d a_{ij} \frac{\partial^2 c}{\partial r_i \partial r_j} + \frac{1}{2} \sum_{i,j=1}^d b_{ij} \frac{\partial c}{\partial r_i} \frac{\partial c}{\partial r_j} + \dots \text{(in component form)}, \tag{1.1.2}
 \end{aligned}$$

where  $\gamma_i := \left. \frac{\partial F(\mathbf{c})}{\partial(\partial c / \partial r_i)} \right|_{\mathbf{c}=\mathbf{c}_L}$ ,  $a_{ij} := \left. \frac{\partial F(\mathbf{c})}{\partial(\partial^2 c / \partial r_i \partial r_j)} \right|_{\mathbf{c}=\mathbf{c}_L}$  and  $b_{ij} := \left. \frac{\partial^2 F(\mathbf{c})}{\partial(\partial c / \partial r_i) \partial(\partial c / \partial r_j)} \right|_{\mathbf{c}=\mathbf{c}_L}$ .

Note that we denoted through this section the classical gradient and higher order derivatives as  $\nabla_{\mathbf{r}}^n$ ,  $n = 1, 2, \dots$  instead of just  $\nabla^n$ , in order to distinguish it from  $\nabla_{\mathbf{c}}^n$  which appears in the free energy expansion 1.1.2. A further term reduction to the above expansion can be achieved by considering a cubic crystal geometry of the mixture (thus we set  $d = 3$ ), in which the tensors  $a_{ij}$  and  $b_{ij}$  reflect the symmetry and the  $\gamma_i$  are components of a polarization vector if the system has a special symmetry direction. In addition, the free energy must be invariant to mirror symmetry, such that upon the reflection  $r_i \rightarrow -r_i$ , (about any vertical plane) to one of the axes, the crystal maintains the same physical features. Furthermore there exists fourfold rotational symmetry about the crystal body, which means that the physical properties remain the same upon a  $90^\circ$  rotation.



Figure 1.1: Representation of crystal symmetries: fourfold axis (left) and mirror plane (right).

Consequently, the definition relations of  $a_{ij}, b_{ij}$  and  $\gamma_i$ , are reduced to:

$$\gamma_i = 0, \quad a_{ij} = \left. \frac{\partial F(\mathbf{c})}{\partial \nabla_{\mathbf{r}}^2 c} \right|_{\mathbf{c}=\mathbf{c}_L} \delta_{ij}, \quad \text{and} \quad b_{ij} = \left. \frac{\partial^2 F(\mathbf{c})}{(\partial \nabla_{\mathbf{r}} c)^2} \right|_{\mathbf{c}=\mathbf{c}_L} \delta_{ij}. \tag{1.1.3}$$

As a result, (1.1.2) reduces to,

$$F(c, \nabla_{\mathbf{r}} c, \nabla_{\mathbf{r}}^2 c, \dots) = f_L^m(c) + a_{ii} \nabla_{\mathbf{r}}^2 c + b_{ii} |\nabla_{\mathbf{r}} c|^2 + \dots \tag{1.1.4}$$

Thus, for the total free energy for  $N$  molecules per unit volume  $\mathcal{F}$  we consequently get:

$$\begin{aligned}
 \mathcal{F}(c) &= N \int_D F(c, \nabla_{\mathbf{r}} c, \nabla_{\mathbf{r}}^2 c, \dots) d\mathbf{r} \\
 &= N \int_D (f_L^m(c) + a_{ii} \nabla_{\mathbf{r}}^2 c + \frac{b_{ii}}{2} |\nabla_{\mathbf{r}} c|^2 + \dots) d\mathbf{r} \\
 &= N \int_D (f_L^m(c) + (b_{ii} - 2\partial_c a_{ii}) \frac{|\nabla_{\mathbf{r}} c|^2}{2} + \dots) d\mathbf{r} + \int_{\partial D} a_{ii} (\nabla_{\mathbf{r}} c \cdot \mathbf{n}) ds. \tag{1.1.5}
 \end{aligned}$$

The last equality follows from the divergence theorem (Gauss and Ostrogradsky [75]),

since

$$\int_D a_{ii} \nabla_{\mathbf{r}}^2 c \, d\mathbf{r} = \int_{\partial D} a_{ii} (\nabla_{\mathbf{r}} c \cdot \mathbf{n}) \, ds - \int_D \partial_{\mathbf{r}} a_{ii} \cdot \nabla_{\mathbf{r}} c \, d\mathbf{r} = \int_{\partial D} a_{ii} (\nabla_{\mathbf{r}} c \cdot \mathbf{n}) \, ds - \int_D \partial_c a_{ii} |\nabla_{\mathbf{r}} c|^2 \, d\mathbf{r}. \quad (1.1.6)$$

Since we are not interested about the external surface effects we can choose homogeneous Neumann boundary conditions on  $\partial D$ , i.e.,  $\partial_n c := \nabla_{\mathbf{r}} c \cdot \mathbf{n} = 0$ , thus the above expression reduces further to

$$\mathcal{F}(c) = \int_D (f_L(c) + \frac{\lambda^2}{2} |\nabla_{\mathbf{r}} c|^2) \, d\mathbf{r}, \quad (1.1.7)$$

in which  $\lambda^2 := N \lambda_N^2 = N(b_{ii} - 2\partial_c a_{ii})$  and we neglected the h.o.t. in the expansion.  $\square$

The first term (local contribution)  $f_L(c) := N f_L^m(c)$  is commonly known as the homogeneous free energy density. The second term (non-local contribution)  $\lambda^2 |\nabla_{\mathbf{r}} c|^2 / 2$  stands for the gradient energy and penalizes the interfacial area, between the distinct phases of the mixture after phase separation and the small parameter  $\lambda$  represents the interaction length, i.e., corresponds to the width of the diffuse interface. We are going to examine in more detail, the process of phase separation and the physical interpretation of the several parameters in the (subsection 1.2.4). Finally, it's worth mentioning that, this type of free energy functional has been first introduced by L. V. Ginzburg and L. D. Landau in 1950 [76] in the context of superconductors theory (a superconductor is simply a charged superfluid), where the complex valued order parameter depends on the superfluid density and defines superconducting order. The theory of superconductivity though is beyond the scope of this project, but more details about superfluids and Ginzburg-Landau theory can be found in [4, 77]. Aiming to understand better the concept of phase separation, we will focus on the study of the free energy of the interface, with properties summarised in the following lemma.

**Lemma 1.1 (Interfacial free energy).** *The minimum interfacial free energy between two isotropic phases  $\alpha$  and  $\beta$  which coexist in the mixture of the species A and B, can be expressed in the following form:*

$$\mathcal{F}_s^{\min}(c) = \sqrt{2}N \int_{c_\alpha}^{c_\beta} (\lambda_N^2 \mathcal{D}f(c))^{1/2} dc, \quad (1.1.8)$$

where  $\mathcal{D}f(c) := f_L^m(c) - f_L^m(c_L)$ .

*Proof.* Lets us consider the interface between two isotropic phases  $\alpha$  and  $\beta$  which coexist in the mixture of the species A and B. The interface under consideration assume to be of a flat shape of area  $\mathcal{A}$ . As a result, since we have one dimensional change in the composition  $c$  between two equilibrium compositions  $c_\alpha$  of phase  $\alpha$  and  $c_\beta$  of phase  $\beta$  respectively, the free energy (1.1.7) reduces to the form:

$$\mathcal{F}(c) = \mathcal{A}N \int_{-\infty}^{\infty} f_L^m(c) + \frac{\lambda_N^2}{2} |\nabla_{\mathbf{r}} c|^2 \, dr, \quad (1.1.9)$$

after neglecting the h.o.t. in the integrand. Since we are dealing with one dimension we may identify the gradient by  $\nabla_{\mathbf{r}} c := \frac{dc}{dr}$ . The interfacial free energy thus, should be the difference per unit area, between the free energy  $\mathcal{F}(c)$  and the free energy of a reference

state  $\mathcal{F}_L(c)$  (the energy for which we assume that the properties of phases are continuous throughout), this is expressed by

$$\mathcal{F}_L(c) = \int_{-\infty}^{\infty} f_L^m(c_L) dr = N \int_{-\infty}^{\infty} (c\mu_B(c_L) + (1-c)\mu_A(c_L)) dr, \quad (1.1.10)$$

where  $c_L = \lim_{r \rightarrow \infty} c$ . The introduced terms  $\mu_A$  and  $\mu_B$  are the partial molar free energies (also known as chemical potentials), of the components  $A$  and  $B$  in phase  $\alpha$  or  $\beta$ . These partial molar free energies referred to the same standard states as  $f_L^m(c)$ . In equilibrium the partial molar free energy of a particular species should be the same in both phases, so in order to calculate  $\mathcal{F}_s(c)$  we take into account this condition. Thus we may rewrite the whole interfacial free energy as

$$\mathcal{F}_s(c) = N \int_{-\infty}^{\infty} \mathcal{D}f(c) + \frac{\lambda_N^2}{2} |\nabla_r c|^2 dr. \quad (1.1.11)$$

According to the basic thermodynamic principles, the equilibrium state of this system, can be identified as the condition in which the composition variation will be such that  $\mathcal{F}_s(c)$  admits a minimum, or equivalently the chemical potentials should not change throughout the system.) In order to minimize the functional  $\mathcal{F}_s(c)$  we shall use basic formulas from the calculus of variations, namely the Euler-Lagrange equation [78]. So if  $\mathcal{J}(c)$  represents the integrand in (1.1.11) one gets the Euler-Lagrange equation,

$$\frac{\partial \mathcal{J}(c)}{\partial c} = \frac{d}{dr} \left( \frac{\partial \mathcal{J}(c)}{\partial (\nabla_r c)} \right), \quad (1.1.12)$$

thus for a stationary point we get the value for the integrand:  $\mathcal{J}(c) - \lambda_N^2 |\nabla_r c|^2 = \text{constant}$ , or since

$$\lim_{r \rightarrow \pm\infty} \mathcal{D}f = 0 \text{ and } \lim_{r \rightarrow \pm\infty} \nabla_r c = 0,$$

the above constant should be zero. Thus, one equivalently obtains  $\frac{2\mathcal{D}f}{\lambda_N^2} = |\nabla_r c|^2$ . Thus as a minimum value for the interfacial free energy one obtains:

$$\mathcal{F}_s^{\min}(c) = 2N \int_{-\infty}^{\infty} \mathcal{D}f(c) dr, \quad (1.1.13)$$

or by changing the variable of integration from  $r$  to the composition  $c$  one can easily derive the expression (1.1.8).  $\square$

One may also interested in the behaviour of the interfacial free energy very close to the critical temperature  $\Theta_c$ , where the two phases have the same composition, which can be denoted by  $c_c$ . An immediate question that eventually comes up, is whether or not there exists any certain relation between  $\mathcal{F}_s$  and the temperature  $\Theta$ ? The answer can be summarised in the following lemma.

**Lemma 1.2 (Behaviour close to the critical point).** *Very close to the critical point  $(c_c, \Theta_c)$  for phase separation, the minimizer of the interfacial free energy (1.1.8) can be expressed in the following form:*

$$\mathcal{F}_s^{\min} |_{\Theta \sim \Theta_c} = (2N/3g)(\lambda_N^2)^{1/2} (\Theta_c - \Theta)^{3/2} b^{3/2} g^{-3}, \quad (1.1.14)$$

where we defined  $b := \frac{1}{2} \partial_{ccc} f_L^m |_{(\Theta_c, c_c)}$  and  $g := \frac{1}{4!} \partial_{cccc} f_L^m |_{(\Theta_c, c_c)}$ .

*Proof.* The idea is to expand in Taylor series  $f_L^m$  by consider it, as a function of the two variables  $\Theta, c$ , over the critical values  $\Theta_c, c_c$ . Thus, we have

$$\begin{aligned} f_L^m |_{\Theta \sim \Theta_c} &= f_L^m(c_c, \Theta_c) + \partial_{\Theta} f_L^m |_{(\Theta_c, c_c)} (\Theta - \Theta_c) + \partial_c f_L^m |_{(\Theta_c, c_c)} (c - c_c) \\ &+ \frac{1}{2} \partial_{cc} f_L^m |_{(\Theta_c, c_c)} (c - c_c)^2 + \frac{1}{2} \partial_{\Theta\Theta} f_L^m |_{(\Theta_c, c_c)} (\Theta - \Theta_c)^2 \\ &+ \partial_{\Theta cc} f_L^m |_{(\Theta_c, c_c)} (\Theta - \Theta_c)(c - c_c) + \text{h.o.t.} \end{aligned} \quad (1.1.15)$$

In order to identify the behaviour of the interfacial free energy close to the critical temperature, we use the above expansion (1.1.15) to derive a form for the quantity  $\mathcal{D}f$  close to  $\Theta_c$ . We can derive a similar expression for  $f_L^m(c_L)$  and we proceed further using the condition that  $\partial_c^n f_L^m |_{(\Theta_c, c_c)} = 0$  for any power  $n \geq 2$ , due to the fact that in the critical point the system is in thermodynamic equilibrium and hence the chemical potential is constant (see also subsection 1.2.4). In addition, the terms associated with  $f_L^m |_{(\Theta_c, c_c)}$  and  $\partial_{\Theta} f_L^m |_{(\Theta_c, c_c)}$  are cancelled in pairs. Furthermore, according to symmetry reasons of  $f_L^m$  about the critical composition  $c_c$  the mixed partial derivatives of  $f_L$  evaluated at the critical point, with odd order with respect to the composition, vanish. As a result, the expansion is finally simplified to

$$\begin{aligned} \mathcal{D}f |_{\Theta \sim \Theta_c} &= f_L^m(c) - f_L^m(c_{\alpha}) \\ &= \frac{1}{2} \partial_{\Theta cc} f_L^m |_{(\Theta_c, c_c)} (\Theta - \Theta_c) ((c - c_c)^2 - (c_{\alpha} - c_c)^2) \\ &+ \frac{1}{4!} ((c - c_c)^4 - (c_{\alpha} - c_c)^4) \partial_{cccc} f_L^m |_{(\Theta_c, c_c)}. \end{aligned} \quad (1.1.16)$$

Therefore, by considering the fact that  $\partial_c \mathcal{D}f |_{c_{\alpha}} = \partial_c \mathcal{D}f |_{c_{\beta}} = 0$ , from equation (1.1.16) we obtain  $\partial_{\Theta cc} f_L^m |_{(\Theta_c, c_c)} (\Theta_c - \Theta) ((c - c_c) + \frac{1}{6} ((c - c_c)^3 \partial_{cccc} f_L^m |_{(\Theta_c, c_c)})) = 0$ , or we can express it alternatively as

$$(\mathcal{D}c_L)^2 = (c_{\alpha} - c_c)^2 = \frac{(\Theta_c - \Theta)b}{2g} = (c_{\beta} - c_c)^2, \quad (1.1.17)$$

where  $b := \frac{1}{2} \partial_{\Theta cc} f_L^m |_{(\Theta_c, c_c)}$  and  $g := \frac{1}{4!} \partial_{cccc} f_L^m |_{(\Theta_c, c_c)}$ . Thus, using the above form, we may rewrite  $\mathcal{D}f$  at the critical point as follows:

$$\mathcal{D}f |_{\Theta \sim \Theta_c} = g((\mathcal{D}c_L)^2 - (\mathcal{D}c)^2)^2, \text{ where } \mathcal{D}c = c - c_c. \quad (1.1.18)$$

Consequently, close enough to the critical point the minimizer of the interfacial free energy (1.1.8) can be expressed in the following form,

$$\mathcal{F}_s^{\min} |_{\Theta \sim \Theta_c} = \sqrt{2}N \int_{-\mathcal{D}c_L}^{\mathcal{D}c_L} (\lambda_{NG}^2)^{1/2} ((\mathcal{D}c_L)^2 - (\mathcal{D}c)^2) d(\mathcal{D}c). \quad (1.1.19)$$

Very close to the critical point, by expanding  $\lambda_N^2$  about this point and neglecting higher order terms, we may assume it is constant. In this context, we can evaluate the above integral by applying the appropriate substitutions and arrive to the expression (1.1.14).  $\square$

As a result, the above analysis suggests that near the critical point the interfacial free energy should be proportional to  $(\Theta_c - \Theta)^{3/2}$ . The interface is characterized by a very small

parameter, called thickness  $l$ , and the interpretation of  $l$  will depend on the particular problem. In the specific case  $l$  could be expressed in terms of the gradient  $c_c$  as follows:

$$l = \frac{c_\alpha - c_\beta}{(dc/dr)_{c_c}} = \sqrt{2} \mathcal{D}_{c_L} \left( \frac{\lambda_N^2}{\max\{\mathcal{D}f|_{\Theta_c - \Theta_c}\}} \right)^{1/2} = \left( \frac{\lambda_N^2}{g} \right)^{1/2} \frac{\sqrt{2}}{\mathcal{D}_{c_L}}. \quad (1.1.20)$$

Thus, close to the critical temperature  $\Theta_c$  using the form we derived for the composition difference  $\mathcal{D}_{c_L}$  the interfacial thickness will be

$$l_{\Theta_c - \Theta_c} = 2 \left( \frac{\lambda_N^2}{b(\Theta_c - \Theta)} \right)^{1/2}. \quad (1.1.21)$$

As a consequence, the thickness  $l$  is an increasing function of temperature and goes to infinite, when the system approaches the critical point.

## 1.2 Minimization of the Ginzburg-Landau/Cahn-Hilliard free energy: The Cahn-Hilliard equation.

Minimization of free energy corresponds to the condition of thermodynamic equilibrium which each system has the tendency to approach (see remark 3.6 for more details). The Cahn-Hilliard/van der Waals model for the equilibrium description of phase separation is therefore to find

$$\min \left\{ \mathcal{F}(c) : c_{av} = |D|^{-1} \int_D c(\mathbf{r}, t) d\mathbf{r} \right\}, \quad (1.2.1)$$

where  $c_{av}$  is considered as the average composition in a uniform temperature of a stable state [79] and  $\mathcal{F}(c)$  denotes the Cahn-Hilliard free energy defined in (1.1.7). This minimum can be mathematically achieved by applying the classical idea of gradient flows, which provides also a dynamic description of the composition  $c$ .

### 1.2.1 General minimization procedure for an Euclidean function: method of gradient descent.

This part is devoted to the motivation of deriving a gradient flow formulation, as an extension of the gradient descent method used to minimize Euclidean functions. Assuming for simplicity a functional  $\mathcal{F}$  depends only in one variable  $c$ , defined for all times in some function space  $\mathcal{Z}(D)$ ,  $D \subset \mathbb{R}^d$ . Starting from the basic idea of the calculus of variations, one can consider a scalar-valued sufficiently smooth function  $c(r)$  in  $\mathbb{R}$ , approaching its local minimum value, based on the idea to take steps proportional to the negative derivative  $-c'(r)$ , until a fixed point is reached. This leads to the following steepest descent method [17, 80]:

$$\frac{r_{i+1} - r_i}{\Delta t} = -c'(r_i), \quad \Delta t \text{ a small enough time step.} \quad (1.2.2)$$

We can extend this idea to the  $d$ -dimensional Euclidean space by considering now a scalar-valued sufficiently smooth function  $c(\mathbf{r}) : D \rightarrow \mathbb{R}$ , where  $D \subset \mathbb{R}^d$  and an initial guess  $\mathbf{r}_0$ , the gradient descent iteratively moves the guess  $\mathbf{r}_0$  towards lower values of  $c$  by taking

steps in the direction of the negative Euclidean gradient of  $c$ , which is a function that assigns to every point  $\mathbf{r} \in D$ , the unique element  $\nabla c(\mathbf{r}) \in \mathbb{R}^d$ , such that:

$$c'(\mathbf{r})\mathbf{r}' := \langle \nabla c(\mathbf{r}), \mathbf{r}' \rangle, \text{ for every } \mathbf{r} \in \mathbb{R}^d, \quad (1.2.3)$$

denotes the directional derivative in the direction of  $\mathbf{r}'$  given by the limit (if that exists):

$$c'(\mathbf{r})\mathbf{r}' := \lim_{k \rightarrow 0} \frac{c(\mathbf{r} + k\mathbf{r}') - c(\mathbf{r})}{k}. \quad (1.2.4)$$

Locally the gradient points into the direction of the maximal slope. Similarly to the one dimensional case the sequence of iterates  $\{\mathbf{r}_i\}$  for  $i = 1, \dots, n \in \mathbb{N}$ , given the initial guess  $\mathbf{r}_0$  of the solution, can be expressed in the form:

$$\frac{\mathbf{r}_{i+1} - \mathbf{r}_i}{\Delta t} = -\nabla c(\mathbf{r}_i). \quad (1.2.5)$$

### 1.2.2 Extension for functionals: gradient flows.

It is straightforward that we can appropriately extend the above idea, where we have to minimize a functional. Following the gradient descent method, in order to solve the minimization problem, one can use the same idea with the iterates in this case to be given by the gradient descent formula (1.2.5), slightly modified and customised for a functional, i.e.,

$$\frac{c_{i+1} - c_i}{\Delta t} = -\nabla_{c_i} \mathcal{F}(c_i), \quad (1.2.6)$$

given an initial guess  $c_0 \in \mathcal{Z}(D)$ . The gradient of  $\mathcal{F}(c_i)$ ,  $i = 1, \dots, n \in \mathbb{N}$  on the right hand side, implicitly could be defined as the linear (in a small perturbation  $k$ ) term of the change in the function  $c$ , given by the Taylor expansion:  $\mathcal{F}(c + kv) = \mathcal{F}(c) + k\langle \nabla_c^{\mathcal{X}_l} \mathcal{F}(c), v \rangle_{\mathcal{Z}(D)} + O(k^2)$ , for  $v \in \mathcal{X}_l(D) \subseteq \mathcal{Z}(D)$ , where the index  $l$  indicates that we can have different function spaces on some occasions. As a result the functional gradient is well defined, using the Gâteaux derivative of  $\mathcal{F}$  at  $c$ , by the following relation

$$\delta_c^{\mathcal{X}_l} \mathcal{F}(c) := \lim_{k \rightarrow 0} \frac{\mathcal{F}(c + kv) - \mathcal{F}(c)}{k} = \langle \nabla_c^{\mathcal{X}_l} \mathcal{F}(c), v \rangle_{\mathcal{Z}(D)}, \quad \forall v \in \mathcal{X}_l(D) \subseteq \mathcal{Z}(D), \quad (1.2.7)$$

which is in other words the directional derivative at  $c$  in the direction of  $v$ . The existence and uniqueness of the gradient for  $\mathcal{X}_l(D) \subseteq \mathcal{Z}(D)$  being Hilbert spaces, follows from the Riesz representation theorem [82, p. 163]. If  $\mathcal{Z}$  is not a Hilbert space though then  $\mathcal{F}$  being Gâteaux-differentiable do not imply the existence of the gradient. After defining the functional gradient one can observe that in order to have the right hand side in (1.2.6) well defined, mathematical consistency requires to take the inner product with the test function  $v \in \mathcal{X}_m(D)$ , on both sides:

$$\lim_{\Delta t \rightarrow 0} \langle (c_{i+1} - c_i) / \Delta t, v \rangle_{L^2(D)} = - \lim_{\Delta t \rightarrow 0} \langle \nabla_{c_i}^{\mathcal{X}_l} \mathcal{F}(c_i), v \rangle_{\mathcal{Z}(D)}, \quad i = 1, \dots, n \in \mathbb{N}. \quad (1.2.8)$$

**Definition 1.1 (Gradient flow).** *The minimization flow of  $c$  for all times  $t > 0$ , following the steepest descent of the functional  $\mathcal{F}$ , is defined as the "gradient flow" of  $\mathcal{F}$  [83, 84] and*

can be expressed by the following weak formulation:

$$\langle \partial_t c, v \rangle_{L^2(D)} = -\delta_c^{\mathcal{X}_i} \mathcal{F}(c), \quad \forall v \in \mathcal{X}_i(D) \subseteq \mathcal{Z}(D), \quad (1.2.9)$$

which can be directly deduced from the previous relationship (1.2.8) for sufficiently large  $n \in \mathbb{N}$ .

**Remark 1.1 (Dissipative behaviour).** *The time rate of change of the functional  $\mathcal{F}$  is negative (corresponds to free energy dissipation [85, 86]), i.e.,*

$$\frac{d\mathcal{F}(c)}{dt} = \langle \nabla_c^{\mathcal{X}_i} \mathcal{F}(c), \partial_t c \rangle_{\mathcal{Z}(D)} = \langle \nabla_c^{\mathcal{X}_i} \mathcal{F}(c), -\nabla_c^{\mathcal{X}_i} \mathcal{F}(c) \rangle_{\mathcal{Z}(D)} = -\|\nabla_c^{\mathcal{X}_i} \mathcal{F}(c)\|_{\mathcal{Z}(D)}^2 \leq 0. \quad (1.2.10)$$

In the same context, we can extend the above idea, by importing a linear symmetric positive semi-definite and invertible operator  $\mathcal{M} : \mathcal{Z}(D) \rightarrow \mathcal{Z}(D)$ , into the gradient flow [84, 87], thus we need to define a new inner product with respect to this operator, namely:

$$\langle \cdot, \cdot \rangle_{\mathcal{M}} = \langle \mathcal{M} \cdot, \cdot \rangle_{\mathcal{Z}(D)}. \quad (1.2.11)$$

Thus, we can define a new gradient flow for  $\mathcal{Z}(D) = L^2(D)$ , starting from (1.2.9) from the following procedure,

$$\begin{aligned} \langle \partial_t c, v \rangle_{L^2(D)} &= -\langle \nabla_c^{L^2} \mathcal{F}(c), v \rangle_{L^2(D)} \\ &= -\langle \mathcal{M}^{-1} \mathcal{M} \nabla_c^{L^2} \mathcal{F}(c), v \rangle_{L^2(D)} \\ &= -\langle \mathcal{M} \nabla_c^{L^2} \mathcal{F}(c), v \rangle_{\mathcal{M}^{-1}} \quad \forall v \in L^2(D). \end{aligned} \quad (1.2.12)$$

This procedure provides the existence of the gradient  $\nabla_c^{\mathcal{M}^{-1}} \mathcal{F}(c)$ , if the  $\nabla_c^{L^2} \mathcal{F}(c)$  also exists and the connection of those by the relationship

$$\mathcal{M} \nabla_c^{L^2} \mathcal{F}(c) = \nabla_c^{\mathcal{M}^{-1}} \mathcal{F}(c). \quad (1.2.13)$$

As a result, one obtains the following evolution equation for the symmetric positive definite linear operator  $\mathcal{M}$ :

$$\partial_t c = -\mathcal{M} \nabla_c^{L^2} \mathcal{F}(c), \quad (1.2.14)$$

which provides the evolution of the initial condition  $c_0$  in the direction of the negative energy gradient. We shall call the triple  $(\mathcal{Z}, \mathcal{F}, \mathcal{M})$ , a gradient system/flow [88]. It is straightforward that, again the free energy is decreasing over time, under the flow (1.2.14) similar as in (1.2.10), namely:

$$\frac{d\mathcal{F}(c)}{dt} = -\langle \nabla_c^{L^2} \mathcal{F}(c), \mathcal{M} \nabla_c^{L^2} \mathcal{F}(c) \rangle_{\mathcal{M}^{-1}} \leq 0. \quad (1.2.15)$$

Suppose now that we are dealing with a set of arbitrary functions  $\mathbf{c} = [c_1, \dots, c_m] \in \mathcal{Z}_1(D) \times \dots \times \mathcal{Z}_m(D)$  for  $D \subset \mathbb{R}^d$  (where  $\mathcal{Z}_i$ 's represent different function spaces). Thus, in order to define the gradient  $\nabla_c^{\mathcal{M}^{-1}} \mathcal{F}(\mathbf{c})$ , we need to make use of a new  $\mathcal{M}$  inner product for two discrete vector fields  $\mathbf{c}, \mathbf{u}$  such as:

$$\langle \mathbf{c}, \mathbf{u} \rangle_{\mathcal{M}} := \langle \mathcal{M} \mathbf{c}, \mathbf{u} \rangle_{L^2(D)}, \quad (1.2.16)$$

where  $\mathcal{M}$  stands for a symmetric positive definite tensor. Therefore, this consequently

implies the following relation between the gradients,

$$\mathcal{M}\nabla_{\mathbf{c}}^{L^2} \mathcal{F}(\mathbf{c}) = \nabla_{\mathbf{c}}^{\mathcal{M}^{-1}} \mathcal{F}(\mathbf{c}). \quad (1.2.17)$$

### 1.2.3 The $L^2$ and $H^{-1}$ gradient flows of the Cahn-Hilliard free energy.

Let us consider again a mixture consisting of two components  $A$  and  $B$  and the related free energy functional (1.1.7) (after neglecting the higher order terms in the expansion),

$$\mathcal{F}(c) = \int_D (f_L(c) + \frac{\lambda^2}{2} |\nabla c|^2) \, d\mathbf{r}, \quad (1.2.18)$$

that has been derived in the previous section, see Theorem 1.1.1. We are interested in examining the time evolution of the composition  $c$ , by considering the minimization of  $\mathcal{F}$ , with respect to the function space  $\mathcal{Z} = L^2(D)$ , where  $D \subset \mathbb{R}^d$  is generally assumed to be a bounded domain with Lipschitz boundary of  $d$  space dimensions. The boundary condition that is considered for the specific derivation, is the homogeneous Neumann, namely  $\partial_n c := \nabla c \cdot \mathbf{n} = 0$ , where  $\mathbf{n}$  stands for the outward normal. The physical meaning of this boundary condition is that, no mass loss occurs across the boundary walls and the total free energy of the mixture decreases in time. This condition describes a contact angle of  $\pi/2$  of the diffused interface and the boundary of the domain.

**Remark 1.2.** *In the sequel and where it is necessary, we will make use of the following notation  $D_T := D \times (0, T)$ , and  $\partial D_T := \partial D \times (0, T)$ , where  $D \subset \mathbb{R}^d$  and  $T \in (0, +\infty)$  the maximum time of observation.*

**Theorem 1.2.1 (The Allen-Cahn equation).** *The  $L^2$ -Gradient flow of the free energy (1.2.18) leads to the Allen-Cahn equation [5], [6]:*

$$\partial_t c = \lambda^2 \Delta c - f'_L(c) \text{ in } D_T, \quad (1.2.19)$$

*with homogeneous Neumann boundary condition  $\partial_n c|_{\partial D_T} = 0$  and some initial condition  $c_{init}(\mathbf{r}) := c(\mathbf{r}, 0) \in H^1(D)$ .*

*Proof.* The Gâteaux differential of  $\mathcal{F}(c)$  at  $c$  in the direction of  $v \in L^2(D)$  ( $L^2$ -gradient), can be formally derived as follows:

$$\begin{aligned} \delta_c^{L^2} \mathcal{F}(c) &:= \langle \nabla_c^{L^2} \mathcal{F}(c), v \rangle_{L^2(D)}, \quad v \in L^2(D) \\ &= \lim_{k \rightarrow 0} \frac{\mathcal{F}(c + kv) - \mathcal{F}(c)}{k} \\ &= \int_D \left( \lim_{k \rightarrow 0} \frac{f_L(c + kv) - f_L(c)}{k} + \lim_{k \rightarrow 0} k |\nabla v|^2 + \lambda^2 \nabla c \cdot \nabla v \right) d\mathbf{r} \\ &= \int_D \left( \lim_{k \rightarrow 0} \frac{f_L(c + kv) - f_L(c)}{k} + \lambda^2 \int_D \nabla c \cdot \nabla v \right) d\mathbf{r} \\ &= \int_D \lim_{k \rightarrow 0} \frac{f_L(c + kv) - f_L(c)}{k} d\mathbf{r} + \lambda^2 \int_{\partial D} v \nabla c \cdot \mathbf{n} \, ds - \lambda^2 \int_D v \Delta c \, d\mathbf{r} \\ &= \int_D \lim_{k \rightarrow 0} \frac{f_L(c + kv) - f_L(c)}{k} d\mathbf{r} - \lambda^2 \int_D v \Delta c \, d\mathbf{r}, \end{aligned} \quad (1.2.20)$$



where we used integration by parts and homogeneous Neumann boundary conditions. Furthermore by plugging the Taylor expansion around  $c$ , namely  $f_L(c+kv) = f_L(c) + kvf'_L(c) + \dots$ , into the first term of the integrand one obtains:  $\delta_c^L \mathcal{F}(c) = \langle f'_L(c) - \lambda^2 \Delta c, v \rangle_{L^2(D)}$  and from the gradient flow formulation one gets then  $\langle \partial_t c, v \rangle_{L^2(D)} = \langle \lambda^2 \Delta c - f'_L(c), v \rangle_{L^2(D)}$ .  $\square$

The quantity  $\mu := f'_L(c) - \lambda^2 \Delta c$  (chemical potential) represents the driving force for the local reduction of  $c$ . The Allen-Cahn equation is a non-mass conserving reaction-diffusion equation and was originally introduced to describe the motion of anti-phase boundaries in crystalline solids (regions where the atoms are configured in the opposite order to those in a perfectly ordered lattice system). The main characteristic in this case is that the phase is not uniquely determined by concentration, temperature and pressure, etc.

**Theorem 1.2.2 (The Cahn-Hilliard equation).** *The  $H^{-1}$ -Gradient flow of the free energy (1.2.18) provides the Cahn-Hilliard equation:*

$$\partial_t c = \Delta(f'_L(c) - \lambda^2 \Delta c) \text{ in } D_T, \quad (1.2.21)$$

with homogeneous Neumann boundary condition  $\partial_n c|_{\partial D_T} = 0$ , no-flux boundary conditions  $\partial_n \mu|_{\partial D} = 0$  and some initial condition  $c_{init}(\mathbf{r}) := c(\mathbf{r}, 0) \in H^1(D)$ .

*Proof.* The starting point in this case is to consider the minimization of the functional (1.2.18), with respect to the function space  $H_{(0)}^1(D)$  and its bounded linear mapping  $H^{-1}(D)$ , i.e.,  $H^{-1}(D) := (H_{(0)}^1(D))'$ , where

$$H_{(0)}^1(D) := \left\{ u \in H^1(D) : \int_D u \, d\mathbf{r} = 0 \right\}, \quad (1.2.22)$$

equipped with the semi-inner product,  $\langle u, v \rangle_{H_{(0)}^1(D)} := \langle \nabla u, \nabla v \rangle_{L^2(D)}$ . Additionally to the homogeneous Neumann condition, one can impose an extra boundary condition for the chemical potential  $\mu$ , namely  $\partial_n \mu|_{\partial D} = 0$  (no-mass flux condition). This reduces further to the following form:

$$\partial_n \Delta c|_{\partial D} = 0, \text{ since } \partial_n f = f' \partial_n c = 0. \quad (1.2.23)$$

The physical meaning of this extra condition is that none of the mixture can pass through the walls. We additionally equip  $H^{-1}(D)$  with the semi-inner product,

$$\langle u, v \rangle_{H^{-1}(D)} := \langle \nabla u^*, \nabla v^* \rangle_{L^2(D)}, \quad \forall u, v \in H^{-1}(D), \quad (1.2.24)$$

where  $v^*, u^* \in H_{(0)}^1(D)$  are such that:

$$\begin{cases} -\Delta j^* = j|_{j=u,v} & \text{in } D, \\ \nabla j^* \cdot \mathbf{n}|_{j=u,v} = 0 & \text{on } \partial D. \end{cases} \quad (1.2.25)$$

Thus, starting from the previously derived in (1.2.20),  $L^2$ -constraint gradient of  $\mathcal{F}$ , one obtains

$$\begin{aligned}
 \delta_c^{L^2} \mathcal{F}(c) &:= \langle \nabla_c^{L^2} \mathcal{F}(c), v \rangle_{L^2(D)} \\
 &= \langle f'_L(c) - \lambda^2 \Delta c, v \rangle_{L^2(D)} \\
 &= \langle f'_L(c) - \lambda^2 \Delta c, -\Delta v^* \rangle_{L^2(D)} \\
 &= \langle \nabla(f'_L(c) - \lambda^2 \Delta c), \nabla v^* \rangle_{L^2(D)} \\
 &= \langle -\Delta(f'_L(c) - \lambda^2 \Delta c), v \rangle_{H^{-1}(D)} \\
 &= \langle \nabla_c^{H^{-1}} \mathcal{F}(c), v \rangle_{H^{-1}(D)}, \quad \forall v \in H_{(0)}^1(D),
 \end{aligned} \tag{1.2.26}$$

where we applied integration by parts, the no flux boundary condition (1.2.23) and the semi-inner product (1.2.24). It turns out that  $\nabla_c^{H^{-1}} \mathcal{F}(c) = -\Delta \nabla_c^{L^2} \mathcal{F}(c)$ .  $\square$

**Remark 1.3 (Formulation with mobility).** *Alternatively, if we consider the variation with respect to the semi-inner product [20, 84]:*

$$\langle u, v \rangle_{H^1(D)} := \langle \nabla u, \nabla v \rangle_{\mathcal{M}} := \langle \mathbb{M} \nabla u, \nabla v \rangle_{L^2(D)}, \quad \forall u, v \in H^1(D), \tag{1.2.27}$$

where  $\mathbb{M}$  could be either a symmetric positive definite tensor (the discrete counterpart of an operator  $\mathcal{M}$  with the same properties as in (1.2.16)), some constant or a function of  $c$ , we obtain

$$\langle \nabla_c^{L^2} \mathcal{F}(c), v \rangle_{H^1(D)} := \langle \mathbb{M} \nabla(f'_L(c) - \lambda^2 \Delta c), \nabla v \rangle_{L^2(D)} = \langle -\operatorname{div}(\mathbb{M} \nabla(f'_L(c) - \lambda^2 \Delta c)), v \rangle_{L^2(D)}, \tag{1.2.28}$$

after integration by parts. As a result of the gradient flow, one obtains the Cahn-Hilliard equation, namely

$$\partial_t c = \operatorname{div}(\mathbb{M} \nabla(f'_L(c) - \lambda^2 \Delta c)) \quad \text{in } D_T, \tag{1.2.29}$$

with initial condition  $c_{\text{init}}(\mathbf{r}) := c(\mathbf{r}, 0) \in H^1(D)$ , no-flux and homogeneous Neumann boundary conditions.

Similar approaches and more details about the gradient flow derivations of the two equations can be found in [74, 91, 92].

**Remark 1.4 (Conservation of mass and free energy dissipation).** *A straightforward property of (1.2.29) is the conservation of the total mass  $\int_D c d\mathbf{r}$ , namely*

$$\frac{d}{dt} \int_D c d\mathbf{r} = \int_D \partial_t c d\mathbf{r} = \int_D \operatorname{div}(\mathbb{M} \nabla \mu) d\mathbf{r} = \int_{\partial D} \mathbb{M}(\nabla \mu \cdot \mathbf{n}) ds = 0, \tag{1.2.30}$$

holds because of the chosen boundary condition. In addition, it holds that the free energy is decreasing over time, i.e.,

$$\frac{d\mathcal{F}(z)}{dt} = \langle \nabla_c^{L^2} \mathcal{F}(c), \partial_t c \rangle_{L^2(D)} := \int_D \mu \operatorname{div}(\mathbb{M} \nabla \mu) d\mathbf{r} = - \int_D \mathbb{M}(\nabla \mu)^2 d\mathbf{r} \leq 0, \tag{1.2.31}$$

in the last equality we used integration by parts.

### 1.2.4 Physical interpretation of the Cahn-Hilliard dynamics

The Cahn-Hilliard equation describes the process of phase separation in binary alloys. The study of phase separation in binary alloys and liquid mixtures [6, 79, 93] has been of interest over the last decades and has its origins in non-equilibrium thermodynamic processes. Some of the examples include binary and ternary metal alloys which are produced when the constituent metals are heated to their liquid phases, liquid mixtures and systems of magnetic spins [94, 95]. In order to understand better this procedure, let us consider again a mixture of two different pure or fairly pure chemical substances, say  $A$  and  $B$ . The process of phase separation, can be defined as the mechanism, by which a mixture of these two or more components from a uniform mixed state, has the tendency to form (after cooling) a fine-grained mixture of two different distinct regions (phases), each of which corresponds to different and stable composition configuration. During this stage, one can observe nucleation and spinodal decomposition, followed by a clear formation of the two distinct phases, in a very short time [96].

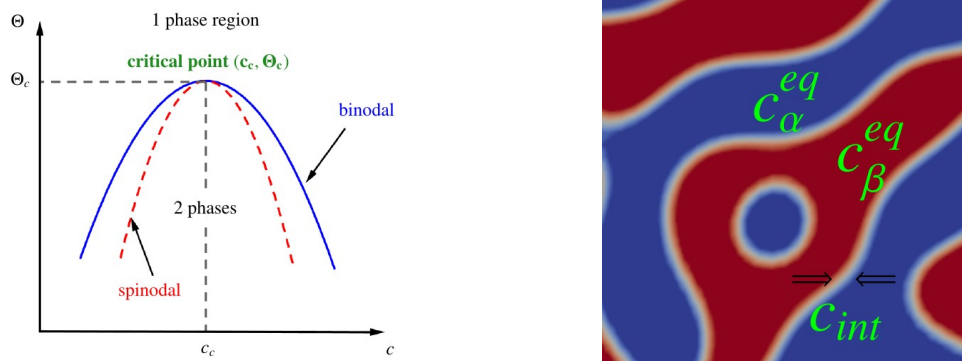


Figure 1.2: Schematic diagram of phase separation (left) and illustration of the composition variation  $c_\beta^{eq} > c_{int} > c_\alpha^{eq}$  (right).

This particular change is observed when the mixture, which forms a single homogeneous phase at some temperature greater than a critical temperature  $\Theta_c$ , is rapidly cooled to a temperature where the homogeneous state is unstable. In the homogeneous state, the respective composition of the components is the same at all locations. In addition, in the heterogeneous case, there are regions locally richer in one of the substances. The critical temperature  $\Theta_c$  could be identified as the temperature at which the two phases attain the same critical composition  $c_c$ . Below this critical temperature, thermodynamic equilibrium corresponds to the coexistence of two phases, one phase rich in species  $B$  and the other phase rich in  $A$ . As a result, this instability leads to composition fluctuations, that are immediately followed by phase separation. The phase diagram in Figure 1.2, represents the evolution of the composition  $c$  (horizontal axis) as a function of the temperature  $\Theta$  (vertical axis).

The binodal curve (or coexistence curve), denotes the condition at which two distinct phases may coexist and divides the phase diagram into the homogeneous and heterogeneous regions. Above this curve any uniform composition is stable. The binodal curve intersects with the spinodal at the critical point  $(c_c, \Theta_c)$  and the region above the binodal corresponds to a one phase region as one can see in the above figure. The condition of

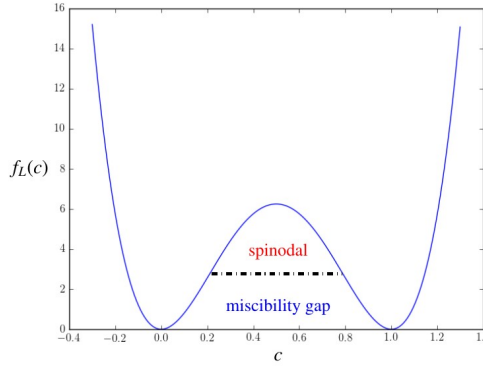


Figure 1.3: Homogeneous free energy density of study  $f_L(c) = 100c^2(1-c)^2$ . The system is considered to be in its energetically favourable position for compositions inside the miscibility gap (between the minimizers of  $f_L(c)$ ).

thermodynamic equilibrium corresponds to the coexistence of the two phases. The collection of points where  $\partial_c^2 f_L(c) = 0$  forms the spinodal curve. Below this curve, the mixture totally separates into two separated values for the composition and the state is unstable. Inside the miscibility gap in Figure 1.3 (for compositions between the minimizers  $c=0$ ,  $c=1$  of  $f_L(c)$ ), a phase-separated system is considered to be in its energetically favourable position.

Whereas, outside the miscibility gap, the system remains homogeneous at equilibrium for any value of the composition. In the chemical spinodal (the region of linear instability, above the dotted line in which  $\partial_c^2 f_L(c) < 0$ ), we observe small composition fluctuations that randomly grow through spinodal decomposition. The state in the region between the two curves (spinodal and binodal) is characterised as metastable. Obviously, the system is stable, only in a uniform temperature greater than the critical temperature  $\Theta_c$ . More details about stability analysis of the Cahn-Hilliard equation can be found in [93, 97, 98]. The thermodynamic description of phase separation is also related to the term quenching and in particular, the Cahn-Hilliard formulation describes well the case of quick quenching where the system is rapidly cooled and undergoes phase separation. Finally, the term critical quenching describes the case where the system evolves through the critical point, see [20, 99].

The interface between the two phases  $\alpha$  and  $\beta$ , is not sharp, but has a finite thickness, let us denote it by  $l$ , in which the composition changes gradually. The interfacial thickness, in the case of the non-uniform mixture of  $A$  and  $B$ , close to the critical temperature  $\Theta_c$ , has been shown to obtain the following expression (see [3] and section 1.1 for more details):

$$l_{\Theta \sim \Theta_c} := 2 \left( \frac{\lambda^2}{b(\Theta_c - \Theta)} \right)^{1/2}, \quad b := \frac{1}{2} \frac{\partial^3 f_L^m}{\partial \Theta \partial c^2} |_{(c_c, \Theta_c)}, \quad \text{with } \Theta \leq \Theta_c. \quad (1.2.32)$$

Thus, the thickness  $l$  is an increasing function of temperature and goes to infinity when the system approaches the critical point  $(c_c, \Theta_c)$ . Inside the interfacial area (thin white region) the composition  $c_{int}$  varies gradually between two equilibrium compositions  $c_\alpha$  in phase  $\alpha$  and  $c_\beta > c_\alpha$  in  $\beta$ , as shown in Figure 1.2.

### 1.2.5 A review on well-posedness of the classical Cahn-Hilliard equation.

The next step towards the analysis of the Cahn-Hilliard equation (1.2.21) is to verify existence and uniqueness of solutions for the problem of the associates (1.2.25). Following the ideas by C. M. Elliot and J. Blowey [79], [100], in combination with the recent review article by D. Lie et al [74], we define a bilinear functional over the space  $H_{(0)}^1(D)$  defined in 1.2.22, i.e.,  $\mathcal{B}: H_{(0)}^1(D) \times H_{(0)}^1(D) \rightarrow \mathbb{R}$ ,  $D \subset \mathbb{R}^d$ ,

which is such that:

$$\mathcal{B}(u^*, v^*) := \int_D \nabla u^* \cdot \nabla v^* \, d\mathbf{r}. \quad (1.2.33)$$

The boundedness of  $\mathcal{B}$  is a result of Hölder's inequality [101, p 48], namely:

$$|\mathcal{B}(u^*, v^*)| \leq \|\nabla u^*\|_{L^2(D)} \|\nabla v^*\|_{L^2(D)} \leq C \|u^*\|_{H_{(0)}^1(D)} \|v^*\|_{H_{(0)}^1(D)}, \quad (1.2.34)$$

for some strictly positive constant  $C$ . Coercivity of  $\mathcal{B}$  is straightforward, as it holds:

$$\mathcal{B}(u^*, u^*) = \|\nabla u^*\|_{L^2(D)}^2, \quad \forall u^* \in H_{(0)}^1(D). \quad (1.2.35)$$

Furthermore, as a consequence of the classical Poincaré inequality [101, p 218], one can deduce for  $u^* \in H_{(0)}^1(D)$  that

$$\|u^*\|_{L^2(D)}^2 = \int_D (u^*)^2 \, d\mathbf{r} = \int_D (u^* - |D|^{-1} \int_D u^*)^2 \, d\mathbf{r} \leq C_D \int_D |\nabla u^*|^2 \, d\mathbf{r} = C_D \mathcal{B}(u^*, u^*), \quad (1.2.36)$$

where  $C_D$  depends on the domain  $D$ , in this case. One can combine the relationships (1.2.35, 1.2.36) and obtain for the  $H_{(0)}^1$ -norm:

$$\|u^*\|_{H_{(0)}^1(D)}^2 := \|\nabla u^*\|_{L^2(D)}^2 + \|u^*\|_{L^2(D)}^2 \leq (C_D + 1) \mathcal{B}(u^*, u^*). \quad (1.2.37)$$

Since we verified existence, uniqueness of the solution  $u^* \in H_{(0)}^1(D)$  of the problem

$$\mathcal{B}(u^*, v^*) = \int_D v v^* \, d\mathbf{r}, \quad (1.2.38)$$

follows from the Lax-Milgram theorem [82, p. 164], for all  $v^* \in H_{(0)}^1(D)$ . We consider now the more general case of the Cahn-Hilliard formulation (1.2.29) with a composition dependent mobility  $\mathbb{M} := \mathbb{M}(c)$ , supplemented again with homogeneous Neumann, no-flux boundary conditions and initial condition  $c_{init}(\mathbf{r}) := c(\mathbf{r}, 0)$ . We shall also make a remark on the Aubin-Lions Lemma, and a special version of Gagliardo-Nirenberg interpolation inequality, which are constantly used in this Thesis.

**Theorem 1.2.3 (Aubin-Lions).** *Let  $\mathcal{Z}(D) \subseteq \mathcal{Z}_1(D) \subseteq \mathcal{Z}_2(D)$  are Banach spaces, with the embedding  $\mathcal{Z}(D) \hookrightarrow \mathcal{Z}_1(D)$  to be compact and the  $\mathcal{Z}_1(D) \hookrightarrow \mathcal{Z}_2(D)$  is considered to be continuous. Then, for  $1 \leq p, q \leq \infty$  the embedding*

$$\{c \in L^p(0, T; \mathcal{Z}(D)) \mid \partial_t c \in L^q(0, T; \mathcal{Z}_2(D))\} \hookrightarrow L^p(0, T; \mathcal{Z}_1(D)), \quad (1.2.39)$$

*is compact for  $p < \infty$  and the embedding*

$$\{c \in L^p(0, T; \mathcal{Z}(D)) \mid \partial_t c \in L^q(0, T; \mathcal{Z}_2(D))\} \hookrightarrow C([0, T]; \mathcal{Z}_1(D)), \quad (1.2.40)$$

*is continuous for  $p = \infty$  and  $q > 1$ . For the proof and more details see [102, 103] and also [104, 105]).*

**Lemma 1.3 (Ladyzhenskaya inequality).** *Let  $D$  be a Lipschitz domain in  $\mathbb{R}^d$ ,  $d = 2, 3$  and  $c \in C_0^\infty(D)$ , then there exist constants  $C_d$  depending only on  $D$  such that,*

$$\|c\|_{L^4(D)} \leq C_d^{1/4} \|c\|_{L^2(D)}^{1-d/4} \|\nabla c\|_{L^2(D)}^{d/4}, \quad d = 2, 3. \quad (1.2.41)$$

For the proof and more details see [106, 107].

Following the basic steps of the proof by C. M. Elliott and H. Garcke [7] and reviewing the main points of the work that has been done in [8, 97, 100, 108, 109], we assume the following conditions.

**Assumption 1.1.** *The mobility coefficient  $\mathbb{M} \in C(\mathbb{R}, \mathbb{R}^+)$  satisfies  $m \leq |\mathbb{M}(c)| \leq M$ , for constants  $M, m > 0$ . Additionally, there exist some constants  $C_0, C_1, C_2, C_3, C_4, C_5 > 0$  such that  $|f'_L(c)| \leq C_0|c|^q + C_1$  and  $C_2|c|^{q+1} - C_3 \leq f_L(c) \leq C_4|c|^{q+1} + C_5$ , for  $q = d/(d-2)$ , if  $d \geq 3$  or  $q \in \mathbb{R}^+$  and arbitrary when  $d = 1, 2$ .*

**Theorem 1.2.4 (Existence of weak solutions for the classical Cahn-Hilliard equation).** *(see [7, Theorem 2]). There exists a pair of functions  $(c, \mu)$ , such that*

$$c \in L^\infty(0, T; H^1(D)) \cap C([0, T]; L^p(D)) \text{ and } \partial_t c \in L^2(0, T; H^{-1}(D)), \quad \mu \in L^2(0, T; H^1(D)), \quad (1.2.42)$$

for  $1 \leq p < 2d/(d-2)$ ,  $d > 3$ , or  $p \in \mathbb{R}^+$ ,  $d = 1, 2$ , where  $D \subset \mathbb{R}^d$  is a bounded domain with Lipschitz boundary. The pair of functions  $(c, \mu)$ , solves the following mixed weak formulation, for the Cahn-Hilliard equation with mobility  $\mathbb{M}(c)$  (which satisfies the assumption Assumption 1.1):

$$\begin{cases} \int_0^T \langle \partial_t c, v \rangle_{H^{-1}(D) \times H^1(D)} dt + \int_{D_T} \mathbb{M}(c) \nabla \mu \cdot \nabla v \, d\mathbf{r} dt = 0, & \forall v \in L^2(0, T; H^1(D)), \\ \int_D \mu \phi \, d\mathbf{r} - \int_D f'_L(c) \phi \, d\mathbf{r} - \lambda^2 \int_D \nabla c \cdot \nabla \phi \, d\mathbf{r} = 0, & \forall \phi \in H^1(D) \text{ and almost } \forall t \in [0, T], \end{cases} \quad (1.2.43)$$

supplemented with initial condition  $c_{init}(\mathbf{r}) := c(\mathbf{r}, 0) \in H^1(D)$ , no-flux  $\mathbb{M}(c) \partial_n \mu = 0$  and homogeneous Neumann  $\partial_n c = 0$  boundary conditions on  $\partial D_T$ .

*Proof.* In order to show the existence of weak solutions, we will first adapt the classical idea of applying a Galerkin approximation, by considering the ansatz:

$$c^N(\mathbf{r}, t) := \sum_{i=1}^N a_i^N(t) \phi_i(\mathbf{r}) \text{ and } \mu^N(\mathbf{r}, t) := \sum_{i=1}^N \beta_i^N(t) \phi_i(\mathbf{r}), \quad (1.2.44)$$

where the  $c^N, \mu^N$ , are approximate solutions of the Cahn-Hilliard problem with no-flux and homogeneous Neumann boundary conditions (i.e.  $\mathbb{M}(c) \partial_n \mu|_{\partial D_T} = 0$  and  $\partial_n c|_{\partial D_T} = 0$ ), by considering an orthonormal basis of the eigenfunctions of the  $-\Delta$ , namely  $\langle \phi_i, \phi_j \rangle_{L^2(D)} = \delta_{ij}$  in  $H^1(D)$ , with the corresponding eigenvalues  $e_j$  (with  $e_1 = 0$ ) and homogeneous Neumann boundary conditions, i.e.,  $\nabla \phi_i \cdot \mathbf{n} = 0$  on  $\partial D_T$ .

$$\begin{cases} \int_D \partial_t c^N \phi_j \, d\mathbf{r} = - \int_D \mathbb{M}(c^N) \nabla \mu^N \cdot \nabla \phi_j \, d\mathbf{r}, \\ \int_D \mu^N \phi_j \, d\mathbf{r} = \lambda^2 \int_D \nabla c^N \cdot \nabla \phi_j \, d\mathbf{r} + \int_D f'_L(c^N) \phi_j \, d\mathbf{r}, \quad j = 1, \dots, N, \\ c^N(\mathbf{r}, 0) = \sum_{i=1}^N \langle c_{init}, \phi_i \rangle_{L^2(D)} \phi_i. \end{cases} \quad (1.2.45)$$

Plugging the approximations expansions (1.2.44) to (2.1.3), provides the following system of ordinary differential equations for  $a_1, \dots, a_N$ , i.e.,

$$\begin{cases} \partial_t a_j^N = - \sum_{k=1}^N \beta_k^N \int_D \mathbb{M} \left( \sum_{i=1}^N a_i^N(t) \phi_i(\mathbf{r}) \right) \nabla \phi_k \cdot \nabla \phi_j \, d\mathbf{r}, \\ \beta_j^N = \lambda^2 e_j a_j^N + \int_D f_L' \left( \sum_{i=1}^N a_i^N(t) \phi_i(\mathbf{r}) \right) \phi_j \, d\mathbf{r}, \quad j = 1, \dots, N, \\ a_j^N(0) = \langle c_{init}, \phi_j \rangle_{L^2(D)}. \end{cases} \quad (1.2.46)$$

An a-priori estimate can be derived, by taking the time derivative of the free energy functional

$$\mathcal{F}(c^N(\mathbf{r}, t)) := \int_D f_L(c^N) + \frac{\lambda^2}{2} |\nabla c^N|^2 \, d\mathbf{r}, \quad (1.2.47)$$

which can be explicitly derived, as follows:

$$\begin{aligned} \frac{d\mathcal{F}}{dt} &= \int_D f_L'(c^N) \partial_t c^N + \lambda^2 \nabla c^N \cdot \nabla \partial_t c^N \, d\mathbf{r} \\ &= \int_D \mu^N \partial_t c^N \, d\mathbf{r} \\ &= - \int_D \mathbb{M}(c^N) |\nabla \mu^N|^2 \, d\mathbf{r}, \end{aligned} \quad (1.2.48)$$

which comes from Green's first identity and the classical Cahn-Hilliard equation, i.e.,  $\partial_t c^N = \operatorname{div}(\mathbb{M}(c^N) \nabla c^N)$ . A further integration of

$$\int_D f_L'(c^N) \partial_t c^N + \lambda^2 \nabla c^N \cdot \nabla \partial_t c^N \, d\mathbf{r} = - \int_D \mathbb{M}(c^N) |\nabla \mu^N|^2 \, d\mathbf{r}, \quad (1.2.49)$$

over the time interval  $(0, T)$ , yields

$$\begin{aligned} \frac{\lambda^2}{2} \int_D |\nabla c^N(\mathbf{r}, T)|^2 \, d\mathbf{r} + \int_{D_T} \mathbb{M}(c^N) |\nabla \mu^N|^2 \, d\mathbf{r} \, dt + \int_D f_L(c^N(\mathbf{r}, T)) \, d\mathbf{r} \\ = \int_D f_L(c^N(\mathbf{r}, 0)) \, d\mathbf{r} + \frac{\lambda^2}{2} \int_D |\nabla c^N(\mathbf{r}, 0)|^2 \, d\mathbf{r}. \end{aligned} \quad (1.2.50)$$

The assumption for the initial condition, i.e.,  $c_{init}(\mathbf{r}) := c(\mathbf{r}, 0) \in H^1(D)$  together with the boundedness of the  $f_L(c^N)$  (see Assumption 1.1) imply the inequality

$$\begin{aligned} \frac{\lambda^2}{2} \int_D |\nabla c^N(\mathbf{r}, T)|^2 \, d\mathbf{r} + \int_{D_T} \mathbb{M}(c^N) |\nabla \mu^N|^2 \, d\mathbf{r} \, dt + \int_D f_L(c^N(\mathbf{r}, T)) \, d\mathbf{r} \\ = \int_D \frac{\lambda^2}{2} |\nabla c^N(\mathbf{r}, 0)|^2 + f_L(c^N(\mathbf{r}, 0)) \, d\mathbf{r} \\ \leq \frac{\lambda^2}{2} \|\nabla c^N(\mathbf{r}, 0)\|_{L^2(D)}^2 + C_4 \|c^N(\mathbf{r}, 0)\|_{L^{q+1}(D)}^{q+1} + C_5 |D|, \text{ by the Assumption 1.1 for } f_L \\ \leq \frac{\lambda^2}{2} \|\nabla c_{init}\|_{L^2(D)}^2 + C_4 C_6 \|c_{init}\|_{H^1(D)}^{q+1} + C_5 |D|, \text{ by Sobolev embedding [101, p 213]} \\ \leq C, \end{aligned} \quad (1.2.51)$$

for some strictly positive constant  $C$  since  $c_{init} \in H^1(D)$ . Furthermore, from the weak formulation  $\int_D \partial_t c^N \phi_j \, d\mathbf{r} = - \int_D \mathbb{M}(c^N) \nabla \mu^N \cdot \nabla \phi_j \, d\mathbf{r}$  for  $j = 1$ , we obtain

$$\int_D \partial_t c^N(\mathbf{r}, t) \, d\mathbf{r} = \int_D (c^N(\mathbf{r}, t) - c^N(\mathbf{r}, 0)) \, d\mathbf{r} = 0, \quad (1.2.52)$$

which simply indicates the conservation of mass. We next consider a projection  $\mathcal{P}^N$  of

$L^2(D)$  onto the  $\text{span}(\phi_1, \dots, \phi_N)$ , defined by

$$\mathcal{P}^N \phi := \sum_{j=1}^N \left( \int_D \phi \phi_j \, d\mathbf{r} \right) \phi_j. \quad (1.2.53)$$

Thus, one can find an upper bound for the integral of  $c^N(\mathbf{r}, t)$  using this projection and Hölder's inequality, namely

$$\begin{aligned} \left| \int_D c^N(\mathbf{r}, t) \, d\mathbf{r} \right| &\leq \left| \int_D c^N(\mathbf{r}, 0) \, d\mathbf{r} \right| = \left| \int_D \mathcal{P}^N c_{init} \, d\mathbf{r} \right| \\ &\leq \|\mathcal{P}^N c_{init}\|_{L^2(D)} |D|^{1/2} \leq \|c_{init}\|_{L^2(D)} |D|^{1/2}. \end{aligned} \quad (1.2.54)$$

The combination of the inequalities (1.2.51, 1.2.54) with the Poincaré-Wirtinger inequality [101, p 218], implies

$$\begin{aligned} \text{ess sup}_{0 < t < T} \|c^N(\mathbf{r}, t)\|_{L^2(D)}^2 &\leq C_P \text{ess sup}_{0 < t < T} \|\nabla c^N(\mathbf{r}, t)\|_{L^2(D)}^2 + C'_P \text{ess sup}_{0 < t < T} \left( \int_D c^N(\mathbf{r}, t) \, d\mathbf{r} \right)^2 \\ &\leq C_P C + C'_P \|c_{init}\|_{L^2(D)}^2 |D|, \end{aligned} \quad (1.2.55)$$

which subsequently provides the estimate

$$\|c^N(\mathbf{r}, t)\|_{L^\infty(0, T; H^1(D))} := \text{ess sup}_{0 < t < T} \|c^N(\mathbf{r}, t)\|_{H^1(D)} \leq C''_P, \text{ for all } N. \quad (1.2.56)$$

This implies that the coefficients  $a_j^N(t)_{j=1, \dots, N}$ , are bounded and as a result a global solution to the system (1.2.46) exists. Furthermore, the inequality (1.2.51) provides the following estimate:

$$\|(\mathbb{M}(c^N))^{1/2} \nabla \mu^N\|_{L^2(D_T)}^2 < C \quad (1.2.57)$$

and subsequently we obtain

$$\begin{aligned} \left| \int_{D_T} \partial_t c^N \phi \, d\mathbf{r} \, dt \right| &= \left| \int_{D_T} \partial_t c^N \mathcal{P}^N \phi \, d\mathbf{r} \, dt \right| \\ &= \left| \int_{D_T} \mathbb{M}(c^N) \nabla \mu^N \cdot \nabla \mathcal{P}^N \phi \, d\mathbf{r} \, dt \right| \\ &\stackrel{\text{Hölder's}}{\leq} \left( \int_{D_T} |\mathbb{M}(c^N) \nabla \mu^N|^2 \, d\mathbf{r} \, dt \right)^{1/2} \left( \int_{D_T} |\nabla \mathcal{P}^N \phi|^2 \, d\mathbf{r} \, dt \right)^{1/2} \\ &\stackrel{|\mathbb{M}(c)| \leq M}{\leq} M^{1/2} \left( \int_{D_T} |(\mathbb{M}(c^N))^{1/2} \nabla \mu^N|^2 \, d\mathbf{r} \, dt \right)^{1/2} \|\nabla \phi\|_{L^2(D_T)} \\ &\stackrel{(1.2.51)}{\leq} (MC)^{1/2} \|\nabla \phi\|_{L^2(D_T)} \\ &\leq C' \|\phi\|_{L^2(0, T; H^1(D))}, \end{aligned} \quad (1.2.58)$$

for all  $\phi \in L^2(0, T; H^1(D))$  from which, we straightforwardly deduce the bound,

$$\|\partial_t c^N\|_{L^2(0, T; H^{-1}(D))} \leq C' \text{ for all } N. \quad (1.2.59)$$

Thus, it turns out that the  $H^{-1}$ -norm of the time derivative of the composition field (over the time interval  $(0, T)$ ), is bounded from above by a constant that depends on the influx  $g$ . In addition, since  $\phi_j$  are eigenvalues of the Laplacian with  $e_1 = 0$ , then from (1.2.46) and the assumption for  $f'_L$ , it follows that:



$$\begin{aligned}
 \left| \int_D \mu^N(\mathbf{r}, t) d\mathbf{r} \right| &= \left| \int_D f'_L(c^N(\mathbf{r}, t)) d\mathbf{r} \right| \leq \int_D |f'_L(c^N(\mathbf{r}, t))| d\mathbf{r} \\
 &\leq |D|^{1/2} \|f'_L(c^N(\mathbf{r}, t))\|_{L^2(D)} \\
 &\leq |D|^{1/2} \left( \int_D (C_0 |c|^q + C_1)^2 d\mathbf{r} \right)^{1/2} \\
 &\leq |D|^{1/2} C_0 \|c^N\|_{L^{2q}(D)} + C_1 |D| \\
 &\leq |D|^{1/2} C_0 \|c^N\|_{H^1(D)} + C_1 |D| \\
 &\leq |D|^{1/2} C_0 C + C_1 |D|,
 \end{aligned} \tag{1.2.60}$$

which follows again by Sobolev embedding and (1.2.56). In addition, from the related assumption for the mobility (1.1) and by the Poincaré-Wirtinger inequality with constants  $C_P, C'_P$ , we obtain using the average  $\{\mu(\mathbf{r}, t)\}_{av} := |D|^{-1} \int_D \mu^N(\mathbf{r}, t) d\mathbf{r}$  that

$$\begin{aligned}
 C_{Pm} \int_D |\nabla \mu^N(\mathbf{r}, t)|^2 d\mathbf{r} &\geq m \|\mu^N(\mathbf{r}, t)\|_{L^2(D)}^2 - m C'_P (\{\mu(\mathbf{r}, t)\}_{av})^2 \\
 &\geq m \|\mu^N(\mathbf{r}, t)\|_{L^2(D)}^2 - m C'_P C'_D,
 \end{aligned} \tag{1.2.61}$$

where  $C'_D := (|D|^{-1/2} C_0 C + C_1)^2$  which comes from the estimate (1.2.60). Hence, on noting that the estimate (1.2.57) holds and by integrating (2.1.47) over time, it follows that

$$m \int_0^T \|\mu^N(\mathbf{r}, t)\|_{L^2(D)}^2 dt \leq m C'_P C'_D T + C_{Pm} \int_0^T \|\nabla \mu^N(\mathbf{r}, t)\|_{L^2(D)}^2 dt \leq C_P C + m C'_P C'_D T \tag{1.2.62}$$

and therefore we can deduce the bound

$$\|\mu^N\|_{L^2(0, T; H^1(D))} \leq C'_{P, m, D, T}, \tag{1.2.63}$$

where  $C'_{P, m, D, T} > 0$  is a constant that depends on the constants  $C_P, C'_D$  the constant  $C$  from (1.2.51), the lower bound  $m$  of the mobility and the maximum time of observation  $T > 0$ . Hence  $\{\mu^N\}$  is a bounded sequence in  $L^2(0, T; H^1(D))$ . Hence by Aubin-Lions Theorem 1.2.3 and the inequalities (1.2.56, 1.2.59), we obtain the following convergence results for a subsequence of  $c^N$  as  $N \rightarrow \infty$  (we can denote the subsequence  $c^N$ ):

$$\begin{aligned}
 c^N &\rightharpoonup c, \quad \text{weakly-}^* \text{ in } L^\infty(0, T; H^1(D)), \\
 c^N &\rightarrow c, \quad \text{strongly in } L^2(0, T; L^p(D)) \text{ and } C([0, T]; L^p(D)), \\
 &\text{for } 1 \leq p < 2d/(d-2), d > 3, \text{ or } p \in \mathbb{R}^+, d = 1, 2.
 \end{aligned} \tag{1.2.64}$$

In addition for the time-derivative we deduce the following convergence result:

$$\partial_t c^N \rightharpoonup \partial_t c, \quad \text{weakly in } L^2(0, T; H^{-1}(D)). \tag{1.2.65}$$

Finally, we can deduce for a subsequence of  $\mu^N$  (still denoted by  $\mu^N$ ) the convergence,

$$\mu^N \rightharpoonup \mu \quad \text{weakly in } L^2(0, T; H^1(D)) \tag{1.2.66}$$

and the proof is completed.  $\square$

Recent and interesting approaches on the analysis of the Cahn-Hilliard equation with influx and dynamic boundary conditions i.e variants of the form  $\partial_t c - \sigma \Delta_{\partial D} \mu + \partial_n \mu = 0, \sigma \geq 0$  on  $\partial D_T$ , can be also found in the work by C. Liu and H. Wu [110] in which they formally

derive the model using an Energetic Variational Approach and study the existence and uniqueness of global weak/strong solutions with or without surface diffusion. Moreover, P. Colli et al in [118, 119], introduced a convective term with a forced velocity field and a mass constraint on the boundary which results the appearance of two Lagrange multipliers [120, Section 17.6], one for the bulk part and the other for the boundary. Finally, the Cahn-Hilliard with reactions model (with nonlinear Newton boundary conditions) coupled to rate-dependent damage processes for the description of the behaviour of electrodes in lithium-ion batteries, has been recently analysed by C. Kraus, C. Heinemann and A. Roggensack [121, 122].

## Chapter 2

# Numerical studies, porous media and homogenization.

In this chapter, we are dealing with various computational aspects related to the Cahn-Hilliard formulation and its variants. We additionally, investigate the corresponding models in the periodic porous media setting and obtain by formal homogenization arguments effective/upscaled approximations. To this end, we generalize the notion of classical two-scale convergence to a reiterated homogenization procedure by considering one additional microscale (three-scale asymptotic expansion). Finally, we are also extending our initial considerations of the classical binary two-phase mixtures, to the more complex case of multiphase ternary alloys, in which due to a variable reduction constraint between the three different substances, we end up to examine a system of two equations, involving the two of the three components of the ternary mixture.

### 2.1 Microscopic formulations, discretization and homogenization of Cahn-Hilliard type equations.

The first step towards numerical studies for the classical Cahn-Hilliard system

$$\begin{cases} \partial_t c = \operatorname{div}(\mathbb{M} \nabla \mu(c)) & \text{in } D_T, \\ \mu(c) := f'_L(c) - \lambda^2 \Delta c & \text{in } D_T, \end{cases} \quad (2.1.1)$$

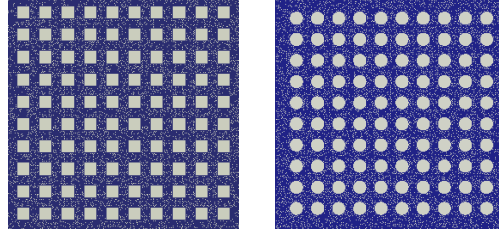
is to obtain an efficient weak formulation by mixed linear finite elements [123], in the space

$$V_h := \{ \phi \in C(\bar{D}) \mid \phi|_K \in \mathcal{P}_1(K), K \in \mathcal{T}_h \}, \quad (2.1.2)$$

where  $\mathcal{T}_h$  denotes a quasi-uniform triangulation of the bounded polygonal domain  $D \subset \mathbb{R}^d$  into triangles (for  $d = 2$ ) or tetrahedrons (for  $d = 3$ ), with mesh size  $h$ . The domain of integration is set to be the unit square  $D = [0, 1] \times [0, 1]$ , for simplicity. We consider the discretization in time by  $t_i = i \Delta t, i \in \mathbb{N}_0$  for  $0 \leq i \leq N$  such that  $t_N = T$ , is the final time-step and  $\Delta t > 0$  denotes the time-step size. We consider the case of constant mobility coefficient  $\mathbb{M} = 1$  for computations and a reasonably small value for the surface parameter (interaction

length),  $\lambda = 0.01$ . All the computations are performed using the Python-FEniCs library [18] for numerical solutions of partial differential equations, based on the finite element method and the perforated meshes are created using the mesh generator of the open source package mshr, which is part of FEniCS.

Figure 2.1: We consider the following types of isotropic periodically perforated domains for computations, which are created by the mesh generator mshr.



**Discrete mixed weak formulation.** We consider the time discretized form of the classical Cahn-Hilliard system's (2.1.1) weak formulation

$$\begin{cases} \int_D \partial_t c v \, d\mathbf{r} = -\mathbb{M} \int_D \nabla \mu \cdot \nabla v \, d\mathbf{r} = 0, \\ \int_D \mu \varphi \, d\mathbf{r} = \lambda^2 \int_D \nabla c \cdot \nabla \varphi \, d\mathbf{r} + \int_D f'_L(c) \varphi \, d\mathbf{r}, \end{cases} \quad (2.1.3)$$

for all  $v, \varphi \in H^1(D)$  and under the hypothesis of constant mobility  $\mathbb{M} > 0$ , by using the  $\theta$ -method which generalizes Crank-Nicholson's method ( $\theta = 1/2$ ) to an arbitrary  $0 < \theta < 1$  [124]:

$$\mu_{i+\theta} = (1-\theta)\mu_i + \theta\mu_{i+1}. \quad (2.1.4)$$

As a result, we obtain the following classical finite element discrete mixed formulation for all  $v, \varphi \in H^1(D)$ :

$$\begin{cases} \int_D \frac{c_{i+1} - c_i}{\Delta t} v \, d\mathbf{r} + \mathbb{M} \int_D \nabla \mu_{i+\theta} \cdot \nabla v \, d\mathbf{r} = 0, \\ \int_D \mu_{i+1} \varphi \, d\mathbf{r} - \int_D (f'_L)^{i+1} \varphi \, d\mathbf{r} - \lambda^2 \int_D \nabla c_{i+1} \cdot \nabla \varphi \, d\mathbf{r} = 0. \end{cases} \quad (2.1.5)$$

A similar formulation holds in the case in which we consider the domain to be a porous medium with a periodic coverage of reference cells, where the solid phase can be given by circular obstacles (or square-shaped obstacles) (see Figure 2.2). The full microscopic problem in the case of neutral wetting (contact angle  $90^\circ$ ) [125–127] with no-flux boundary conditions and initial condition  $c^\varepsilon(\mathbf{r}, 0)$ , can be formulated as follows:

$$\begin{cases} \partial_t c^\varepsilon = \operatorname{div} \left( \mathbb{M} \nabla (f'_L(c^\varepsilon)) - \lambda^2 \Delta c^\varepsilon \right) & \text{in } D_T^\varepsilon, \\ \partial_n c^\varepsilon = \partial_n \Delta c^\varepsilon = 0 & \text{on } \partial D_T^\varepsilon. \end{cases} \quad (2.1.6)$$

**Remark 2.1.** In the more general case inhomogeneous boundary conditions of the form  $\nabla c^\varepsilon \cdot \mathbf{n} = \varepsilon Q$  may appear, due to a surface energy contribution to the Cahn-Hilliard free energy. The parameter  $Q = -s\gamma/C_h$  accounts for the wetting properties of the pore walls and depends on the Cahn number  $C_h = \lambda/L$  and the fraction  $\gamma := 2\sqrt{2}c_e/3\sigma_{ig}$ , where  $c_e$  is the local equilibrium

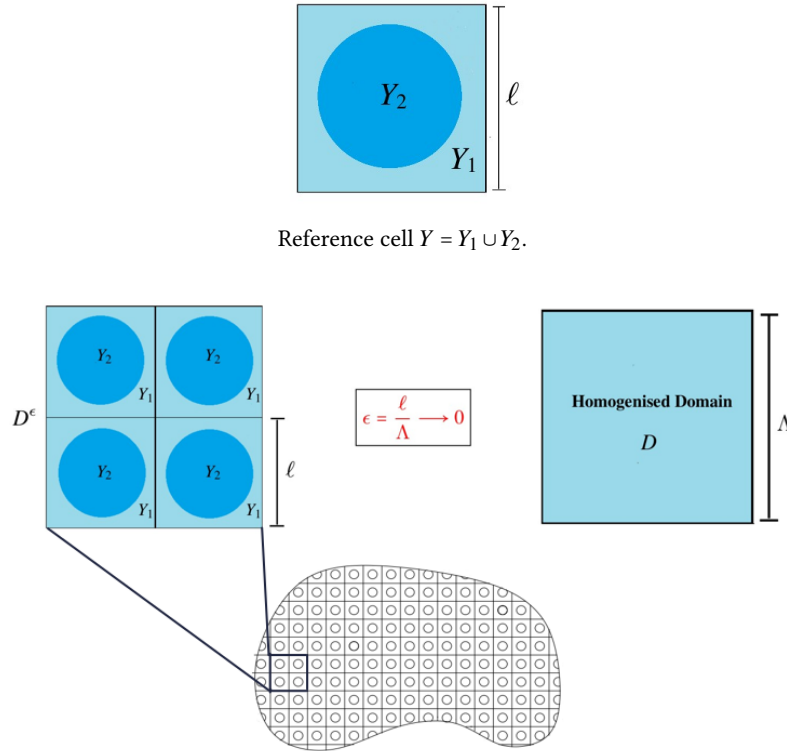
limiting value of the free energy  $\mathcal{F}$  and  $\sigma_{lg}$  is the liquid-gas surface tension. The choice of  $s > 0$  indicates that the pore walls are hydrophilic and for  $s < 0$  hydrophobic. Hence,  $s = 0$  stands for a contact angle of 90 degrees, i.e., the case of neutral wetting ( $Q = 0$ ), which is the situation of interest in this project.

A well-accepted approximation is then the exact periodic covering of the porous medium by a finite number of single reference cells  $Y := (0, \ell)^d \subset \mathbb{R}^d$ . Hence, we can define the perforated domain of length  $\Lambda$  and heterogeneity  $\varepsilon := \ell/\Lambda$  by

$$D^\varepsilon := \cup_{\mathbf{z} \in \mathbf{Z}^d} \varepsilon (Y + \mathbf{z}), \quad (2.1.7)$$

where  $Y := Y_1 \cup Y_2$  and more precisely  $Y_1$  stands for the pore phase of each cell (e.g. liquid or gas phase in wetting problems) and  $Y_2$  the corresponding solid phase, see Figure 2.2. The

Figure 2.2: The idea of upscaling: Representation in two dimensions of the isotropic perforated domain which is composed of subdomains  $D^\varepsilon$  of characteristic length  $\Lambda$ , and is covered by a periodic replacement of reference cells  $Y$  of characteristic length  $\ell$ . As the heterogeneity  $\varepsilon := \ell/\Lambda$  becomes infinitely small, the perforated domain can be approximated by homogeneous one. (The figure of the perforated domain in grayscale, has been taken by G. Allaire Notes on Homogenization, École Polytechnique.)



2-d representation of the perforated domain and its homogeneous approximation as  $\varepsilon \rightarrow 0$ .

discrete mixed weak formulation scheme for the model is the same as (2.1.5) adapted in the porous media setting and can be compactly rewritten with the help of the following identifications, summarised in the next statement.

### Discretization scheme for the microscopic Cahn-Hilliard system.

We discretize the microscopic problem (2.1.21) by mixed linear finite elements in space and we compute numerical approximations in time by the  $\theta$ -method which generalizes

Crank–Nicholson’s, as mentioned earlier. To this end, we define the mass matrix by  $\mathbb{G} := \{(\varphi_i, \varphi_j)\}_{1 \leq i, j \leq d}$  (where  $\{\varphi_j\}_{j=1}^d$  linear finite element basis on  $V_h$ ), the stiffness matrix  $\mathbb{S} := \{(\nabla \varphi_i, \nabla \varphi_j)\}_{1 \leq i, j \leq d}$  and the nonlinear matrix  $\mathbb{K}(\mathbf{c}_{n+1}^{\varepsilon, l}) := \{(\mathbf{c}_{n+1}^{\varepsilon, l})^2 \varphi_i, \varphi_j\}_{1 \leq i, j \leq d}$ . We denote by  $\langle \nabla^k \phi_i, \nabla^k \phi_j \rangle$ ,  $k=0, 1$  the usual  $L^2$ -scalar product  $\int_D \nabla^k \phi_i \cdot \nabla^k \phi_j \, d\mathbf{r}$ ,  $k=0, 1$ . In addition, we denote by  $c_{h, \Delta t}^\varepsilon := \sum_{j=1}^d c_j^n \varphi_j(\mathbf{r})$  the finite element approximation of the microscopic solution  $c^\varepsilon$  for  $t_n = n\Delta t$ . The index  $l \in N, 0 \leq l \leq L$ , denotes the iteration level in the scheme, linearized by a fixed point iteration. The scheme also consists of the  $\theta$ -method:  $\boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1} := (1-\theta)\boldsymbol{\mu}_n^\varepsilon + \theta\boldsymbol{\mu}_{n+1}^{\varepsilon, l+1}$ ,  $0 \leq \theta \leq 1$ .

Therefore, the following mixed finite element scheme can be applied for mobility  $\mathbb{M} = m\mathbb{I}$ ,  $m > 0$  [20]:

$$\begin{cases} \mathbb{G}\mathbf{c}_{n+1}^{\varepsilon, l+1} + m\Delta t\mathbb{S}\boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1} = \mathbb{G}\mathbf{c}_n^\varepsilon, \\ \mathbb{G}\boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1} + \mathbb{K}(\mathbf{c}_{n+1}^{\varepsilon, l})\mathbf{c}_{n+1}^{\varepsilon, l+1} - \frac{1}{2}\mathbb{G}\mathbf{c}_{n+1}^{\varepsilon, l+1} - \lambda^2\mathbb{S}\mathbf{c}_{n+1}^{\varepsilon, l+1} = 0, \end{cases} \quad (2.1.8)$$

where  $(\mathbf{c}_{n+1}^{\varepsilon, l+1}, \boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1})$  with  $\boldsymbol{\mu}_{n+\theta}^{\varepsilon, l+1} := \{\mu_{j, n+\theta}^{\varepsilon, l+1}\}_{j=1}^d$  and  $\mathbf{c}_{n+1}^{\varepsilon, l+1} := \{c_{j, n+1}^{\varepsilon, l+1}\}_{j=1}^d$ , are coefficient vectors of the related finite element functions. Finally we considered in the discretization scheme, the following form of the homogeneous free energy:  $f_L(c) = (1/4)c^2(1-c)^2$ , the derivative of which appears in the definition of the Cahn-Hilliard chemical potential, i.e.,  $\mu(c) := f_L'(c) - \lambda^2\Delta c$ . In the same context we introduce the following function space, which is constantly used in the sequel:

$$H_{per}^1(Y) := \left\{ c \in \bar{H}_{per}^1(Y) \mid M_Y(c) := |Y|^{-1} \int_Y c \, dy = 0 \right\}, \quad (2.1.9)$$

where  $\bar{H}_{per}^1(Y)$  stands for the closure of  $C_{per}^\infty(Y)$  in the  $H^1$ -norm.

An effective/homogenised macroscopic equation can be derived from the Cahn-Hilliard formulation in porous media, with the help of basic principles of homogenisation theory [12] and more precisely by applying a two-scale asymptotic expansion of the form

$$c^\varepsilon(\mathbf{r}, t) = \sum_{i=0}^{\infty} \varepsilon^i c_i(\mathbf{r}, \mathbf{y}, t) := c_0(\mathbf{r}, \mathbf{y}, t) + \varepsilon c_1(\mathbf{r}, \mathbf{y}, t) + \varepsilon^2 c_2(\mathbf{r}, \mathbf{y}, t) + \dots, \quad (2.1.10)$$

where  $\mathbf{y} := \mathbf{r}/\varepsilon \in Y$  stands for the microscale. Plugging this ansatz to the microscopic formulation, leads to a sequence of problems where a solvability constraint on the problem for  $c_2$ , provides the upscaled Cahn-Hilliard equation (derived by M. Schmuck et al in [13, 128, 129]) for an infinitely small value of the heterogeneity  $\varepsilon \rightarrow 0$  (for the idea of upscaling see Figure 2.2). The upscaled equation, in the case of isotropic mobility  $\mathbb{M} = m\{\delta_{ij}\}_{1 \leq i, j \leq d}$  with  $m > 0$  and porosity  $p := |Y_1|/|Y|$ , reads:

$$\begin{cases} p\partial_t c_0 = \operatorname{div}(m\mathbb{D}\nabla f_L'(c_0)) - p^{-1}\lambda^2 \operatorname{div}(m\mathbb{D}\nabla[\operatorname{div}(\mathbb{D}\nabla c_0)]) & \text{in } D_T, \\ \mathbf{n} \cdot \mathbb{D}\nabla c_0 = \mathbf{n} \cdot \mathbb{D}\nabla \Delta c_0 = 0 & \text{on } \partial D_T. \end{cases} \quad (2.1.11)$$

In the above equation,  $\mathbb{D} := \{\mathbb{D}_{ij}\}_{1 \leq i, j \leq d}$  stands for a tensorial quantity (effective tensor) with elements defined by:

$$\mathbb{D}_{ij} := \mathcal{M}_{Y_1} \left( \delta_{ij} - \frac{\partial \xi^j(\mathbf{y})}{\partial y_i} \right) := \frac{1}{|Y|} \int_{Y_1} \left( \delta_{ij} - \frac{\partial \xi^j(\mathbf{y})}{\partial y_i} \right) d\mathbf{y}, \quad (2.1.12)$$

where the correctors  $\xi^j(\mathbf{y}) \in H_{per}^1(Y_1)$  for  $1 \leq j \leq d$  are unique, in the sense of distributions,

solutions of the following reference cell problems:

$$\begin{cases} -\sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi^k) = 0. \end{cases} \quad (2.1.13)$$

**Remark 2.2.** *It has been rigorously shown in [130, Theorem 1], that for smooth enough data, Lipschitz boundary  $\partial D^\varepsilon$  and isotropic mobility  $\mathbb{M} = m\mathbb{I}$ , the error quantities  $E_\varepsilon^c := c^\varepsilon - (c_0 + \varepsilon c_1)$  and  $E_\varepsilon^w := w^\varepsilon - (w_0 + \varepsilon w_1)$  with*

$$\begin{cases} w_1 := -\sum_{k=1}^d \xi_w^k(\mathbf{y}) \partial_{r_k} w_0(\mathbf{r}, t), \\ c_1 := -\sum_{k=1}^d \xi_c^k(\mathbf{y}) \partial_{r_k} c_0(\mathbf{r}, t), \end{cases} \quad (2.1.14)$$

*of the solutions of the following splitting formulation for  $-\Delta c^\varepsilon = w^\varepsilon$ , for the microscopic problem (2.1.6), i.e.,*

$$\begin{cases} \partial_t (-\Delta)^{-1} w^\varepsilon = \operatorname{div}(\mathbb{M} \nabla)(f_L'(c^\varepsilon) + \lambda^2 w^\varepsilon) & \text{in } D_T^\varepsilon, \\ \partial_n w^\varepsilon = -\partial_n \Delta c^\varepsilon = \partial_n c^\varepsilon = 0 & \text{on } \partial D_T^\varepsilon, \end{cases} \quad (2.1.15)$$

*satisfy for  $0 \leq t \leq T < \infty$  and polynomial free energy, the error estimates:*

$$\begin{cases} \|E_\varepsilon^w(\cdot, t)\|_{L^2(D^\varepsilon)} + c(m, \lambda, k) \int_0^t \|\mathcal{A}_\varepsilon E_\varepsilon^w(\cdot, s)\|_{L^2(D^\varepsilon)} ds \leq \varepsilon^{1/2} C(T, D, m, k, \lambda), \\ \|E_\varepsilon^\phi(\cdot, t)\|_{H^1(D^\varepsilon)} \leq \varepsilon^{1/4} C(T, D, m, k, \lambda), \end{cases} \quad (2.1.16)$$

*where the constants  $C(T, D, m, k, \lambda), c(m, \lambda, k) > 0$ , are independent of the heterogeneity  $\varepsilon$ .*

**Remark 2.3.** *Consequently, we can adapt the discretization scheme (2.1.8) for the microscopic formulation (2.1.6) to derive one for the homogenized model (2.1.11) with the same definitions for the quantities involved, as follows:*

$$\begin{cases} p \mathbb{G} \mathbf{c}_{n+1}^{0,l+1} + m \Delta t \hat{\mathbb{S}} \boldsymbol{\mu}_{n+\theta}^{0,l+1} = p \mathbb{G} \mathbf{c}_n^0, \\ \mathbb{G} \boldsymbol{\mu}_{n+\theta}^{0,l+1} + \mathbb{K}(c_{n+1}^{0,l}) \mathbf{c}_{n+1}^{0,l+1} - \frac{1}{2} \mathbb{G} \mathbf{c}_{n+1}^{0,l+1} - \lambda^2 p^{-1} \hat{\mathbb{S}} \mathbf{c}_{n+1}^{0,l+1} = 0, \end{cases} \quad (2.1.17)$$

*in which we additionally introduced the effective stiffness matrix defined by  $\hat{\mathbb{S}} := \{\hat{s}_{ij}\}_{i,j=1}^d$ , where  $\hat{s}_{ij} := \langle \mathbb{D} \nabla \phi_i, \nabla \phi_j \rangle$ .*

A recent computational study on the behaviour of the  $L^2$ -error between the upscaled solution and the solution of the microscopic problem (see [20]), which can be defined by  $E_\varepsilon^{L^2} := \|c^\varepsilon - c_0\|_{L^2(D^\varepsilon)}$ , where  $D^\varepsilon$  the periodic porous medium with circular perforations, suggests that the convergence rate coincides with the analytically derived upper bound of  $\mathcal{O}(\varepsilon^{1/4})$  based on a truncation argument for the constant involved in the estimate (see [130] for more details). It is worth mentioning that for different parameters of the model such as different time step size, or number of time steps and different initial conditions, the upscaled error admits computationally various convergence rates for the

same type of perforations, but generally better than  $\mathcal{O}(\varepsilon^{1/4})$ . Examples include an  $\mathcal{O}(\varepsilon^2)$

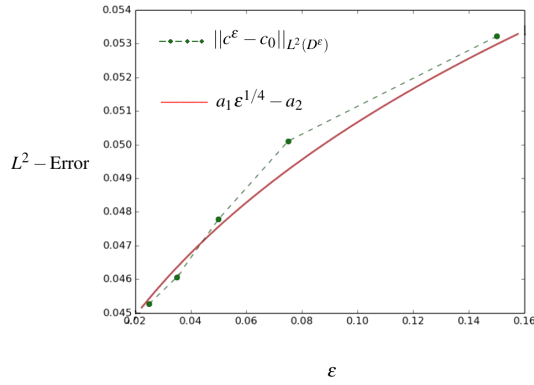


Figure 2.3: Possible convergence rates of the upscaled Cahn-Hilliard equation (2.1.11) with  $m = 1$ , porosity  $p = 0.5$  and surface parameter  $\lambda = 0.01$ . The error  $E_\varepsilon^{L^2} := \|c^\varepsilon - c_0\|_{L^2(D^\varepsilon)}$  is investigated after 5 time steps with time-step size  $\Delta t = 10^{-6}$  and for fixed mesh size  $h = 1/100$ .

convergence rate, i.e.,  $a'_1\varepsilon^2 + a'_2$ ,  $a_1, a'_2$  positive constants, or a rate of  $a_1\varepsilon^{1/4} - a_2$ ,  $a_1, a_2 > 0$  are constants such that  $a_1\varepsilon^{1/4} - a_2 \leq a_1\varepsilon^{1/4}$  and other, as illustrated in Figure 2.3 and Figure 2.4 and constructed with the help of the FEniCs library. Since the error estimates grow in

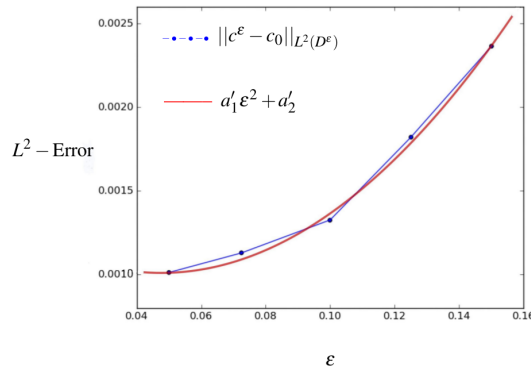


Figure 2.4: Possible convergence rates of the upscaled Cahn-Hilliard equation (2.1.11) with  $m = 1$ , porosity  $p = 0.5$  and surface parameter  $\lambda = 0.01$ . The error  $E_\varepsilon^{L^2} := \|c^\varepsilon - c_0\|_{L^2(D^\varepsilon)}$  is investigated after 5 time steps with time-step size  $\Delta t = 10^{-6}$  and for fixed mesh size  $h = 1/100$ .

time (see Remark 2.2 and [27]) the (exact) initial conditions are defined on the perforated domain, the relaxation time is expected to be very short with the numerical scheme (2.1.17) of the upscaled problem and hence the error is being examined after the first 5 time steps for vanishing heterogeneity  $\varepsilon \rightarrow 0$ . The exact error quantity used for the numerics is  $E_\varepsilon^{L^2} := \|c^\varepsilon - c_0\|_{L^2(D^\varepsilon)}$ , where  $c^\varepsilon$  is a linear finite element solution of the discretization scheme (2.1.8) of the microscopic Cahn-Hilliard formulation and  $c_0$  is a solution of the scheme (2.1.17) approximating the homogenized equation.

In light of the above, it may be of interest to verify certain dependence of the numerical parameters mentioned above and the convergence rate for the same type of periodic perforations, as we so far be aware of the fact that geometry and regularity of the boundary influence the size of the estimated error bound, as well as the discretization of the boundary geometry, since the resolution in this case demands a larger number of grid points to resolve the curvature appropriately, than in the case of flat surfaces. Hence, for square shaped perforations we generally expect a better convergence rate, which has



been computationally shown to be close to  $\mathcal{O}(\varepsilon)$ , (see[20]).

**Definition 2.1 (Local thermodynamic equilibrium).** *The key requirement for the derivation of the effective equation, is the assumption of local thermodynamic equilibrium, in which we require that the chemical potential  $\mu(c) := f'_L(c) - \lambda^2 \Delta c$ , varies over the different reference cells and remains constant on each particular cell  $Y$  and not on the macroscale. Equivalently the derived upscaled chemical potential  $\mu_0(c_0) := f'_L(c_0) - p^{-1} \lambda^2 \operatorname{div}(\mathbb{D} \nabla c_0)$  satisfies the same property, i.e.,  $\partial_{r_k} \mu_0(c_0(\mathbf{r})) = 0$ , in  $D \times Y$ .*

This constraint consequently leads to linearisation of the first derivative of the homogeneous free energy  $f'_L(c^\varepsilon)$ , around the upscaled solution  $c_0$ . The method that applied for the derivation of the upscaled equations relies on the use of a formal asymptotic expansion, by introducing the microscale variable  $\frac{\mathbf{r}}{\varepsilon} =: \mathbf{y} \in Y$ . Moreover, a consequence of Local Thermodynamic Equilibrium (see definition 2.1) and the linearization of the nonlinear free energy density around the homogenized/upscaled solution  $c_0$ , i.e.,  $f_L(c^\varepsilon) = f_L(c_0) + f'_L(c_0)(c^\varepsilon - c_0) + \dots$ , is that we end up with the classical (linear) cell problem (2.1.13).

**Remark 2.4.** *The homogenized equation (2.1.11) is valid when the interfacial width is smaller than the characteristic pore size  $\ell$ . This particular case is more often observed in real world applications, where it is assumed that solid–fluid or fluid–fluid interfaces are much smaller than the pore size. If this would not be the case, then such materials would not be suitable for applications since too much energy to pump fluids through such a medium, is required. Consequently, an interfacial width smaller than  $\ell$  forms a vital requirement in modelling porous media, since it also guarantees the well-accepted property of Local Thermodynamic Equilibrium [20, 131–133].*

A weak formulation to the above problem (2.1.13) can be obtained by multiplying with a test function  $v^k \in H_{per}^1(Y_1) := \{v^k \text{ is } Y_1\text{-periodic, } v^k \in H^1(Y_1)\}$  and integrate over the whole domain  $Y_1$ , then one gets for  $k = 1, 2$ :

$$\sum_{i=1}^d \int_{Y_1} \frac{\partial y_i}{\partial y_k} \frac{\partial v^k}{\partial y_i} d\mathbf{y} = \sum_{i,j=1}^d \int_{Y_1} \delta_{ij} \frac{\partial \xi^k}{\partial y_j} \frac{\partial v^k}{\partial y_i} d\mathbf{y} - \sum_{i,j=1}^d \int_{\partial Y_1} v^k (\delta_{ik} - \delta_{ij} \frac{\partial \xi^k}{\partial y_j}) n_i ds^1 \quad \text{in } Y_1, \quad (2.1.18)$$

supplemented with the related boundary condition for the  $Y$ -periodic  $\xi^k$ 's:

$$\sum_{i,j=1}^d n_i \frac{\partial \xi^k}{\partial y_j} \delta_{ij} = \sum_{i=1}^d n_i \delta_{ik} \quad \text{on } \partial Y_2, \quad (2.1.19)$$

which due to the related boundary condition, is simplified to the final form

$$\begin{cases} \sum_{i=1}^d \int_{Y_1} \frac{\partial y_i}{\partial y_k} \frac{\partial v^k}{\partial y_i} d\mathbf{y} = \sum_{i,j=1}^d \int_{Y_1} \delta_{ij} \frac{\partial \xi^k}{\partial y_j} \frac{\partial v^k}{\partial y_i} d\mathbf{y} & \text{in } Y_1, \\ \sum_i \int_{\partial Y_1} v^k n_i \frac{\partial \xi^k}{\partial y_i} ds^1 = d \int_{\partial Y_1} v^k n_k ds^1 & \text{on } \partial Y_2, \\ \xi^k \text{ is } Y\text{-periodic.} \end{cases} \quad (2.1.20)$$

The numerical implementation of the weak formulation (2.1.20) by the FEniCs library, provides the plots of the corresponding corrector functions  $\xi^k$ ,  $k = 1, 2$ , which for porosity  $p = 0.9$  are shown in Figure 2.5. Just for reference, the related effective tensor  $\mathbb{D}$  defined in

(2.1.12) in the case of circular periodic perforations reads

$$\mathbb{D} = \begin{bmatrix} 8.19320388e-01 & 2.18689492e-07 \\ 2.18689492e-07 & 8.19321348e-01 \end{bmatrix}$$

and similarly in the case of square-shaped perforations, is given by

$$\mathbb{D} = \begin{bmatrix} 8.04050527e-01 & 1.60999833e-05 \\ 1.60999833e-05 & 8.04053707e-01 \end{bmatrix}.$$

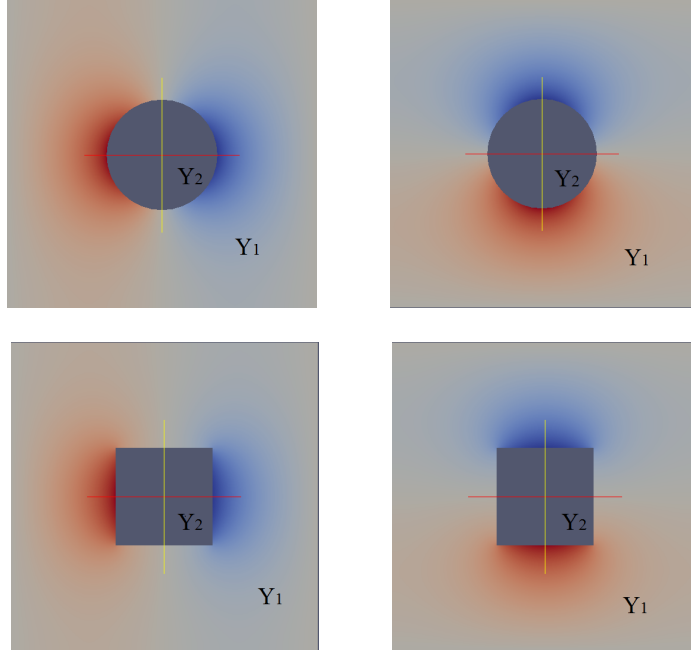


Figure 2.5: Plots for the correctors  $\xi^1$  (left column) and  $\xi^2$  (right column), solving the elliptic reference cell problem (2.1.13), for a reference cell  $Y$  containing a single circular (top) and square shaped (bottom) solid obstacle  $Y_2 := Y \setminus Y_1$ , where  $Y_1$  is the pore space (see also [20]).

A reader who is interested in more details about the computational study on the homogenised/effective Cahn-Hilliard equation can search for more details in [20] and for more details about the derivation and analysis in the articles [13, 129]. The derivation of the upscaled classical Cahn-Hilliard formulation is illustrated for a similar problem in the following paragraph.

### 2.1.1 Upscaled Allen-Cahn/Cahn-Hilliard equations.

We investigate a variant model of the classical Cahn-Hilliard equation with constant mobility  $\mathbb{M} > 0$ , which was first introduced by G. Karali and M. Katsoulakis [9] as a more simplified model of a mesoscopic formulation for multiple microscopic mechanisms, in simultaneously interacting surface processes. The full model consists of a Cahn-Hilliard term  $\operatorname{div}(\mathbb{M}\nabla\mu)$  which corresponds to surface diffusion and an Allen-Cahn chemical potential term  $\mu := \mu(c) := f'_L(c) - \lambda^2\Delta c$  that corresponds to adsorption/desorption. Hence, due to the presence of two types of evolution in the same equation the formulation has been given the representative name Allen-Cahn/Cahn-Hilliard and can be expressed as follows:

**Definition 2.2 (Allen-Cahn/Cahn-Hilliard formulation).**

$$\begin{cases} \partial_t c = \operatorname{div}(\mathbb{M}\nabla\mu) - \mu & \text{in } D_T, \\ \partial_n c = \partial_n \mu = \partial_n \Delta c = 0 & \text{on } \partial D_T. \end{cases} \quad (2.1.21)$$

More precisely equation (2.1.21) can be derived by the classical Cahn-Hilliard formulation (2.1.1) with appropriate rescaling close to the critical temperature, see [9] for more details. Moreover, existence and uniqueness of weak solutions has been studied by G. Karali and Y. Nagase [10] for the constant mobility case and by X. Zhang and C. Liu [11], for the degenerate mobility case. The proofs follow similar lines (with the appropriate modifications) as the one provided in Theorem 1.2.4 for the classical Cahn-Hilliard and therefore we are not getting into details on the analysis part. In this subsection, we are mainly interested in the porous media setting of the problem of the Allen-Cahn/Cahn-Hilliard and on the derivation of effective/upscaled equations for this model.

**Remark 2.5 (Dissipation of energy and non-conservation of mass).** *Similarly as for the classical Cahn-Hilliard, we observe again a decrease in the Cahn-Hilliard free energy  $\mathcal{F}(c) := \int_D f_L(c) + \lambda^2 |\nabla c|^2 / 2 \, d\mathbf{r}$  over time, i.e.,*

$$\frac{d\mathcal{F}(z)}{dt} = \langle \nabla_c^2 \mathcal{F}(c), \partial_t c \rangle_{L^2(D)} := - \int_D \mu (1 - \operatorname{div}(\mathbb{M}\nabla)) \mu \, d\mathbf{r} = - \int_D (\mathbb{M}(\nabla\mu)^2 + \mu^2) \, d\mathbf{r} \leq 0, \quad \mathbb{M} > 0. \quad (2.1.22)$$

*On the contrary this equation is non-mass conserving since*

$$\frac{d}{dt} \int_D c \, d\mathbf{r} = \int_D \partial_t c \, d\mathbf{r} = \int_D \operatorname{div}(\mathbb{M}\nabla\mu) - \mu \, d\mathbf{r} = \int_{\partial D} \mathbb{M}(\nabla\mu \cdot \mathbf{n}) \, ds - \int_D \mu \, d\mathbf{r} = - \int_D \mu \, d\mathbf{r}. \quad (2.1.23)$$

In the subsection 2.2.2 we provide computational results that clearly validate that the mass is not conserved, in this case and more precisely we observe total loss of mass under curve shortening flow in a short time frame (see Figure 2.11), for a double well potential of the form  $f_L(c) := 100c^2(1-c)^2$  and constant mobility  $\mathbb{M} = m\mathbb{I}$ ,  $m > 0$  or in other words the specific flow fully validates the Gage-Hamilton and Grayson theorem for non-convex curves, i.e., "the non-convex evolving curve after some time becomes convex and circular as it shrinks, before collapses to a point" [134, 135].

**Remark 2.6 (Microscopic Allen-Cahn/Cahn-Hilliard model).** We further introduce the same problem in the porous media setting in the particular case of an isotropic mobility coefficient  $\mathbb{M} := m\mathbb{I}$ , for some constant  $m > 0$ , i.e.,

$$\begin{cases} \partial_t c^\varepsilon = -(1 - \operatorname{div}(\mathbb{M}\nabla))\mu^\varepsilon & \text{in } D_T^\varepsilon, \\ \mu^\varepsilon := f_L'(c^\varepsilon) - \lambda^2 \Delta c^\varepsilon & \text{in } D_T^\varepsilon, \\ \partial_n c^\varepsilon = \partial_n \mu^\varepsilon = \partial_n \Delta c^\varepsilon = 0 & \text{on } \partial D_T^\varepsilon. \end{cases} \quad (2.1.24)$$

It is straightforward to add a chemical potential term to the discretization scheme for the classical Cahn-Hilliard problem (2.1.8), as follows:

$$\begin{cases} \mathbb{G}\mathbf{c}_{n+1}^{\varepsilon,l+1} + m\Delta t \mathbb{S}\boldsymbol{\mu}_{n+\theta}^{\varepsilon,l+1} + \mathbb{G}\boldsymbol{\mu}_{n+\theta}^{\varepsilon,l+1} = \mathbb{G}\mathbf{c}_n^\varepsilon, \\ \mathbb{G}\boldsymbol{\mu}_{n+\theta}^{\varepsilon,l+1} + \mathbb{K}(\mathbf{c}_{n+1}^{\varepsilon,l})\mathbf{c}_{n+1}^{\varepsilon,l+1} - \frac{1}{2}\mathbb{G}\mathbf{c}_{n+1}^{\varepsilon,l+1} - \lambda^2 \mathbb{S}\mathbf{c}_{n+1}^{\varepsilon,l+1} = 0, \end{cases} \quad (2.1.25)$$

where we make use of the same definitions for the related matrices  $\mathbb{G}, \mathbb{S}$  and  $\mathbb{K}$  as in (2.1.8) and subsequently the coefficients vectors  $(\mathbf{c}_{n+1}^{\varepsilon,l+1}, \boldsymbol{\mu}_{n+\theta}^{\varepsilon,l+1})$  with  $\boldsymbol{\mu}^{\varepsilon,l+1} := \{\mu_{j,n}^{\varepsilon,l+1}\}_{j=1}^J$  and  $\mathbf{c}^{\varepsilon,l+1} := \{c_{j,n}^{\varepsilon,l+1}\}_{j=1}^J$ .

Existence of weak solutions for the microscopic model (2.1.24), can be verified in the same way as for the classical homogeneous Cahn-Hilliard formulation in Theorem 1.2.4. The result is summarised in the following Theorem 2.1.1. Furthermore, we subsequently investigate two-scale convergence arguments and derive a homogenized model. We shall motivate the development of the homogenization procedure using similar arguments, as in [12, 136–143, 145–147].

**Lemma 2.1.** *Let  $c^\varepsilon \in W^{1,p}(D^\varepsilon)$ ,  $1 \leq p < d$ . Then  $c^\varepsilon \in L^{p^*}(D^\varepsilon)$ , with  $p^* = dp/(d-p)$  and there exists a constant  $K > 0$  independent of  $\varepsilon$ , such that the following inequality holds:*

$$\|c^\varepsilon\|_{L^{p^*}(D^\varepsilon)} \leq K \|c^\varepsilon\|_{W^{1,p}(D^\varepsilon)}, \quad (2.1.26)$$

which means that  $W^{1,p}(D^\varepsilon) \hookrightarrow L^{p^*}(D^\varepsilon)$ . For the proof of (2.1.26) we refer to [139, Theorem 2.10].

**Lemma 2.2 (Extension).** *Any function  $c^\varepsilon \in W^{1,p}(D^\varepsilon)$ ,  $1 \leq p \leq \infty$  admits an extension  $\tilde{c}^\varepsilon \in W^{1,p}(D)$  defined in all  $D$  and is such that  $\|\tilde{c}^\varepsilon\|_{W^{1,p}(D)} \leq C \|c^\varepsilon\|_{W^{1,p}(D^\varepsilon)}$ , where  $C$  is a constant independent of  $\varepsilon$ . For the proof and more details see [139, 153–156].*

**Assumption 2.1.** *We assume the existence of an initial condition  $c_0 \in H^1(D^\varepsilon)$  with  $|c_0|_{L^2(D^\varepsilon)} \leq 1$  independent of  $\varepsilon$ . Also there exist constants  $C_0, C_1, C_2, C_3, C_4, C_5 > 0$  such that  $|f_L'(c^\varepsilon)| \leq C_0 |c^\varepsilon|^{q-1} + C_1$  and  $C_2 |c^\varepsilon|^q - C_3 \leq f_L(c^\varepsilon) \leq C_4 |c^\varepsilon|^q + C_5$ , for  $q = 2d/(d-2)$ , if  $d \geq 3$  or  $q \in \mathbb{R}^+$  and arbitrary when  $d = 1, 2$  and  $f_L(c^\varepsilon) \geq 0$ .*

**Theorem 2.1.1 (Existence of weak solutions for the microscopic problem (2.1.24)).** *There exists a pair of solutions  $(c^\varepsilon, \mu^\varepsilon)$  of (2.1.24), such that*

$$c^\varepsilon \in L^\infty(0, T; H^1(D^\varepsilon)), \partial_t c^\varepsilon \in L^2(0, T; H^{-1}(D^\varepsilon)) \text{ and } \mu^\varepsilon \in L^2(0, T, H^1(D^\varepsilon)), \quad (2.1.27)$$

which are solutions of the following weak microscopic formulation

$$\begin{cases} \int_0^T \langle \partial_t c^\varepsilon, \varphi \rangle_{H^{-1}(D^\varepsilon) \times H^1(D^\varepsilon)} dt = - \int_{D^\varepsilon} \mathbb{M} \nabla \mu^\varepsilon \cdot \nabla \varphi \, d\mathbf{r} \, dt - \int_{D^\varepsilon} \mu^\varepsilon \varphi \, d\mathbf{r} \, dt, \\ \int_{D^\varepsilon} \mu^\varepsilon \phi \, d\mathbf{r} = \lambda^2 \int_{D^\varepsilon} \nabla c^\varepsilon \cdot \nabla \phi \, d\mathbf{r} + \int_{D^\varepsilon} f'_L(c^\varepsilon) \phi \, d\mathbf{r}, \end{cases} \quad (2.1.28)$$

for all  $\varphi \in L^2(0, T; H^1(D^\varepsilon))$  and  $\phi \in H^1(D^\varepsilon)$  and almost all  $t \in [0, T]$ , with some initial condition  $c_{init}^\varepsilon := c^\varepsilon(0, \mathbf{r}) \in H^1(D^\varepsilon)$ .

*Proof.* Following exactly the same procedure as in the proof of Theorem 1.2.4, we can derive an energy type estimate by taking the time derivative of the free energy functional in the  $D^\varepsilon$  setting, i.e.,

$$\mathcal{F}(c^\varepsilon(\mathbf{r}, t)) := \int_{D^\varepsilon} f_L(c^\varepsilon) + \frac{\lambda^2}{2} |\nabla c^\varepsilon|^2 \, d\mathbf{r}, \quad (2.1.29)$$

which implies

$$\int_{D^\varepsilon} f_L(c^\varepsilon) \partial_t c^\varepsilon + \lambda^2 \nabla c^\varepsilon \cdot \nabla \partial_t c^\varepsilon \, d\mathbf{r} = - \int_{D^\varepsilon} \mathbb{M}(c^\varepsilon) |\nabla \mu^\varepsilon|^2 \, d\mathbf{r}. \quad (2.1.30)$$

A further integration over the time interval  $(0, T)$ , yields

$$\begin{aligned} & \frac{\lambda^2}{2} \int_{D^\varepsilon} |\nabla c^\varepsilon(\mathbf{r}, T)|^2 \, d\mathbf{r} + \int_{D^\varepsilon} |\mu^\varepsilon|^2 \, d\mathbf{r} \, dt + \int_{D^\varepsilon} \mathbb{M} |\nabla \mu^\varepsilon|^2 \, d\mathbf{r} \, dt + \int_{D^\varepsilon} f_L(c^\varepsilon(\mathbf{r}, T)) \, d\mathbf{r} \\ & = \int_{D^\varepsilon} f_L(c^\varepsilon(\mathbf{r}, 0)) \, d\mathbf{r} + \frac{\lambda^2}{2} \int_{D^\varepsilon} |\nabla c^\varepsilon(\mathbf{r}, 0)|^2 \, d\mathbf{r}. \end{aligned} \quad (2.1.31)$$

The assumption for the initial condition together with the boundedness of the homogeneous free energy density  $f_L(c^\varepsilon)$  stated in Assumption 2.1, imply the subsequent inequality:

$$\begin{aligned} & \frac{\lambda^2}{2} \int_{D^\varepsilon} |\nabla c^\varepsilon(\mathbf{r}, T)|^2 \, d\mathbf{r} + \int_{D^\varepsilon} |\mu^\varepsilon|^2 \, d\mathbf{r} \, dt + \int_{D^\varepsilon} \mathbb{M} |\nabla \mu^\varepsilon|^2 \, d\mathbf{r} \, dt + \int_{D^\varepsilon} f_L(c^\varepsilon(\mathbf{r}, T)) \, d\mathbf{r} \\ & \leq \lambda^2 \|\nabla c_{init}^\varepsilon\|_{L^2(D^\varepsilon)}^2 + C_4 C_6 \|c_{init}^\varepsilon\|_{H^1(D^\varepsilon)}^q + C_5 |D^\varepsilon|, \text{ due to Lemma 2.1 for } p=2 \\ & \leq C + C_5 |D|, \end{aligned} \quad (2.1.32)$$

for some strictly positive constant  $C$ , since  $c_{init}^\varepsilon \in H^1(D^\varepsilon)$  by assumption. In addition, the non-negativity of  $f_L$  applied to the inequality (2.1.32) implies further

$$\frac{\lambda^2}{2} \|\nabla c^\varepsilon\|_{L^\infty(0, T; L^2(D^\varepsilon))} + \|\nabla \mu^\varepsilon\|_{L^2(D^\varepsilon)} + \|\mu^\varepsilon\|_{L^2(D^\varepsilon)} \leq C'. \quad (2.1.33)$$

**Remark 2.7 (Extension of the solutions).** *The assumptions on the microscopic structure of  $D^\varepsilon$  ensure that there exists an extension  $(\tilde{c}^\varepsilon, \tilde{\mu}^\varepsilon)$  of the microscopic solution  $(c^\varepsilon, \mu^\varepsilon)$  to the macroscopic domain  $D$ , which is such that*

$$\|\tilde{c}^\varepsilon\|_{L^2(D)} \leq C_1 \|c^\varepsilon\|_{L^2(D^\varepsilon)}, \quad \|\nabla \tilde{c}^\varepsilon\|_{L^2(D)} \leq C_1 \|\nabla c^\varepsilon\|_{L^2(D^\varepsilon)} \quad (2.1.34)$$

and also

$$\|\tilde{\mu}^\varepsilon\|_{L^2(D)} \leq C_2 \|\mu^\varepsilon\|_{L^2(D^\varepsilon)}, \quad \|\nabla \tilde{\mu}^\varepsilon\|_{L^2(D)} \leq C_2 \|\nabla \mu^\varepsilon\|_{L^2(D^\varepsilon)}, \quad (2.1.35)$$

for  $\varepsilon$ -independent constants  $C_1, C_2 > 0$ .

In view of Remark 2.7 we can deduce the corresponding of (2.1.33) estimate for the extensions, i.e.,

$$\frac{\lambda^2}{2} \|\nabla \tilde{c}^\varepsilon\|_{L^\infty(0,T;L^2(D))} + \|\nabla \tilde{\mu}^\varepsilon\|_{L^2(D_T)} + \|\tilde{\mu}^\varepsilon\|_{L^2(D_T)} \leq C'_\varepsilon. \quad (2.1.36)$$

Moreover, one can find an upper bound for the mean of  $c^\varepsilon(\mathbf{r}, t)$  over  $D^\varepsilon$  using Hölder's inequality, namely

$$\left| \int_{D^\varepsilon} c^\varepsilon(\mathbf{r}, t) d\mathbf{r} \right| \leq \left| \int_{D^\varepsilon} c^\varepsilon(\mathbf{r}, 0) d\mathbf{r} \right| \leq \|c_{init}^\varepsilon(\mathbf{r})\|_{L^2(D^\varepsilon)} |D^\varepsilon|^{1/2} \leq C' |D|^{1/2}, \text{ since } c_{init}^\varepsilon \in H^1(D^\varepsilon). \quad (2.1.37)$$

In light of Remark 2.7 and the estimate 2.1.36 we can apply the Poincaré-Wirtinger inequality [101, p 218] to the norm of the corresponding extension  $\|\nabla \tilde{c}^\varepsilon\|_{L^2(D)}$  due to the fact that the constant in the Poincaré type inequalities depends on the geometry of the domain of integration and hence we can not apply those directly to the microscopic solutions. Hence, we can deduce from 2.1.34 and the Poincaré-Wirtinger inequality that

$$\|c^\varepsilon - \int_D \tilde{c}^\varepsilon d\mathbf{r}\|_{L^2(D)} \leq C_P \|\nabla \tilde{c}^\varepsilon\|_{L^2(D)} \leq C_1 C_P \|\nabla c^\varepsilon\|_{L^2(D^\varepsilon)}. \quad (2.1.38)$$

Then we have

$$\|c^\varepsilon - \int_D \tilde{c}^\varepsilon d\mathbf{r}\|_{L^2(D^\varepsilon)} \leq \|c^\varepsilon - \int_D \tilde{c}^\varepsilon d\mathbf{r}\|_{L^2(D)} \leq C_1 C_P \|\nabla c^\varepsilon\|_{L^2(D^\varepsilon)} \quad (2.1.39)$$

and by taking the mean value of  $c^\varepsilon - \int_D \tilde{c}^\varepsilon d\mathbf{r}$  over  $D^\varepsilon$ , we obtain

$$\left| \int_{D^\varepsilon} c^\varepsilon - \int_D \tilde{c}^\varepsilon d\mathbf{r} \right| \leq C_1 C_P \|\nabla c^\varepsilon\|_{L^2(D^\varepsilon)}. \quad (2.1.40)$$

This implies that the Poincaré-Wirtinger inequality holds in the perforated domain  $D^\varepsilon$  (see [157, Prop. 5.24] and also [158]), i.e.,

$$\|c^\varepsilon - \int_{D^\varepsilon} c^\varepsilon d\mathbf{r}\|_{L^2(D^\varepsilon)} \leq C'_P \|\nabla c^\varepsilon\|_{L^2(D^\varepsilon)}, \quad (2.1.41)$$

where  $C'_P > 0$  is actually a constant independent of  $\varepsilon$ .

$$\begin{aligned} \text{ess sup}_{0 < t < T} \|c^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)}^2 &\leq C_P \text{ess sup}_{0 < t < T} \|\nabla c^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)}^2 + C'_P \text{ess sup}_{0 < t < T} \left( \int_{D^\varepsilon} c^\varepsilon(\mathbf{r}, t) d\mathbf{r} \right)^2 \\ &\leq C_P C + C'_P C_1 \|c^\varepsilon(\mathbf{r}, 0)\|_{L^2(D^\varepsilon)} |D^\varepsilon|^{1/2} \\ &\leq C'_{D,P}. \end{aligned} \quad (2.1.42)$$

This subsequently provides the estimate

$$\|c^\varepsilon(\mathbf{r}, t)\|_{L^\infty(0,T;H^1(D^\varepsilon))} := \text{ess sup}_{0 < t < T} \|c^\varepsilon(\mathbf{r}, t)\|_{H^1(D^\varepsilon)} \leq C''_{D,P}. \quad (2.1.43)$$

In addition, it is easy to deduce an upper bound as a consequence of Hölder's inequality, as follows:

$$\begin{aligned} \left| \langle \partial_t c^\varepsilon, \phi \rangle_{H^{-1}(D^\varepsilon) \times H^1(D^\varepsilon)} \right| &\leq \mathbb{M} \|\nabla \mu^\varepsilon\|_{L^2(D^\varepsilon)} \|\nabla \phi\|_{L^2(D^\varepsilon)} + \|\mu^\varepsilon\|_{L^2(D^\varepsilon)} \|\phi\|_{L^2(D^\varepsilon)}, \text{ for all } \phi \in L^2(0, T; H^1(D^\varepsilon)) \\ &\leq \left( \mathbb{M} \|\nabla \mu^\varepsilon\|_{L^2(D^\varepsilon)} + \|\mu^\varepsilon\|_{L^2(D^\varepsilon)} \right) \|\phi\|_{H^1(D^\varepsilon)} \\ &\leq C' \|\phi\|_{H^1(D^\varepsilon)}, \text{ by (2.1.33)}. \end{aligned} \quad (2.1.44)$$

This implies the bound  $\|\partial_t c^\varepsilon\|_{L^2(0,T;H^{-1}(D))} \leq C'$ . Finally from the relationship

$$\int_{D^\varepsilon} \mu^\varepsilon \phi \, d\mathbf{r} = \lambda^2 \int_{D^\varepsilon} \nabla c^\varepsilon \cdot \nabla \phi \, d\mathbf{r} + \int_{D^\varepsilon} f'_L(c^\varepsilon) \phi \, d\mathbf{r}, \quad (2.1.45)$$

for  $\phi = 1$  we obtain:  $\int_{D^\varepsilon} \mu^\varepsilon \, d\mathbf{r} = \int_{D^\varepsilon} f'_L(c^\varepsilon) \, d\mathbf{r}$ , which provides the following bound:

$$\begin{aligned} \left| \int_{D^\varepsilon} \mu^\varepsilon(\mathbf{r}, t) \, d\mathbf{r} \right| &= \left| \int_{D^\varepsilon} f'_L(c^\varepsilon(\mathbf{r}, t)) \, d\mathbf{r} \right| \leq \int_{D^\varepsilon} |f'_L(c^\varepsilon(\mathbf{r}, t))| \, d\mathbf{r} \\ &\leq |D^\varepsilon|^{1/2} \|f'_L(c^\varepsilon(\mathbf{r}, t))\|_{L^2(D^\varepsilon)} \\ &\leq |D|^{1/2} \left( \int_{D^\varepsilon} (C_0 |c^\varepsilon|^q + C_1)^2 \, d\mathbf{r} \right)^{1/2} \\ &\leq |D|^{1/2} C_0 \|c^\varepsilon\|_{L^{2q}(D^\varepsilon)} + C_1 |D^\varepsilon| \\ &\leq |D|^{1/2} C_0 \|c^\varepsilon\|_{H^1(D^\varepsilon)} + C_1 |D| \\ &\leq C''_{D,P}, \end{aligned} \quad (2.1.46)$$

by Sobolev embedding in the version of Lemma 2.1 and the estimate 2.1.43. Finally, following the proof of Theorem 1.2.4, we based on the assumption for the mobility (1.1) and by the Poincaré-Wirtinger inequality in  $D^\varepsilon$  with constants  $C_P, C'_P$  [157, Prop. 5.24], we obtain using the average  $\{\mu^\varepsilon(\mathbf{r}, t)\}_{av} := |D^\varepsilon|^{-1} \int_{D^\varepsilon} \mu^\varepsilon(\mathbf{r}, t) \, d\mathbf{r}$  that

$$\begin{aligned} C_{Pm} \int_{D^\varepsilon} |\nabla \mu^\varepsilon(\mathbf{r}, t)|^2 \, d\mathbf{r} &\geq m \|\mu^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)}^2 - m C'_P \left( \{\mu^\varepsilon(\mathbf{r}, t)\}_{av} \right)^2 \\ &\geq m \|\mu^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)}^2 - m C'_P C'_D, \end{aligned} \quad (2.1.47)$$

where  $C'_D := (|D|^{-1/2} C_0 C + C_1)^2$  which comes from the estimate (2.1.46). Hence, by integrating (2.1.47) over time, it follows that

$$m \int_0^T \|\mu^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)}^2 \, dt \leq m C'_P C'_D T + C_{Pm} \int_0^T \|\nabla \mu^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)}^2 \, dt \leq C_P C + m C'_P C'_D T \quad (2.1.48)$$

and therefore we can deduce the bound

$$\|\mu^\varepsilon\|_{L^2(0,T;H^1(D^\varepsilon))} \leq C'_{P,m,D,T}, \quad (2.1.49)$$

where  $C'_{P,m,D,T} > 0$  is a constant independent of  $\varepsilon$  which depends on the constants  $C_P, C'_D$  the constant  $C$  from (2.1.32), the lower bound  $m$  of the mobility and the maximum time of observation  $T > 0$ . Hence, it turns out that  $\{\mu^\varepsilon\}$  is a bounded sequence in  $L^2(0, T; H^1(D^\varepsilon))$ .  $\square$

In the sequel (see subsection 2.1.3 and subsection 2.1.2), we examine the homogenization procedure for the microscopic Allen-Cahn/Cahn-Hilliard equation (2.1.24) by applying to different upscaling techniques. The first one follows the homogenization procedure applied by M. Schmuck et al for the classical microscopic Cahn-Hilliard formulation (2.1.6) in [13, 128] and is based on the idea of applying a formal two-scale asymptotic expansion, by introducing a microscale variable  $\mathbf{r}/\varepsilon := \mathbf{y} \in Y$  and considering  $\mathbf{r} \in D$  and  $\mathbf{y} \in Y$  as two separated variables. The homogenization result of this upscaling method is summarised in Theorem 2.1.4. It is worth mentioning that following the different technique, i.e., by a rigorous two-scale convergence approach, we end up with the same upscaled equation for which the result is summarised in Theorem 2.1.5. We subsequently state some useful Lemmas and Definitions which are necessary for the

homogenization procedure. In the context of the two-scale asymptotic expansions there exist two convergence statements, related to the upscaling of this type of systems (see [17, 148–150] for more details).

**Definition 2.3 (Two-scale convergence).** *A sequence of functions  $\{c^\varepsilon\}_{\varepsilon>0}$  in  $L^2(D_T)$  is said to two-scale converge to a limit  $c_0 \in L^2(D_T \times Y)$  if, for any function  $\varphi \in L^2(D_T, C_{per}^\infty(Y))$ , we have*

$$\lim_{\varepsilon \rightarrow 0} \int_{D_T} c^\varepsilon(\mathbf{r}, t) \varphi(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \, d\mathbf{r} \, dt = \frac{1}{|Y|} \int_{D_T \times Y} c_0(\mathbf{r}, \mathbf{y}, t) \varphi(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{r} \, d\mathbf{y} \, dt, \quad (2.1.50)$$

in which  $C_{per}^\infty(Y)$  stands for the space of  $Y$ -periodic in  $\mathbf{y}$ ,  $C^\infty$ -functions. For the proof of this statement and more details, see [17, Definition 1.1.] and also [151].

**Lemma 2.3** ([152]). *For every bounded sequence  $\{c^\varepsilon\}_{\varepsilon>0}$  in  $L^2(D_T)$  there exists a subsequence (still can be denoted by  $\{c^\varepsilon\}_{\varepsilon>0}$ ) and a function  $c \in L^2(D_T \times Y)$ , such that this subsequence two-scale converges to  $c$ .*

**Lemma 2.4** ([152]). *Let  $\{c^\varepsilon\}_{\varepsilon>0}$  be strongly convergent to  $c \in L^2(D_T)$ , then  $\{c^\varepsilon\}_{\varepsilon>0}$  converges to  $c_1(\mathbf{r}, \mathbf{y}, t) = c(\mathbf{r}, t)$ , in the two-scale sense.*

**Theorem 2.1.2 (Strong convergence).** *Let  $c^\varepsilon$  be a sequence of functions in  $L^2(D_T)$ , which two-scale to a limit  $c_0(\mathbf{r}, \mathbf{y}, t) \in L^2(D_T \times Y)$ , then the following arguments hold:  $c^\varepsilon$  converges weakly in  $L^2(D_T)$  to  $c(\mathbf{r}, t) = \frac{1}{|Y|} \int_Y c_0(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{y}$  and*

$$\lim_{\varepsilon \rightarrow 0} \|c^\varepsilon\|_{L^2(D_T)}^2 \geq |Y|^{-1} \|c_0\|_{L^2(D_T \times Y)}^2 \geq \|c\|_{L^2(D_T)}^2. \quad (2.1.51)$$

Assuming further that  $c_0(\mathbf{r}, \mathbf{y}, t)$  is smooth enough and  $\lim_{\varepsilon \rightarrow 0} \|c^\varepsilon\|_{L^2(D_T)}^2 = |Y|^{-1} \|c_0\|_{L^2(D_T \times Y)}^2$ , then we deduce the following strong convergence result:

$$\lim_{\varepsilon \rightarrow 0} \|c^\varepsilon(\mathbf{r}, t) - c_0(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t)\|_{L^2(D_T)}^2 = 0. \quad (2.1.52)$$

For the proof and more details see also [17, Theorem 0.2.] and [12].

**Lemma 2.5.** ([17, 152]) *In addition, for a bounded sequence  $\{c^\varepsilon\}_{\varepsilon>0}$  in  $L^2(0, T; H^1(D))$ , there exists functions  $c_0 \in L^2(0, T; H^1(D))$  and  $c_1 \in L^2(D_T; H_{per}^1(Y))$  (where the function space  $H_{per}^1$  is defined in (2.1.9)), such that (up to a subsequence) the following convergence argument, holds:*

$$\left\{ \begin{array}{l} c^\varepsilon \rightharpoonup c_0 \text{ weakly in } L^2(0, T; H^1(D)), \\ \lim_{\varepsilon \rightarrow 0} \int_{D_T} \nabla_{\mathbf{r}} c^\varepsilon(\mathbf{r}, t) \cdot \boldsymbol{\varphi}(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \, d\mathbf{r} \, dt = \frac{1}{|Y|} \int_{D_T \times Y} (\nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t)) \cdot \boldsymbol{\varphi}(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{r} \, d\mathbf{y} \, dt, \end{array} \right. \quad (2.1.53)$$

for all vector-valued test functions  $\boldsymbol{\varphi}$  in  $L^2(D_T, C_{per}^\infty(Y))_d := \{L^2(D_T, C_{per}^\infty(Y)) \times L^2(D_T, C_{per}^\infty(Y)) \times \dots\}$ .

**Definition 2.4 (Unfolding operator).** *Let us consider the extension  $\tilde{c}^\varepsilon$  defined in a homogeneous domain  $D_T$  of a function  $c^\varepsilon$  defined over the perforated domain  $D_T^\varepsilon$  (see Remark 2.7). An unfolding operator is linear and continuous mapping, defined by  $\mathcal{T}_\varepsilon : L^p(0, T; L^q(D)) \rightarrow L^p(0, T; L^q(D \times Y))$ ,  $p \in [1, +\infty]$ ,  $q \in [1, +\infty)$  and transforms the function  $\tilde{c}^\varepsilon$  on  $D_T$  into a function  $\mathcal{T}_\varepsilon \tilde{c}^\varepsilon$  on  $D_T \times Y$ , in the sense that The action of  $\mathcal{T}_\varepsilon$ , can be formally defined as:*

$$\mathcal{T}_\varepsilon \tilde{c}^\varepsilon(\mathbf{r}, \mathbf{y}, t) := \tilde{c}^\varepsilon \left( \varepsilon \left[ \frac{\mathbf{r}}{\varepsilon} \right]_Y + \varepsilon \mathbf{y}, t \right), \text{ for all } \mathbf{r} \in D, \mathbf{y} \in Y, \quad (2.1.54)$$



where  $[\cdot]_Y$  denotes the unique integer  $k_i \in \mathbb{Z}^d$  combination  $\sum_{i=1}^d k_i e_i$  of the periods (where  $e_i$  is the  $i$ -th canonical basis vector of  $\mathbb{R}^d$ ), such that  $\left\{ \frac{\mathbf{r}}{\varepsilon} \right\}_Y := \frac{\mathbf{r}}{\varepsilon} - \left[ \frac{\mathbf{r}}{\varepsilon} \right]_Y$ , belongs to  $Y$ . Analogously for the function  $c^\varepsilon \in L^p(0, T; L^q(D^\varepsilon))$ , we can define the related unfolding operator  $\mathcal{T}_\varepsilon^{Y_1}$  by

$$\mathcal{T}_\varepsilon^{Y_1} c^\varepsilon(\mathbf{r}, \mathbf{y}, t) := c^\varepsilon \left( \varepsilon \left[ \frac{\mathbf{r}}{\varepsilon} \right]_Y + \varepsilon \mathbf{y}, t \right), \text{ for all } \mathbf{r} \in D, \mathbf{y} \in Y_1. \quad (2.1.55)$$

For more details on this definition we refer to [158–161].

**Remark 2.8.** We also note that the unfolding operator preserves the integral up to a multiplicative constant  $|Y|$ , i.e.,

$$\int_{D_T \times Y} \mathcal{T}_\varepsilon \tilde{c}^\varepsilon(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{r} \, d\mathbf{y} \, dt = |Y| \int_{D_T} \tilde{c}^\varepsilon(\mathbf{r}, t) \, d\mathbf{r} \, dt, \quad (2.1.56)$$

for all  $\tilde{c}^\varepsilon \in L^1(D_T)$  or equivalently

$$\|\mathcal{T}_\varepsilon \tilde{c}^\varepsilon\|_{L^p(D_T \times Y)} = |Y|^{1/p} \|\tilde{c}^\varepsilon\|_{L^p(D_T)}, \quad (2.1.57)$$

for all  $\tilde{c}^\varepsilon \in L^p(D_T)$ . For more properties and the related proof of the integral preserving property (2.1.56) we refer to [12, 158–160, 162–164].

**Lemma 2.6.** Let  $p, q \in [1, \infty)$ ,  $\{w^\varepsilon\}_{\varepsilon>0}$  a sequence in  $L^q(0, T; L^p(D))$  and  $w_0$  a function in  $L^q(0, T; L^p(D))$ . Then the following convergence results hold:

$$\begin{aligned} \mathcal{T}_\varepsilon(w_0) &\rightarrow w_0, \text{ strongly in } L^q(0, T; L^p(D \times Y)), \\ \text{if } w^\varepsilon &\rightarrow w_0 \text{ strongly in } L^q(0, T; L^p(D)), \text{ then } \mathcal{T}_\varepsilon(w^\varepsilon) \rightarrow w_0, \text{ strongly in } L^q(0, T; L^p(D \times Y)). \end{aligned} \quad (2.1.58)$$

For the proof and more details on convergence using unfolding operators, we refer to [159, 164–166] and also [158, Lemma 5.1, 6.1].

**Lemma 2.7.** Let  $p \in (1, \infty)$  and  $\{w^\varepsilon\}_{\varepsilon>0}$  a sequence in  $L^\infty(0, T; W_0^{1,p}(D))$ . such that

$$\|\nabla w^\varepsilon\|_{L^\infty(0, T; L^p(D))} \leq C. \quad (2.1.59)$$

Then there exist  $w_0 \in L^\infty(0, T; W_0^{1,p}(D))$  and  $w_1 \in L^\infty(0, T; L^p(D, W_{per}^{1,p}(Y)))$  such that up to a subsequence,

$$\begin{aligned} \mathcal{T}_\varepsilon(w^\varepsilon) &\rightarrow w_0, \text{ weakly* in } L^\infty(0, T; L^p(D, W^{1,p}(Y))), \\ \mathcal{T}_\varepsilon(\nabla_{\mathbf{r}} w^\varepsilon) &\rightarrow \nabla_{\mathbf{r}} w_0 + \nabla_{\mathbf{y}} w_1, \text{ weakly* in } L^\infty(0, T; L^p(D \times Y)). \end{aligned} \quad (2.1.60)$$

For the proof and more details, we refer to [159, 164–166] and also [158, Lemma 5.1, 6.1].

**Theorem 2.1.3 (Strong integral equicontinuity-Riesz-Fréchet-Kolmogorov).** Let  $\mathcal{Z}(D)$  is a separable Banach space of finite dimension and  $\mathcal{U}$  a bounded family of functions in  $L^p(0, T; \mathcal{Z}(D))$ ,  $1 \leq p < \infty$ , then  $\mathcal{U}$  is totally bounded in  $L^p(0, T; \mathcal{Z}(D))$  if and only if,

$$\lim_{\tau \rightarrow 0^+} \int_0^{T-\tau} \|\partial_\tau c(\mathbf{r}, t) - c(\mathbf{r}, t)\|_{\mathcal{Z}(D)}^p \, dt = 0, \text{ uniformly for } c \in \mathcal{U}, \quad (2.1.61)$$

where  $\partial_\tau c(\mathbf{r}, t) := c(\mathbf{r}, t + \tau)$ . Therefore, there exists a non-decreasing and concave modulus of continuity  $q: [0, +\infty) \rightarrow [0, +\infty)$  with  $\lim_{\tau \rightarrow 0^+} q(\tau) = 0$  such that

$$\left( \int_0^{T-\tau} \|\partial_\tau c(\mathbf{r}, t) - c(\mathbf{r}, t)\|_{\mathcal{Z}(D)}^p \, dt \right)^{1/p} \leq q(\tau), \quad \forall \tau \in (0, T), c \in \mathcal{U}. \quad (2.1.62)$$

For the proof and more details see [167, Theorem IV.26] or [168, Theorem 1] and also [169, 170].

**Lemma 2.8 (By-parts integration formula).** *Let  $(\mathcal{Z}(D), \mathcal{H}(D), \mathcal{Z}^{-1}(D))$  with  $\mathcal{Z}(D) \subset \mathcal{H}(D) \cong \mathcal{H}^{-1}(D) \subset \mathcal{Z}^{-1}(D)$  form a Gelfand triple (or evolution triple), where  $\mathcal{Z}(D), \mathcal{Z}^{-1}(D)$  are Banach spaces and  $\mathcal{H}(D)$  a Hilbert space and*

$$W^{1,p,q}(0,T; \mathcal{Z}(D), \mathcal{Z}^{-1}(D)) = \left\{ c \in L^p(0,T; \mathcal{Z}(D)), \partial_t c \in L^q(0,T; \mathcal{Z}^{-1}(D)), q = p/(p-1) \right\} \subset C([0,T]; \mathcal{H}(D)), \quad (2.1.63)$$

with  $\partial_t c$  denoting the distributional derivative of  $c$  understood as an abstract linear operator with its action to be formally defined by  $\partial_t c(\phi) := - \int_0^T c \partial_t \phi \, dt$ , for all  $\phi \in C_0^\infty(0,T)$ . Then for all  $c, \phi \in W^{1,p,q}$  and  $0 \leq t_1, t_2 \leq T$ , the following integration formula holds:

$$\int_{t_1}^{t_2} \frac{d}{dt} \langle c, \phi \rangle_{\mathcal{H}(D)} = \int_{t_1}^{t_2} \langle \partial_t c, \phi \rangle_{\mathcal{Z}^{-1}(D) \times \mathcal{Z}(D)} \, dt + \int_{t_1}^{t_2} \langle c, \partial_t \phi \rangle_{\mathcal{Z}(D) \times \mathcal{Z}^{-1}(D)} \, dt, \quad (2.1.64)$$

where  $\int_{t_1}^{t_2} \frac{d}{dt} \langle c, \phi \rangle_{\mathcal{H}(D)} := \langle c(\mathbf{r}, t_2), \phi(\mathbf{r}, t_2) \rangle_{\mathcal{H}(D)} - \langle c(\mathbf{r}, t_1), \phi(\mathbf{r}, t_1) \rangle_{\mathcal{H}(D)}$ . For the proof and more details, see [113, Lemma 7.3] and also [114, Lemma 2.1].

**Remark 2.9.** Note that the space  $W^{1,p,q}(0,T; \mathcal{Z}(D), \mathcal{Z}^{-1}(D))$ , where  $\mathcal{Z}(D), \mathcal{Z}^{-1}(D)$  are Banach spaces, is also a Banach space itself and is called Sobolev-Bochner space [113, 115] and is equipped with the norm

$$\|c\|_{W^{1,p,q}(0,T; \mathcal{Z}(D), \mathcal{Z}^{-1}(D))} := \|c\|_{L^p(0,T; \mathcal{Z}(D))} + \|\partial_t c\|_{L^q(0,T; \mathcal{Z}^{-1}(D))}, \quad q = p/(p-1). \quad (2.1.65)$$

**Remark 2.10.** The formula (2.1.64) for  $c = \phi$  implies

$$\frac{1}{2} \|c(\mathbf{r}, t_2)\|_{\mathcal{H}(D)}^2 - \frac{1}{2} \|c(\mathbf{r}, t_1)\|_{\mathcal{H}(D)}^2 = \int_{t_1}^{t_2} \langle \partial_t c, c \rangle_{\mathcal{Z}^{-1}(D) \times \mathcal{Z}(D)} \, dt \quad (2.1.66)$$

and hence the function  $t \mapsto \frac{1}{2} \|c(\mathbf{r}, t)\|_{\mathcal{H}(D)}^2$  is absolutely continuous with respect to  $t$ , see also [113].

### 2.1.2 Homogenization with the help of a two-scale asymptotic expansion.

The following homogenization procedure is a heuristic method and is based on a formal two-scale asymptotic expansion, as explained in many textbooks such as for example [12, 149] and subsequently has been recently applied to the classical microscopic Cahn-Hilliard formulation (2.1.6) in [13, 128, 129]. The homogenization result makes use of the recently proposed splitting strategy for the homogenization of fourth order problems (see [128]) and will be explained in the sequel (see Definition 2.5). To this end, we also consider the following ansatz, which accounts for the multiscale characteristics of the problem:

$$c^\varepsilon(\mathbf{r}, t) = \sum_{i=0}^{\infty} \varepsilon^i c_i(\mathbf{r}, \mathbf{y}, t), \quad (2.1.67)$$

where  $c_i$  are  $\mathbf{y}$ -periodic and  $c_0$  is  $\mathcal{O}(\varepsilon^0)$ . The assumption of the existence of the extra spatial microscale  $\mathbf{y} := \mathbf{r}/\varepsilon$  provides also the two-scale property for spatial differentiation, namely

$$\nabla \rightarrow \nabla_{\mathbf{r}} + \varepsilon^{-1} \nabla_{\mathbf{y}}. \quad (2.1.68)$$

**Remark 2.11.** *The assumption for the existence of two independent variables namely, the "slow" macroscopic variable  $\mathbf{r}$  and the "fast" microscopic variable  $\mathbf{y}$ , provides the following expressions for the Laplace operator  $\Delta$ :*

$$\Delta \rightarrow \varepsilon^{-2} \mathcal{B}_0 + \varepsilon^{-1} \mathcal{B}_1 + \mathcal{B}_2, \quad (2.1.69)$$

with the identifications

$$\begin{cases} \mathcal{B}_0 := \sum_{i,j=1}^d \partial_{y_i} (\delta_{ij} \partial_{y_j}), \mathcal{B}_2 := \sum_{i,j=1}^d \partial_{r_i} (\delta_{ij} \partial_{r_j}), \\ \mathcal{B}_1 := \sum_{i,j=1}^d \partial_{r_i} (\delta_{ij} \partial_{y_j}) + \partial_{y_i} (\delta_{ij} \partial_{r_j}). \end{cases} \quad (2.1.70)$$

Similarly for the operator  $\operatorname{div}(m\mathbb{I}\nabla)$ , we obtain

$$\operatorname{div}(m\mathbb{I}\nabla) \rightarrow m(\varepsilon^{-2} \mathcal{B}_0 + \varepsilon^{-1} \mathcal{B}_1 + \mathcal{B}_2), \quad (2.1.71)$$

where coefficients in all the operators defined above, are periodic functions of  $\mathbf{y}$ .

**Remark 2.12.** (*Fredholm Alternative* ([171], [172, p 7])).

For  $\mathbf{y}$ -periodic tensors  $\mathbb{C}_{(i+1)}, \mathbb{C}_i$  and source term  $K_s$ , the local balance equation at some order of  $\varepsilon$ ,

$$\nabla_{\mathbf{y}} \cdot \mathbb{C}_{(i+1)} + \nabla_{\mathbf{r}} \cdot \mathbb{C}_i = K_s, \quad (2.1.72)$$

admits a unique homogenized solution if and only if

$$\int_Y \nabla_{\mathbf{r}} \cdot \mathbb{C}_i \, d\mathbf{y} = \int_Y K_s \, d\mathbf{y}. \quad (2.1.73)$$

Therefore the main issue is to correctly identify each time this source term  $K_s$  and the related tensor  $\mathbb{C}_i$ , in the particular  $\varepsilon^i$  order balance equation, as it appears. In addition, we can approximate the derivative of the homogeneous free energy density  $f'_L(c^\varepsilon)$  by the Taylor expansion over  $c_0$  (the leading order term in the expansion (2.1.67)), as follows:

$$f'_L(c^\varepsilon) \approx f'_L(c_0) + f''_L(c_0)(c^\varepsilon - c_0) + 1/2 f'''_L(c_0)(c^\varepsilon - c_0)^2 + \dots \quad (2.1.74)$$

**Definition 2.5 (Splitting microscopic formulation).** *We introduce an equivalent formulation to the (2.1.24) setting, by identifying  $c^\varepsilon = (-\Delta)^{-1} w^\varepsilon$  in the  $H^2_{(0)}$ -sense, i.e. for all  $\phi \in H^2_{(0)}(D)$  it subsequently holds that  $\langle -\Delta c, \phi \rangle_{L^2(D)} = \langle -\Delta(-\Delta)^{-1} w, \phi \rangle_{L^2(D)} = \langle w, \phi \rangle_{L^2(D)}$ . This identification implies the following reformulation of (2.1.24),*

$$\begin{cases} \partial_r (-\Delta)^{-1} w^\varepsilon = -(1 - \operatorname{div}(m\mathbb{I}\nabla)) (f'_L(c^\varepsilon) + \lambda^2 w^\varepsilon) & \text{in } D_T^\varepsilon, \\ \text{with } w^\varepsilon := \Delta c^\varepsilon & \text{in } D_T^\varepsilon, \\ \partial_n w^\varepsilon = -\partial_n \Delta c^\varepsilon = \partial_n c^\varepsilon = 0 & \text{on } \partial D_T^\varepsilon. \end{cases} \quad (2.1.75)$$

This splitting strategy for homogenization [128], guarantees the existence of weak solutions of the Cahn-Hilliard type equation under the arguments of J. Cahn, A. Novick-Cohen,

C. M. Elliott et al [7, 8, 97] discussed in the subsection 1.2.5 as well as subsection 2.1.1 and the gradient flow derivation of the Cahn-Hilliard equation with the help of the associate functions and the related  $H^{-1}$ -semi-inner product (see the details in theorem 1.2.2).

**Theorem 2.1.4 (Effective Allen-Cahn/Cahn-Hilliard equations).** *We assume that the assumption for local thermodynamic equilibrium (2.1) holds and that the macroscopic chemical potential  $\mu_0(c_0) := f'_L(c_0) - p^{-1}\lambda^2 \operatorname{div}(\mathbb{D}\nabla c_0)$  satisfies the scale separation property with initial condition  $c_{init,0}(\mathbf{r}) := c_0(\mathbf{r}, 0) \in H^1(D)$ . Under these considerations the microscopic formulation (2.1.75) after averaging over the microscale and applying a two-scale asymptotic expansion, admit the following effective macroscopic form:*

$$p\partial_t c_0 = m \operatorname{div}(\mathbb{D}\nabla f'_L(c_0)) - \lambda^2 p^{-1} m \operatorname{div}(\mathbb{D}\nabla [\operatorname{div}(\mathbb{D}\nabla c_0)]) - p f'_L(c_0) + \lambda^2 \operatorname{div}(\mathbb{D}\nabla c_0) \text{ in } D_T, \quad (2.1.76)$$

with homogeneous Neumann  $\mathbb{D}\nabla_n c_0 = 0$  and no-flux  $\mathbb{D}\nabla_n \operatorname{div}(\mathbb{D}\nabla c_0) = 0$  boundary conditions on  $\partial D_T$ . The elements of the effective tensor  $\mathbb{D} := \{\mathbb{D}_{ij}\}_{1 \leq i, j \leq d}$  are defined by

$$\mathbb{D}_{ij} := \frac{1}{|Y|} \int_{Y_1} \left( \delta_{ij} - \frac{\partial \xi^j(\mathbf{y})}{\partial y_i} \right) d\mathbf{y} \text{ for all } i, j = 1, \dots, d. \quad (2.1.77)$$

where the correctors  $\xi^j(\mathbf{y}) \in H^1_{per}(Y_1)$  for  $1 \leq j \leq d$  are unique, in the sense of distributions, solutions of the following reference cell problems:

$$\begin{cases} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi^k) = 0. \end{cases} \quad (2.1.78)$$

*Proof.* We will apply the two-scale asymptotic expansion

$$z^\varepsilon(\mathbf{r}, t) = \sum_{i=0}^{\infty} \varepsilon^i z_i(\mathbf{r}, \mathbf{y}, t), \quad z = \{c, w\}, \quad (2.1.79)$$

to the splitting formulation (2.1.75) and with the help of (2.1.74) and the operators  $\mathcal{B}_i$  we obtain:

$$\begin{aligned} & \partial_t (-\Delta)^{-1} (w_0 + \varepsilon w_1 + \varepsilon^2 w_2 + \dots) + [(f'_L(c_0) + f''_L(c_0)(\varepsilon c_1 + \varepsilon^2 c_2 + \dots) + \dots + \lambda^2 (w_0 + \varepsilon w_1 + \varepsilon^2 w_2 + \dots))] \\ & = m(\varepsilon^{-2} \mathcal{B}_0 + \varepsilon^{-1} \mathcal{B}_1 + \mathcal{B}_2) [(f'_L(c_0) + f''_L(c_0)(\varepsilon c_1 + \varepsilon^2 c_2 + \dots) + \dots + \lambda^2 (w_0 + \varepsilon w_1 + \varepsilon^2 w_2 + \dots))] \text{ in } (Y_1)_T, \end{aligned} \quad (2.1.80)$$

where we defined  $(Y_1)_T := Y_1 \times (0, T)$  and analogously for the related boundary. We additionally obtain the corresponding boundary conditions, i.e.,  $\mathbf{n} \cdot (\varepsilon^{-1} \nabla_{\mathbf{y}} + \nabla_{\mathbf{r}})(z_0 + \varepsilon z_1 + \dots) = 0$ ,  $z = \{w, c\}$ . This provides the following sequence of problems, depending on the particular order of the heterogeneity  $\varepsilon$ :

$$\mathcal{O}(\varepsilon^{-2}) : \begin{cases} \lambda^2 m \mathcal{B}_0 w_0 + m \mathcal{B}_0 f'_L(c_0) = 0 & \text{in } (Y_1)_T, \\ \mathcal{B}_0 c_0 = 0 & \text{in } (Y_1)_T. \end{cases} \quad (2.1.81)$$

Moreover,

$$\mathcal{O}(\varepsilon^{-1}) : \begin{cases} -\lambda^2 m \mathcal{B}_1 w_0 - \lambda^2 m \mathcal{B}_0 w_1 = m \mathcal{B}_1 f'_L(c_0) + m \mathcal{B}_0 f''_L(c_0) c_1 & \text{in } (Y_1)_T, \\ -\mathcal{B}_1 c_0 = \mathcal{B}_0 c_1 & \text{in } (Y_1)_T, \\ \mathbf{n} \cdot \nabla_{\mathbf{y}} z_0 = 0, z = \{c, w\} & \text{on } (\partial Y_2)_T \end{cases} \quad (2.1.82)$$

and finally the  $\mathcal{O}(\varepsilon^0)$  problems can be expressed as follows:

$$\mathcal{O}(\varepsilon^0) : \begin{cases} -\partial_t \mathcal{B}_2^{-1} w_0 + f'_L(c_0) + \lambda^2 w_0 = m \mathcal{B}_1 f''_L(c_0) c_1 + m \mathcal{B}_2 f'_L(c_0) + \lambda^2 m \mathcal{B}_2 w_0 \\ + m \mathcal{B}_0 f''_L(c_0) c_2 + m \mathcal{B}_0 c_2 + m \mathcal{B}_0 f'''_L(c_0) c_1^2 / 2 + m \lambda^2 \mathcal{B}_0 w_2 + m \lambda^2 \mathcal{B}_1 w_1 & \text{in } (Y_1)_T, \\ -\mathcal{B}_0 c_2 - \mathcal{B}_1 c_1 - \mathcal{B}_2 c_0 = -w_0 & \text{in } (Y_1)_T, \\ \mathbf{n} \cdot (\nabla_{\mathbf{y}} z_1 + \nabla_{\mathbf{r}} z_0) = 0, z = \{c, w\} & \text{on } (\partial Y_2)_T. \end{cases} \quad (2.1.83)$$

The  $\mathcal{O}(\varepsilon^{-2})$  problem implies that the leading order terms  $c_0$  and  $w_0$  are independent of the microscale  $\mathbf{y}$ , which provides the suggestion to make the following assumption for  $w_1$  and  $c_1$  (the same as discussed in the previous example for Cahn-Hilliard):

$$w_1(\mathbf{r}, \mathbf{y}, t) = - \sum_{k=1}^d \xi_w^k(\mathbf{y}) \partial_{r_k} w_0(\mathbf{r}, t) \text{ and } c_1(\mathbf{r}, \mathbf{y}, t) = - \sum_{k=1}^d \xi_c^k(\mathbf{y}) \partial_{r_k} c_0(\mathbf{r}, t) \text{ in } L^2(D_T; H_{per}^1(Y)). \quad (2.1.84)$$

Plugging the expressions (2.1.84) into the relationship  $-\mathcal{B}_1 c_0 = \mathcal{B}_0 c_1$  and taking into account the boundary condition  $\mathbf{n} \cdot (\nabla_{\mathbf{y}} c_1 + \nabla_{\mathbf{r}} c_0) = 0$ , we obtain an equation for the correctors  $\xi_w^k(\mathbf{y})$  and  $\xi_c^k(\mathbf{y})$ , i.e.,

$$\begin{cases} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ij} \left( \frac{\partial (y_k - \xi_c^k(\mathbf{y}))}{\partial y_j} \right) \right) = - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_c^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi_c^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi_c^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi_c^k) = 0, \end{cases} \quad (2.1.85)$$

for which Fredholm alternative (see Remark 2.12) guaranties the existence of a unique solution in  $H_{per}^1(Y)$  (up to an additive constant) to the problem (2.1.85). The first equation in the  $\mathcal{O}(\varepsilon^{-1})$  problem provides that

$$-\lambda^2 \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_w^k(\mathbf{y})}{\partial y_j} \right) \frac{\partial w_0}{\partial r_k} = \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_c^k(\mathbf{y})}{\partial y_j} \right) \frac{\partial f'_L(c_0)}{\partial r_k}, \quad (2.1.86)$$

supplemented with the boundary condition

$$\sum_{k,i,j=1}^d n_i \left\{ \left( \delta_{ij} \frac{\partial \xi_w^k(\mathbf{y})}{\partial y_j} - \delta_{ik} \right) + \left( -\delta_{ij} \frac{\partial \xi_c^k(\mathbf{y})}{\partial y_j} + \delta_{ik} \right) \right\} = 0, \text{ on } \partial Y_2 \quad (2.1.87)$$

and  $\mathcal{M}_{Y_1}(\xi_w^k) = 0$ . Hence, due to the assumption of a scale separated chemical potential, i.e.,

$$\frac{\partial f'_L(c_0)}{\partial r_k} := f''_L(c_0) \frac{\partial c_0}{\partial r_k} = \lambda^2 \frac{\partial w_0}{\partial r_k}, \quad (2.1.88)$$

(Local Thermodynamic Equilibrium, as discussed earlier), we can deduce the reference cell problem:

$$\sum_{k,i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_w^k}{\partial y_j} \right) = \sum_{k,i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_c^k}{\partial y_j} \right) \text{ in } Y_1, \quad (2.1.89)$$

which additionally provides that  $\xi^k(\mathbf{y}) := \xi_c^k(\mathbf{y}) = \xi_w^k(\mathbf{y})$ . Finally, the upscaled equations can be obtained by solving the  $\mathcal{O}(\varepsilon^0)$  problem, which by Fredholm alternative (2.1.73) is simplified to

$$\int_{Y_1} \left( -\partial_t \mathcal{B}_2^{-1} w_0 + f'_L(c_0) + \lambda^2 w_0 \right) d\mathbf{y} = \int_{Y_1} \left( m\mathcal{B}_1 f''_L(c_0) c_1 + m\mathcal{B}_2 f'_L(c_0) + \lambda^2 m\mathcal{B}_2 w_0 + m\lambda^2 \mathcal{B}_1 w_1 \right) d\mathbf{y} \quad (2.1.90)$$

and

$$-\sum_{k,i=1}^d \left[ \sum_{j=1}^d \int_{Y_1} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi^k(\mathbf{y})}{\partial y_j} \right) d\mathbf{y} \right] \frac{\partial^2 c_0}{\partial r_i \partial r_k} = |Y_1| w_0, \quad (2.1.91)$$

which can be written in a more compact form as  $-\operatorname{div}(\mathbb{D} \nabla c_0) = p w_0$ ,  $p := |Y_1|/|Y|$ . From this we also deduce the related boundary condition  $\mathbb{D} \nabla_{\mathbf{n}} w_0 := -p^{-1} \mathbb{D} \nabla_{\mathbf{n}} \operatorname{div}(\mathbb{D} \nabla c_0) = 0$ . In addition the two last terms in (2.1.90) imply that

$$\begin{aligned} \lambda^2 m \operatorname{div}(\mathbb{D} \nabla w_0) &:= \lambda^2 m \sum_{k,i=1}^d \left[ \sum_{j=1}^d \int_{Y_1} \frac{\partial}{\partial r_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi^k(\mathbf{y})}{\partial y_j} \right) d\mathbf{y} \right] \frac{\partial w_0}{\partial r_k} \\ &:= \int_{Y_1} \lambda^2 m \mathcal{B}_2 w_0 + m \lambda^2 \mathcal{B}_1 w_1 d\mathbf{y}. \end{aligned} \quad (2.1.92)$$

Finally the remaining terms on the right-hand side of (2.1.90) provide that

$$\begin{aligned} m\mathcal{B}_1 f''_L(c_0) c_1 &:= -\sum_{i,j=1}^d m \frac{\partial}{\partial r_i} \left( f''_L(c_0) \sum_{k=1}^d \frac{\partial \xi^k(\mathbf{y})}{\partial y_j} \frac{\partial c_0}{\partial r_k} \right) - \sum_{i,j=1}^d m \frac{\partial}{\partial y_i} \left( f''_L(c_0) \sum_{k=1}^d \xi^k(\mathbf{y}) \frac{\partial^2 c_0}{\partial r_k \partial r_j} \right) \\ &= -m \sum_{k,i,j=1}^d \frac{\partial \xi^k(\mathbf{y})}{\partial y_j} \frac{\partial^2 f'_L(c_0)}{\partial r_k \partial r_i}, \end{aligned} \quad (2.1.93)$$

where the second term disappeared due to integration by parts. Hence, we can identify the sum of  $m\mathcal{B}_1 f''_L(c_0) c_1$  and  $m\mathcal{B}_2 f'_L(c_0)$  appearing in (2.1.90) by

$$m \operatorname{div}(\mathbb{D} \nabla f'_L(c_0)) := m\mathcal{B}_2 f'_L(c_0) + m\mathcal{B}_1 f''_L(c_0) c_1, \quad (2.1.94)$$

where the elements of the effective tensor  $\mathbb{D}$  can be clearly defined by

$$\mathbb{D}_{ij} := \mathcal{M}_{Y_1} \left( \delta_{ij} - \frac{\partial \xi^j(\mathbf{y})}{\partial y_i} \right) := \frac{1}{|Y|} \int_{Y_1} \left( \delta_{ij} - \frac{\partial \xi^j(\mathbf{y})}{\partial y_i} \right) d\mathbf{y} \text{ for all } i, j = 1, \dots, d. \quad (2.1.95)$$

Therefore the upscaled equation (2.1.90) under the above assumption and for isotropic mobility  $\mathbb{M} := m\mathbb{I}$ , finally reads

$$p \partial_t c_0 = m \operatorname{div}(\mathbb{D} \nabla f'_L(c_0)) - \lambda^2 p^{-1} m \operatorname{div}(\mathbb{D} \nabla [\operatorname{div}(\mathbb{D} \nabla c_0)]) - p f'_L(c_0) + \lambda^2 \operatorname{div}(\mathbb{D} \nabla c_0) \text{ in } D_T \quad (2.1.96)$$

and the proof is completed.  $\square$

**Lemma 2.9 (Symmetry and positive definiteness of the effective tensor).** *The effective tensor  $\mathbb{D} := \{\mathbb{D}_{ij}\}_{1 \leq i, j \leq d}$  defined in (2.1.95) is symmetric and positive definite (see also [136, Prop. 3.2.], [12] and also [173, Chap. 1.1.2-1.1.3]).*

*Proof.* We consider the weak formulation of the cell problem (2.1.85), i.e.,

$$\int_{Y_1} \left( \mathbf{e}_j - \nabla_{\mathbf{y}} \xi^j(\mathbf{y}) \right) \cdot \nabla_{\mathbf{y}} \varphi(\mathbf{y}) d\mathbf{y} = 0, \text{ for all } Y\text{-periodic } \varphi(\mathbf{y}). \quad (2.1.97)$$

Hence, we obtain

$$\begin{aligned} 0 &= \int_{Y_1} (\mathbf{e}_j - \nabla_{\mathbf{y}} \xi^j(\mathbf{y})) \cdot \nabla_{\mathbf{y}} \xi^i(\mathbf{y}) \, d\mathbf{y} \\ &= \int_{Y_1} \mathbf{e}_j \cdot \nabla_{\mathbf{y}} \xi^i(\mathbf{y}) \, d\mathbf{y} - \int_{Y_1} \nabla_{\mathbf{y}} \xi^j(\mathbf{y}) \cdot \nabla_{\mathbf{y}} \xi^i(\mathbf{y}) \, d\mathbf{y}, \end{aligned} \quad (2.1.98)$$

and thus,

$$\begin{aligned} \int_{Y_1} \mathbf{e}_j \cdot \nabla_{\mathbf{y}} \xi^i(\mathbf{y}) \, d\mathbf{y} &= \int_{Y_1} \nabla_{\mathbf{y}} \xi^j(\mathbf{y}) \cdot \nabla_{\mathbf{y}} \xi^i(\mathbf{y}) \, d\mathbf{y} \\ &= \int_{Y_1} \nabla_{\mathbf{y}} \xi^i(\mathbf{y}) \cdot \nabla_{\mathbf{y}} \xi^j(\mathbf{y}) \, d\mathbf{y} \\ &= \int_{Y_1} \mathbf{e}_i \cdot \nabla_{\mathbf{y}} \xi^j(\mathbf{y}) \, d\mathbf{y}, \end{aligned} \quad (2.1.99)$$

from which it directly follows that  $\mathbb{D}_{ij} = \mathbb{D}_{ji}$ . Moreover, in order to show positive definiteness, we consider for real numbers  $u_i$  that

$$u_i \mathbb{D}_{ij} u_j = \frac{1}{|Y|} u_i \int_{Y_1} (\mathbf{e}_j - \nabla_{\mathbf{y}} \xi^j(\mathbf{y})) \, d\mathbf{y} u_j = \frac{1}{|Y|} \int_{Y_1} \nabla_{\mathbf{y}} (u_j (y_j - \xi^j(\mathbf{y}))) \cdot \nabla_{\mathbf{y}} (u_i (y_i - \xi^i(\mathbf{y}))) \, d\mathbf{y}. \quad (2.1.100)$$

The sum over all these terms for  $i, j = 1, \dots, d$  is positive whenever one of the  $u_i$ 's differs from zero, which implies that the effective tensor is positive definite.  $\square$

**Remark 2.13 (Discretization of the homogenized equations).** *It is straightforward to adapt the previously discussed discretization scheme for the microscopic problem, to the homogenized Allen-Cahn/Cahn-Hilliard equations 2.1.96), as follows:*

$$\begin{cases} p \mathbb{G} \mathbf{c}_{n+1}^{0,l+1} + m \Delta t \hat{\mathbb{S}} \boldsymbol{\mu}_{n+\theta}^{0,l+1} - p \mathbb{G} \boldsymbol{\mu}_{n+\theta}^{0,l+1} = p \mathbb{G} \mathbf{c}_n^0, \\ \mathbb{G} \boldsymbol{\mu}_{n+\theta}^{0,l+1} + \mathbb{K} (c_{n+1}^{0,l}) \mathbf{c}_{n+1}^{0,l+1} - \frac{1}{2} \mathbb{G} \mathbf{c}_{n+1}^{0,l+1} - \lambda^2 p^{-1} \hat{\mathbb{S}} \mathbf{c}_{n+1}^{0,l+1} = 0. \end{cases} \quad (2.1.101)$$

In the above, we make use of the same definitions for the related matrices  $\mathbb{G}, \mathbb{K}$  and additionally we introduce the effective stiffness matrix defined by  $\hat{\mathbb{S}} := \{\hat{s}_{ij}\}_{i,j=1}^J$  where  $\hat{s}_{ij} := \langle \mathbb{D} \nabla \phi_i, \nabla \phi_j \rangle$ , as in (2.1.8) and subsequently the coefficients vectors  $(\mathbf{c}_{n+1}^{\varepsilon,l+1}, \boldsymbol{\mu}_{n+\theta}^{\varepsilon,l+1})$  with  $\boldsymbol{\mu}^{\varepsilon,l+1} := \{\mu_{j,n}^{\varepsilon,l+1}\}_{j=1}^J$  and  $\mathbf{c}^{\varepsilon,l+1} := \{c_{j,n}^{\varepsilon,l+1}\}_{j=1}^J$ .

### 2.1.3 Derivation of homogenized/upscaled equations via a rigorous two-scale convergence approach.

**Theorem 2.1.5 (Homogenized Allen-Cahn/Cahn-Hilliard system).** *Let  $(c^\varepsilon, \mu^\varepsilon)$  be a weak solution of the microscopic Allen-Cahn/Cahn-Hilliard problem (2.1.24) in  $d \leq 3$  dimensions. Assuming also that the extended initial condition converges, i.e.,  $\widetilde{c_{init}^\varepsilon} \xrightarrow{\varepsilon \rightarrow 0} c_{init,0}$  in  $L^2(D)$ , then the two pairs of limit functions  $c_0, \mu_0 \in L^2(0, T; H^1(D))$  and  $c_1, \mu_1 \in L^2(D_T; H_{per}^1(Y))$  from Lemma 2.10 satisfy the following homogenized/macroscopic Allen-Cahn/Cahn-Hilliard system for isotropic mobility  $\mathbb{M} := m \mathbb{I} := m \{\delta_{ij}\}_{1 \leq i, j \leq d}$ ,  $m > 0$  and porosity  $p := |Y_1|/|Y|$ , i.e.,*

$$\begin{cases} p \partial_t c_0(\mathbf{r}, t) = m \operatorname{div}(\mathbb{D} \nabla \mu_0(\mathbf{r}, t)) - p \mu_0(\mathbf{r}, t) & \text{in } D_T, \\ \mu_0(\mathbf{r}, t) = f'_L(c_0(\mathbf{r}, t)) - p^{-1} \lambda^2 \operatorname{div}(\mathbb{D} \nabla c_0(\mathbf{r}, t)) & \text{in } D_T, \\ c_{init,0}(\mathbf{r}) := c_0(\mathbf{r}, 0) & \text{in } D, \end{cases} \quad (2.1.102)$$

supplemented with homogeneous Neumann and no-flux boundary conditions on  $\partial D_T$ , i.e.,

$$\mathbb{D}\nabla_n c_0 = 0 \text{ and } \mathbb{D}\nabla_n \operatorname{div}(\mathbb{D}\nabla c_0) = 0. \quad (2.1.103)$$

The elements of the effective tensor  $\mathbb{D} := \{\mathbb{D}_{ij}\}_{1 \leq i, j \leq d}$  are defined by

$$\mathbb{D}_{ij} := \frac{1}{|Y|} \int_{Y_1} \left( \delta_{ij} - \frac{\partial \xi^j(\mathbf{y})}{\partial y_i} \right) d\mathbf{y} \text{ for all } i, j = 1, \dots, d, \quad (2.1.104)$$

in which the correctors functions  $\xi^k(\mathbf{y}) \in H_{per}^1(Y_1)$  are unique, in the sense of distributions, solutions of the following reference cell problems:

$$\begin{cases} -\sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi^k) = 0. \end{cases} \quad (2.1.105)$$

Before we start by formally applying the two-scale limits to the system (2.1.24), we have to examine some necessary arguments, associated with the proof. The one indicates the existence of extension of the microscopic solution to the macroscopic domain and the other one provides the strong convergence of limiting functions and the related convergence of the nonlinear bulk free energy term. To prove the convergence of solutions of the microscopic problems to the solutions of the corresponding macroscopic equations, we have to derive an additional equicontinuous a priori estimate with respect to the time variable. This will allow us to obtain compactness properties for a sequence of solutions of the microscopic problem (2.1.24). Hence, in light of Theorem 2.1.3 we aim to obtain an upper bound for the norm  $\|\partial_\tau c^\varepsilon(\mathbf{r}, t) - c^\varepsilon(\mathbf{r}, t)\|_{\mathcal{Z}(D^\varepsilon)}$  on a suitable function space  $\mathcal{Z}$ , where we defined  $\partial_\tau c^\varepsilon(\mathbf{r}, t) := c^\varepsilon(\mathbf{r}, t + \tau)$ . To do this, following the articles by A. Jüngel and M. Ptashnyk on the analysis and homogenization of cross diffusion systems and more precisely the proofs of [174, Theorem 2], [161, Lemma 4], we will make use of an admissible test function

$$\begin{cases} \varphi(\mathbf{r}, t) = \int_{t-\tau}^t \left( \partial_\tau c^\varepsilon(\mathbf{r}, s) - c^\varepsilon(\mathbf{r}, s) \right) k(s) ds, \quad \forall \tau \in (0, T), \\ \varphi(\mathbf{r}, 0) = \varphi(\mathbf{r}, T) = 0 \end{cases} \quad (2.1.106)$$

and in which we defined  $k(s) = 1$ , for  $s \in (0, T - \tau)$ ,  $k(s) = 0$ , for  $s \in [-\tau, 0] \cup [T - \tau, T]$ , in the first weak formulation in (2.1.28), i.e.,

$$0 = \int_0^T \langle \partial_t c^\varepsilon, \varphi \rangle_{H^{-1}(D^\varepsilon) \times H^1(D^\varepsilon)} dt + \int_{D_\varepsilon^c} \mathbb{M} \nabla \mu^\varepsilon \cdot \nabla \varphi d\mathbf{r} dt + \int_{D_\varepsilon^c} \mu^\varepsilon \varphi d\mathbf{r} dt =: I_1 + I_2 + I_3. \quad (2.1.107)$$

We then integrate by parts in the integral  $I_1$ , taking into account that  $\varphi(\mathbf{r}, 0) = \varphi(\mathbf{r}, T) = 0$  and we subsequently obtain



$$\begin{aligned}
 I_1 &:= \int_0^T \langle \partial_t c^\varepsilon, \varphi \rangle_{H^{-1}(D^\varepsilon) \times H^1(D^\varepsilon)} dt \\
 &= - \int_{D_t^\varepsilon} c^\varepsilon \partial_t \varphi \, d\mathbf{r} \, dt \\
 &= - \int_0^{T-\tau} \int_{D^\varepsilon} c^\varepsilon (\partial_\tau c^\varepsilon - c^\varepsilon) \, d\mathbf{r} \, dt + \int_\tau^T \int_{D^\varepsilon} c^\varepsilon (c^\varepsilon - \partial_{-\tau} c^\varepsilon) \, d\mathbf{r} \, dt \\
 &= - \int_0^{T-\tau} \int_{D^\varepsilon} c^\varepsilon (\partial_\tau c^\varepsilon - c^\varepsilon) \, d\mathbf{r} \, dt + \int_0^{T-\tau} \int_{D^\varepsilon} \partial_\tau c^\varepsilon (\partial_\tau c^\varepsilon - c^\varepsilon) \, d\mathbf{r} \, dt \\
 &= \int_0^{T-\tau} \int_{D^\varepsilon} (\partial_\tau c^\varepsilon - c^\varepsilon)^2 \, d\mathbf{r} \, dt. \tag{2.1.108}
 \end{aligned}$$

In the same way, for the integral  $I_2$  we deduce

$$\begin{aligned}
 I_2 &:= \int_0^T \int_{D^\varepsilon} \int_{t-\tau}^t \mathbb{M} \nabla \mu^\varepsilon(\mathbf{r}, t) \cdot \nabla (\partial_\tau c^\varepsilon(\mathbf{r}, s) - c^\varepsilon(\mathbf{r}, s)) k(s) \, ds \, d\mathbf{r} \, dt \\
 &= \int_{D_{T-\tau}^\varepsilon} \int_t^{t+\tau} \mathbb{M} \nabla \mu^\varepsilon(\mathbf{r}, s) \cdot \nabla (\partial_\tau c^\varepsilon(\mathbf{r}, t) - c^\varepsilon(\mathbf{r}, t)) \, ds \, d\mathbf{r} \, dt, \tag{2.1.109}
 \end{aligned}$$

in which we made use of the following relation [161, Lemma 4]:

$$\int_0^T f(t) \int_{t-\tau}^t g(s) \, ds \, dt = \int_0^{T-\tau} \int_t^{t+\tau} f(s) \, ds \, g(t) \, dt, \tag{2.1.110}$$

with  $g(t) = 0$  for  $t \in [-\tau, 0] \cup [T-\tau, T]$ . Hence, the classical Hölder's inequality yields

$$\begin{aligned}
 |I_2| &\leq \int_0^{T-\tau} \int_t^{t+\tau} \|\mathbb{M} \nabla \mu^\varepsilon(\mathbf{r}, s)\|_{L^2(D^\varepsilon)} \left( \|\nabla \partial_\tau c^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)} + \|\nabla c^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)} \right) \, ds \, dt \\
 &\leq m C_D \tau^{1/2} \int_0^{T-\tau} \left( \|\nabla \partial_\tau c^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)} + \|\nabla c^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)} \right) \, dt, \text{ since } \mathbb{M} := m \mathbb{I} \\
 &\leq C'_{D,m} \tau^{1/2} \tag{2.1.111}
 \end{aligned}$$

and we similarly obtain

$$|I_3| \leq \int_0^{T-\tau} \int_t^{t+\tau} \|\mu^\varepsilon(\mathbf{r}, s)\|_{L^2(D^\varepsilon)} \left( \|\partial_\tau c^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)} + \|c^\varepsilon(\mathbf{r}, t)\|_{L^2(D^\varepsilon)} \right) \, ds \, dt \leq C'_D \tau^{1/2}, \tag{2.1.112}$$

which follows from the estimates (2.1.43) and (2.1.49). As a result, putting the bounds (2.1.111), (2.1.112) together with (2.1.108) implies

$$\|\partial_\tau c^\varepsilon(\mathbf{r}, t) - c^\varepsilon(\mathbf{r}, t)\|_{L^2(D_{T-\tau}^\varepsilon)} \leq C''_{D,m} \tau^{1/4}. \tag{2.1.113}$$

Consequently Theorem 2.1.3 implies the strong integral equicontinuity

$$\lim_{\tau \rightarrow 0^+} \|\partial_\tau c^\varepsilon(\mathbf{r}, t) - c^\varepsilon(\mathbf{r}, t)\|_{L^2(D_{T-\tau}^\varepsilon)} = 0 \tag{2.1.114}$$

and the boundedness in  $L^2(D_T^\varepsilon)$ .

**Remark 2.14.** *An additional estimate can be obtained from the bound (2.1.43), i.e.,*

$$\|\tilde{c}^\varepsilon(\mathbf{r}, t)\|_{L^\infty(0,T,H^1(D))} \leq C''. \tag{2.1.115}$$

*and Ladyzhenskaya inequality (see Lemma 1.3) by considering the extended solution  $\tilde{c}^\varepsilon$ , directly as follows:*

$$\|\tilde{c}^\varepsilon\|_{L^4(D)} \leq C_d^{1/4} \|\tilde{c}^\varepsilon\|_{L^2(D)}^{1-d/4} \|\nabla \tilde{c}^\varepsilon\|_{L^2(D)}^{d/4} \leq C''_{D,d}, \quad d = 2, 3, \tag{2.1.116}$$

where the constant  $C''_{D,d} > 0$  is independent of  $\varepsilon$ .

**Lemma 2.10 (Two-scale convergence).** *Assuming that the extended initial condition converges, i.e.,  $\widetilde{c_{init}^\varepsilon} \xrightarrow{\varepsilon \rightarrow 0} c_{init,0}$  in  $L^2(D)$ , then there exist two pairs of limiting functions  $c_0, \mu_0 \in L^2(0, T; H^1(D))$  and  $c_1, \mu_1 \in L^2(D_T; H^1_{per}(Y))$ , such that the related (not relabeled) subsequences  $\widetilde{c^\varepsilon}$  and  $\widetilde{\mu^\varepsilon}$ , satisfy the following convergence results as  $\varepsilon \rightarrow 0$ :*

$$\begin{aligned}
 (i) \quad & \{\widetilde{c^\varepsilon}\}_{\varepsilon > 0} \text{ converges in the two-scale sense to } c_0, \\
 (ii) \quad & \{\nabla_{\mathbf{r}} \widetilde{c^\varepsilon}\}_{\varepsilon > 0} \text{ converges in the two-scale sense to } \nabla_{\mathbf{r}} c_0 + \nabla_{\mathbf{y}} c_1, \\
 (iii) \quad & \{\widetilde{\mu^\varepsilon}\}_{\varepsilon > 0} \text{ converges in the two-scale sense to } \mu_0, \\
 (iv) \quad & \{\nabla_{\mathbf{r}} \widetilde{\mu^\varepsilon}\}_{\varepsilon > 0} \text{ converges in the two-scale sense to } \nabla_{\mathbf{r}} \mu_0 + \nabla_{\mathbf{y}} \mu_1.
 \end{aligned} \tag{2.1.117}$$

*Proof.* The convergence in all arguments follows from the estimate (2.1.32), as a result of Lemma 2.5 and Lemma 2.3.  $\square$

**Lemma 2.11 (Strong convergence and nonlinear term).** *We obtain with the help of the unfolding operator discussed in Definition 2.4, the following convergence results:*

$$\begin{aligned}
 (i) \quad & \{\widetilde{c^\varepsilon}\}_{\varepsilon > 0} \text{ converges to } c_0 \text{ strongly in } L^2(D_T), \\
 (ii) \quad & \mathcal{T}_\varepsilon(\widetilde{c^\varepsilon}) \text{ converges to } c_0 \text{ strongly in } L^2(D_T \times Y), \\
 (iii) \quad & \mathcal{T}^\varepsilon(\nabla_{\mathbf{r}} \widetilde{\mu^\varepsilon}) \text{ converges weakly to } \nabla_{\mathbf{r}} \mu_0 + \nabla_{\mathbf{y}} \mu_1 \text{ in } L^2(D_T \times Y), \\
 (iv) \quad & f'_L(\widetilde{c^\varepsilon}) \text{ is two-scale convergent to } f'_L(c).
 \end{aligned} \tag{2.1.118}$$

*Proof.* (i) In light of Remark 2.7 and the estimates (2.1.43), (2.1.113), there exists a subsequence (not relabeled and still denoted by the same symbol) of the extension  $\{\widetilde{c^\varepsilon}\}_{\varepsilon > 0}$  such that  $\{\widetilde{c^\varepsilon}\}_{\varepsilon > 0} \xrightarrow{\varepsilon \rightarrow 0} c_0$ , strongly in  $L^2(D_T)$ , by Theorem 2.1.3. The convergence in (ii) and (iii) holds straightforwardly by Lemma 2.6 and Lemma 2.7 due to the estimates (2.1.43) and (2.1.49).

In order to show the argument (iv), we note that the weak two-scale convergence of  $f'_L(\widetilde{c^\varepsilon})$  to  $f'_L(c_0)$  is equivalent to the weak convergence  $\mathcal{T}_\varepsilon(f'_L(\widetilde{c^\varepsilon})) := f'_L(\mathcal{T}_\varepsilon(\widetilde{c^\varepsilon})) \rightharpoonup f'_L(c_0)$ . Then by the integral conservation property of the unfolding operator (2.1.159), we obtain with the help of the estimate (2.1.116) the following inequality:

$$\|\mathcal{T}_\varepsilon(\widetilde{c^\varepsilon})\|_{L^4(D_T \times Y)} = |Y|^{1/4} \|\widetilde{c^\varepsilon}\|_{L^4(D_T)} = \|\widetilde{c^\varepsilon}\|_{L^4(D_T)} \leq C''_D, \tag{2.1.119}$$

since we assumed that the porous medium consists of periodically distributed reference cells of unit volume, i.e.,  $Y := (0, 1)^d$ ,  $d = 2, 3$  and hence  $|Y| = 1$ .

Furthermore, since  $f_L(c) := (c^2 - 1)^2/4$  and also  $f'_L(c) = c^3 - c$  then, pointwise convergence and the generalized Lebesgue dominated convergence theorem in  $L^p$ -spaces (see[176]), due to the bound (2.1.119), imply that for all test functions  $\varphi \in C_0(D_T; C^\infty_{per}(Y))$ :

$$\begin{aligned}
 & \left| \int_{D_T \times Y} f'_L(\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)) \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt - \int_{D_T \times Y} f'_L(c_0) \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \right| \\
 & \stackrel{\text{Triangle}}{\leq} \int_{D_T \times Y} |f'_L(\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)) - f'_L(c_0)| \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \\
 & = \int_{D_T \times Y} |([\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)]^3 - \mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) - c_0^3 + c_0) \varphi| \, d\mathbf{r} \, d\mathbf{y} \, dt \\
 & \stackrel{\text{Triangle}}{\leq} \int_{D_T \times Y} |([\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)]^3 - c_0^3) \varphi| \, d\mathbf{r} \, d\mathbf{y} \, dt + \int_{D_T \times Y} |(\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) - c_0) \varphi| \, d\mathbf{r} \, d\mathbf{y} \, dt \\
 & \stackrel{\text{Hölder's}}{\leq} \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) - c_0\|_{L^2(D_T \times Y)} \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)^2 + \mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)c_0 + c_0^2\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)} \\
 & \quad + \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) - c_0\|_{L^2(D_T \times Y)} \|\varphi\|_{L^2(D_T \times Y)}. \tag{2.1.120}
 \end{aligned}$$

Hence, the strong convergence  $\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) \xrightarrow{\varepsilon \rightarrow 0} c_0$  in  $L^2(D_T \times Y)$  implies

$$\begin{aligned}
 & \lim_{\varepsilon \rightarrow 0} \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) - c_0\|_{L^2(D_T \times Y)} \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) (\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) + c_0) + c_0^2\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)} \\
 & \quad + \lim_{\varepsilon \rightarrow 0} \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) - c_0\|_{L^2(D_T \times Y)} \|\varphi\|_{L^2(D_T \times Y)} = 0, \tag{2.1.121}
 \end{aligned}$$

since

$$\begin{aligned}
 \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) (\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) + c_0) + c_0^2\|_{L^2(D_T \times Y)}^2 &= \int_{D_T \times Y} [\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)]^2 (\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) + c_0)^2 \, d\mathbf{r} \, d\mathbf{y} \, dt \\
 & \quad + 2 \int_{D_T \times Y} \mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) (\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon) + c_0) c_0^2 \, d\mathbf{r} \, d\mathbf{y} \, dt \\
 & \quad + \int_{D_T \times Y} |c_0|^4 \, d\mathbf{r} \, d\mathbf{y} \, dt \\
 & \leq C_1 \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)\|_{L^4(D_T \times Y)}^4 + C_2 |Y| \|c_0\|_{L^4(D_T)}^4 \\
 & \quad + 2|Y| \|\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)\|_{L^2(D_T \times Y)} \|c_0\|_{L^2(D_T)} \\
 & \leq C_D''', \tag{2.1.122}
 \end{aligned}$$

which follows by Hölder's and Young's inequality as well as the bound (2.1.119) and the estimate (2.1.116). As a result

$$\lim_{\varepsilon \rightarrow 0} \int_{D_T \times Y} f'_L(\mathcal{T}_\varepsilon(\tilde{c}^\varepsilon)) \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt = \int_{D_T \times Y} f'_L(c_0) \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \tag{2.1.123}$$

and the Proof of Lemma 2.15 has been completed.  $\square$

*Proof of Theorem 2.1.5.* We are able to proceed now to the formal derivation of the up-scaled model (2.1.163) stated in the theorem. Following classical rigorous homogenization arguments and the procedure discussed in detail in [12, 17, 138, 139, 141–144], we will prove that the limiting functions from the previous Lemma 2.15 satisfy the macroscopic equations (2.1.163). To this end, we choose test functions  $\phi_0 \in C_0^\infty(D_T)$  and  $\phi_1 \in C_0^\infty(D_T; C_{per}^\infty(Y))$  such that  $\phi^\varepsilon(\mathbf{r}, t) = \phi_0(\mathbf{r}, t) + \varepsilon \phi_1(\mathbf{r}, \varepsilon^{-1}\mathbf{r}, t)$ . Hence, we obtain for all test functions  $\phi^\varepsilon \in L^2(0, T; H^1(D^\varepsilon))$ , in the weak formulation (2.1.28):

$$\int_0^T \langle \partial_t c^\varepsilon, \phi^\varepsilon \rangle_{H^{-1}(D^\varepsilon) \times H^1(D^\varepsilon)} \, dt = - \int_{D_T^\varepsilon} \mathbb{M} \nabla \mu^\varepsilon \cdot \nabla \phi^\varepsilon \, d\mathbf{r} \, dt - \int_{D_T^\varepsilon} \mu^\varepsilon \phi^\varepsilon \, d\mathbf{r} \, dt \tag{2.1.124}$$

Therefore, we can deduce by definition of the test function in terms of  $\phi_0$  and  $\phi_1$  that

$$\begin{aligned}
 & - \int_{D_T^\varepsilon} c^\varepsilon(\mathbf{r}, t) \left( \partial_t \phi_0(\mathbf{r}, t) + \varepsilon \partial_t \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 & + \int_{D_T^\varepsilon} \mu^\varepsilon(\mathbf{r}, t) \left( \phi_0(\mathbf{r}, t) + \varepsilon \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 & = -\mathbb{M} \int_{D_T^\varepsilon} \nabla_{\mathbf{r}} \mu^\varepsilon(\mathbf{r}, t) \cdot \left( \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) + \varepsilon \nabla_{\mathbf{r}} \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \quad (2.1.125)
 \end{aligned}$$

In order to proceed further with the convergence we recall the following properties.

**Remark 2.15.** ([161, Remark 14]) *We can obtain the extension by zero in  $D \setminus D^\varepsilon$  with the help of the characteristic function  $\chi_{D^\varepsilon}(\mathbf{r})$  as follows: a) if  $\|z^\varepsilon\|_{L^2(D^\varepsilon)} \leq C'$  for  $z = \{c, \mu\}$ , then  $\|\tilde{z}^\varepsilon\|_{L^2(D)} \leq C'$  and there exists  $z_0 \in L^2(D \times Y)$  such that, up to a subsequence,  $\tilde{z}^\varepsilon \rightharpoonup \chi_{Y_1} z_0$ ,  $z = \{c, \mu\}$  two-scale, where we define the characteristic function over the pore-phase  $Y_1$  by*

$$\chi_{Y_1}(\mathbf{y}) = \begin{cases} 1 & \text{for } \mathbf{y} \in Y_1, \\ 0 & \text{for } \mathbf{y} \in Y \setminus \bar{Y}_1. \end{cases} \quad (2.1.126)$$

Hence, it holds

$$\begin{aligned}
 & \lim_{\varepsilon \rightarrow 0} \int_{D^\varepsilon} z^\varepsilon(\mathbf{r}) \varphi(\mathbf{r}, \varepsilon^{-1} \mathbf{r}) d\mathbf{r} = \lim_{\varepsilon \rightarrow 0} \int_D \tilde{z}^\varepsilon(\mathbf{r}) \varphi(\mathbf{r}, \varepsilon^{-1} \mathbf{r}) d\mathbf{r} \\
 & = \lim_{\varepsilon \rightarrow 0} \int_D \tilde{z}^\varepsilon(\mathbf{r}) \chi_{D^\varepsilon}(\mathbf{r}) \varphi(\mathbf{r}, \varepsilon^{-1} \mathbf{r}) d\mathbf{r} = \frac{1}{|Y|} \int_{D \times Y} \chi_{Y_1}(\mathbf{y}) z_0(\mathbf{r}, \mathbf{y}) \varphi(\mathbf{r}, \varepsilon^{-1} \mathbf{r}) d\mathbf{r} d\mathbf{y}, \quad z = \{c, \mu\} \quad (2.1.127)
 \end{aligned}$$

for any smooth  $Y$ -periodic function  $\varphi : D \times Y \rightarrow \mathbb{R}$ . b) Moreover, if  $z^\varepsilon \rightharpoonup z_0$ ,  $z = \{c, \mu\}$  two-scale with  $c \in L^p(D \times Y)$ , then

$$z^\varepsilon \rightharpoonup \frac{1}{|Y|} \int_Y z_0(\mathbf{r}, \mathbf{y}) d\mathbf{y} \text{ weakly in } L^p(D) \text{ for } p \in [1, +\infty), \quad z = \{c, \mu\}. \quad (2.1.128)$$

The above convergence arguments can be very naturally extended for both space and time-dependent functions.

As a result, in view of Remark 2.15 we can pass to the limit in the two-scale sense, as follows:

$$\begin{aligned}
 0 & = - \lim_{\varepsilon \rightarrow 0} \int_{D_T^\varepsilon} \chi_{Y_1}(\varepsilon^{-1} \mathbf{r}) c^\varepsilon(\mathbf{r}, t) \left( \partial_t \phi_0(\mathbf{r}, t) + \varepsilon \partial_t \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 & + \lim_{\varepsilon \rightarrow 0} \int_{D_T^\varepsilon} \chi_{Y_1}(\varepsilon^{-1} \mathbf{r}) \mu^\varepsilon(\mathbf{r}, t) \left( \phi_0(\mathbf{r}, t) + \varepsilon \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 & + \lim_{\varepsilon \rightarrow 0} \mathbb{M} \int_{D_T^\varepsilon} \chi_{Y_1}(\varepsilon^{-1} \mathbf{r}) \nabla_{\mathbf{r}} \mu^\varepsilon(\mathbf{r}, t) \cdot \left( \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) + \varepsilon \nabla_{\mathbf{r}} \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt, \\
 & = - \int_{D_T \times Y_1} \chi_{Y_1}(\mathbf{y}) c_0(\mathbf{r}, t) \partial_t \phi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} dt + \int_{D_T \times Y_1} \chi(\mathbf{y}) \mu_0(\mathbf{r}, t) \phi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} dt \\
 & + \mathbb{M} \int_{D_T \times Y_1} \chi_{Y_1}(\mathbf{y}) \left( \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \left( \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) \right) d\mathbf{r} d\mathbf{y} dt \\
 & = -|Y_1| \int_{D_T} c_0(\mathbf{r}, t) \partial_t \phi_0(\mathbf{r}, t) d\mathbf{r} dt + |Y_1| \int_{D_T} \chi_{Y_1}(\mathbf{y}) \mu_0(\mathbf{r}, t) \phi_0(\mathbf{r}, t) d\mathbf{r} dt \\
 & + \mathbb{M} \int_{D_T \times Y_1} \left( \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \left( \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) \right) d\mathbf{r} d\mathbf{y} dt, \quad (2.1.129)
 \end{aligned}$$

where we used the fact that  $\chi_{Y_1}(\mathbf{y}) = 1$  over each pore space  $Y_1$ . Therefore, if we choose  $\phi_0 = 0$  and  $\phi_1 \neq 0$  in (2.1.129), we obtain

$$\mathbb{M} \int_{D_T \times Y_1} \left( \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} dt = 0, \quad (2.1.130)$$

which implies after integration by parts:

$$\begin{cases} \nabla_{\mathbf{y}} \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) = -\Delta_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) & \text{in } D_T \times Y_1, \\ [\nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \mu_1^{av}(\mathbf{r}, t)] \cdot \mathbf{n} = 0 & \text{on } \partial D_T, \end{cases} \quad (2.1.131)$$

where  $\mu_1^{av}(\mathbf{r}, t) := |Y_1|^{-1} \int_{Y_1} \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{y}$ . This relation suggests to make the assumption that  $\mu_1$  depends linearly on  $\nabla_{\mathbf{r}} \mu_0$  and it can be expressed by the following scale separation ansatz,

$$\mu_1(\mathbf{r}, \mathbf{y}, t) = - \sum_{k=1}^d \xi_{\mu}^k(\mathbf{y}) \frac{\partial \mu_0(\mathbf{r}, t)}{\partial r_k} + \beta(\mathbf{r}) \text{ in } L^2(D_T, H_{per}^1(Y)/\mathbb{R}), \quad (2.1.132)$$

where  $\beta(\mathbf{r})$  is arbitrary and for simplicity can be chosen to be zero, i.e.,  $(\beta(\mathbf{r}) = 0)$ . Inserting the ansatz (2.1.294) into the boundary condition  $[\nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \mu_1^{av}(\mathbf{r}, t)] \cdot \mathbf{n} = 0$  on  $\partial D_T$  implies the no-flux condition in (2.1.103). The correctors  $\xi_{\mu}^k(\mathbf{y})$  are solutions of the following reference cell problem (if one takes into account the related boundary conditions):

$$\begin{cases} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left[ \delta_{ij} \left( \frac{\partial (y_k - \xi_{\mu}^k(\mathbf{y}))}{\partial y_j} \right) \right] = - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_{\mu}^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi_{\mu}^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi_{\mu}^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi_{\mu}^k) = 0, \end{cases} \quad (2.1.133)$$

for which Fredholm alternative (see Remark 2.12) ensures that there exists a unique solution in  $H_{per}^1(Y)$  (up to an additive constant) to the problem (2.1.133). In the same way, on noting again that  $\mathcal{X}(\mathbf{y}) = 1$  in  $Y_1$ , if we choose  $\phi_1 = 0$  and  $\phi_0 \neq 0$  in (2.1.129), we consequently obtain

$$\begin{aligned} -|Y_1| \int_{D_T} c_0(\mathbf{r}, t) \partial_t \phi_0(\mathbf{r}, t) \, d\mathbf{r} \, dt + |Y_1| \int_{D_T} \mu_0(\mathbf{r}, t) \phi_0(\mathbf{r}, t) \, d\mathbf{r} \, dt \\ = -\mathbb{M} \int_{D_T \times Y_1} (\nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t)) \cdot \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) \, d\mathbf{r} \, d\mathbf{y} \, dt. \end{aligned} \quad (2.1.134)$$

This yields to the following homogenized relationship,

$$\partial_t c_0(\mathbf{r}, t) + \mu_0(\mathbf{r}, t) - \mathbb{M} \Delta_{\mathbf{r}} \mu_0(\mathbf{r}, t) - \mathbb{M} \nabla_{\mathbf{r}} \cdot \left( |Y_1|^{-1} \int_{Y_1} \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{y} \right) = 0 \quad \text{in } D_T. \quad (2.1.135)$$

In addition, we set  $\varphi^{\varepsilon}(\mathbf{r}, t) = \varphi_0(\mathbf{r}, t) + \varepsilon \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t)$  in  $C_0^{\infty}(D_T; C_{per}^{\infty}(Y))$  to the weak formulation for the microscopic chemical potential  $\mu^{\varepsilon}$ , i.e.,

$$\begin{aligned} \int_{D_T^{\varepsilon}} \mu^{\varepsilon}(\mathbf{r}, t) \varphi^{\varepsilon}(\mathbf{r}, t) \, d\mathbf{r} \, dt = \lambda^2 \int_{D_T^{\varepsilon}} \nabla_{\mathbf{r}} c^{\varepsilon}(\mathbf{r}, t) \cdot \nabla_{\mathbf{r}} \varphi^{\varepsilon}(\mathbf{r}, t) \, d\mathbf{r} \, dt \\ + \int_{D_T^{\varepsilon}} f'_L(c^{\varepsilon}) \varphi^{\varepsilon}(\mathbf{r}, t) \, d\mathbf{r} \, dt \end{aligned} \quad (2.1.136)$$

and by passing to the limit  $\varepsilon \rightarrow 0$  with the help of the characteristic function  $\mathcal{X}(\varepsilon^{-1} \mathbf{r})$  similarly as above, we can deduce that

$$\begin{aligned}
 \int_{D_T \times Y_1} \mu_0(\mathbf{r}, t) \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dt &= \lambda^2 \int_{D_T \times Y_1} (\nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t)) \cdot \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dt \\
 &\quad + \lambda^2 \int_{D_T \times Y_1} (\nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t)) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{r} \, dy \, dt \\
 &\quad + \int_{D_T \times Y_1} f'_L(c_0(\mathbf{r}, t)) \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dt. \tag{2.1.137}
 \end{aligned}$$

This can be reduced further to  $\int_{D_T \times Y_1} (\nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t)) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{r} \, dy \, dt = 0$  for  $\varphi_0 = 0$ , which additionally yields

$$\begin{cases} -\Delta_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) = \nabla_{\mathbf{y}} \cdot \nabla_{\mathbf{r}} c_0(\mathbf{r}, t) & \text{in } D_T \times Y_1, \\ [\nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + c_1^{av}(\mathbf{r}, t)] \cdot \mathbf{n} = 0 & \text{on } \partial D_T, \end{cases} \tag{2.1.138}$$

where  $c_1^{av}(\mathbf{r}, t) := |Y_1|^{-1} \int_{Y_1} \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) \, dy$ . This relation suggests again that  $c_1$  depends linearly on  $\nabla_{\mathbf{r}} c_0$  and thus we can consider the following scale separation ansatz,

$$c_1(\mathbf{y}, \mathbf{r}, t) = - \sum_{k=1}^d \xi_c^k(\mathbf{y}) \frac{\partial c_0(\mathbf{r}, t)}{\partial r_k} + \alpha(\mathbf{r}) \text{ in } L^2(D_T, H_{per}^1(Y)/\mathbb{R}), \tag{2.1.139}$$

where  $\alpha(\mathbf{r})$  is arbitrary (for simplicity  $\alpha(\mathbf{r}) = 0$ ). The correctors  $\xi_c^k(\mathbf{y})$  are solutions of the following reference cell problem, which comes out from (2.1.138):

$$\begin{cases} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_c^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi_c^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi_c^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi_c^k) = 0. \end{cases} \tag{2.1.140}$$

Moreover, (2.1.133) and (2.1.140) provide that  $\xi^k(\mathbf{y}) := \xi_c^k(\mathbf{y}) = \xi_{\mu}^k(\mathbf{y})$ . Inserting the ansatz (2.1.139) into the boundary condition  $[\nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + c_1^{av}(\mathbf{r}, t)] \cdot \mathbf{n} = 0$  on  $\partial D_T$  implies the following homogeneous Neumann boundary condition  $\mathbb{D} \nabla_{\mathbf{n}} c_0 = 0$ . The elements of the effective tensor  $\mathbb{D} := \{\mathbb{D}_{ij}\}_{1 \leq i, j \leq d}$  are defined by

$$\mathbb{D}_{ij} := \frac{1}{|Y|} \int_{Y_1} \left( \delta_{ij} - \frac{\partial \xi^j(\mathbf{y})}{\partial y_i} \right) \, d\mathbf{y} \text{ for all } i, j = 1, \dots, d. \tag{2.1.141}$$

Analogously the choice  $\varphi_1 = 0$  implies

$$\begin{aligned}
 \int_{D_T \times Y_1} \mu_0(\mathbf{r}, t) \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dt &= \lambda^2 \int_{D_T \times Y_1} (\nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t)) \cdot \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dt \\
 &\quad + \int_{D_T \times Y_1} f'_L(c_0(\mathbf{r}, t)) \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dt. \tag{2.1.142}
 \end{aligned}$$

Also by inserting the ansatz (2.1.132) into the boundary condition  $[\nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \mu_1^{av}(\mathbf{r}, t)] \cdot \mathbf{n} = 0$  on  $\partial D_T$  yields the no-flux boundary condition

$$\mathbb{D} \nabla_{\mathbf{n}} \mu_0 := \mathbf{n} \cdot \mathbb{D} f''(c_0) \nabla c_0 - p^{-1} \lambda^2 \mathbb{D} \nabla_{\mathbf{n}} \text{div}(\mathbb{D} \nabla c_0) = -p^{-1} \lambda^2 \mathbb{D} \nabla_{\mathbf{n}} \text{div}(\mathbb{D} \nabla c_0) = 0 \tag{2.1.143}$$

and the derivation of the homogenized system (2.1.163), is completed.  $\square$

**Remark 2.16.** *It is worth mentioning that although the applied homogenization methods for the proofs of Theorem 2.1.5 and Theorem 2.1.4 have many technical differences, the resulting upscaled equation is the same. The method of two-scale asymptotic yields heuristically*

the correct form of the homogenized equation, but it does not yield a correct proof of the homogenization procedure. The reason is that the ansatz

$$z^\varepsilon(\mathbf{r}, t) = \sum_{i=0}^{\infty} \varepsilon^i z_i(\mathbf{r}, \mathbf{y}, t), \quad z = \{c, w\}, \quad (2.1.144)$$

is correct only if you consider all terms and hence the first two terms give you only a first order approximation. For example, it does not include possible boundary layers in the vicinity of  $\partial D^\varepsilon$  (for more details, see e.g., [177], [178]).

#### 2.1.4 Homogenized Allen-Cahn/Cahn-Hilliard equations, derived by a reiterated rigorous three-scale convergence approach.

**A brief introduction to reiterated homogenization.** If we consider a composite medium constructed by different types of inclusions in a matrix material (matrix-inclusion composites) with different sizes and various periodicities (see for example Figure 2.7), then the upscaling procedure can be generalised and the several microscopic variables have to be taken into account [179–181]. Hence, as an extension of the classical two-scale case explained in the previous subsection, we further assume that this sequence of separated length-scales of periodic oscillations depend on the same reference scaling parameter  $\varepsilon \rightarrow 0$ . Therefore, apart from  $\mathbf{r}$ , we introduce  $n-1$  additional microscale variables  $\mathbf{y}_i := \mathbf{r}/\varepsilon_i, i = 1, \dots, n$  and we consider  $\mathbf{r}, \mathbf{y}_1, \dots, \mathbf{y}_n$ , as  $n$  separated variables. The parameters  $\varepsilon_1(\varepsilon)$  and  $\varepsilon_2(\varepsilon)$  satisfy the properties,

$$\lim_{\varepsilon \rightarrow 0} \varepsilon_i(\varepsilon) = 0, i = 1, \dots, n-1 \text{ and } \lim_{\varepsilon \rightarrow 0} \frac{\varepsilon_{i+1}(\varepsilon)}{\varepsilon_i(\varepsilon)} = 0, \quad (2.1.145)$$

which indicates the separation of the scales, i.e, the are of different order of magnitude.

The next step is to consider a generalized ansatz which accounts for the multiscale characteristics of the problem:

$$c^\varepsilon(\mathbf{r}, t) := c_0(\mathbf{r}, \mathbf{y}_1, \dots, \mathbf{y}_n, t) + \sum_{i=1}^n \sum_{k=1}^{\infty} \varepsilon_i^k c_k(\mathbf{r}, \mathbf{y}_1, \dots, \mathbf{y}_n, t), \quad (2.1.146)$$

In the same context, G. Allaire and M. Briane [181] extended the classical two-scale convergence statement (see Definition 2.3) and introduced the notion of multiscale convergence, summarised in the Definition 2.6 below.

**Definition 2.6 (Multiscale convergence).** *A sequence of functions  $\{c^\varepsilon\}_{\varepsilon>0}$  in  $L^2(D_T)$   $(n+1)$ -scale converges (up to a subsequence) to a limit  $c_0(\mathbf{r}, \mathbf{y}_1, \dots, \mathbf{y}_n, t) \in L^2(D_T \times Y^1 \times Y^2 \times \dots \times Y^n)$  if for all  $\varphi \in L^2(D_T, C_{per}^\infty(Y^1, \dots, Y^n))$  it holds,*

$$\begin{aligned} & \lim_{\varepsilon \rightarrow 0} \int_{D_T} c^\varepsilon(\mathbf{r}, t) \varphi(\mathbf{r}, \varepsilon_1^{-1} \mathbf{r}, \varepsilon_2^{-1} \mathbf{r}, \dots, \varepsilon_n^{-1} \mathbf{r}, t) \, d\mathbf{r} \, dt \\ &= \frac{1}{\prod_{i=1}^n |Y^i|} \int_{D_T \times Y^1 \times \dots \times Y^n} c_0(\mathbf{r}, \mathbf{y}_1, \dots, \mathbf{y}_n, t) \varphi(\mathbf{r}, \mathbf{y}_1, \dots, \mathbf{y}_n, t) \, d\mathbf{r} \, d\mathbf{y}_1 \dots d\mathbf{y}_n \, dt. \end{aligned} \quad (2.1.147)$$

Note that each different reference cell  $Y^i, i = 1, \dots, n$  is decomposed in terms of its own solid obstacle and pore-space parts, i.e.,  $Y^i := Y_1^i \cup Y_2^i$  as defined in Figure 2.2. See also [181, Theo. 1.1. and Def. 2.3.] for more details on this definition.

**Lemma 2.12** ([181]). *For any bounded sequence  $\{c^\varepsilon\}_{\varepsilon>0}$  in  $L^2(0,T;H^1(D))$ , there exist a function  $c_0 \in L^2(0,T;H^1(D))$  and  $k = 1, \dots, n$  functions  $c_k \in L^2(D_T \times Y^1 \times \dots \times Y^{k-1}; H_{per}^1(Y_k))$ , such that (up to a subsequence) the following convergence argument holds:*

$$\begin{cases} c^\varepsilon \xrightarrow{(n+1)\text{-scale}} c_0(\mathbf{r}, t), \\ \nabla_{\mathbf{r}} c^\varepsilon \xrightarrow{(n+1)\text{-scale}} \nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \sum_{k=1}^n \nabla_{\mathbf{y}_k} c_k(\mathbf{r}, \mathbf{y}_1, \dots, \mathbf{y}_n, t). \end{cases} \quad (2.1.148)$$

**The three-scale composite geometry.** We define the domain  $D^\varepsilon$  as an open bounded domain in  $\mathbb{R}^d$ ,  $d = 2, 3$  with Lipschitz continuous boundary  $\partial D^\varepsilon$ , as earlier and represents a periodic composite material possessing two hierarchical levels of organization characterized by the small parameters  $\varepsilon = \ell_1/L \ll 1$  and  $\varepsilon_1(\varepsilon) := \ell_2/L \ll 1$  such that  $0 < \varepsilon_1(\varepsilon) < \varepsilon$  and where the inclusions do not intersect the boundaries. The small perforations of size  $\varepsilon$  periodically distributed with period  $\varepsilon$  and the very small perforations of size  $\varepsilon\varepsilon_1(\varepsilon)$  periodically distributed with periodicity  $\varepsilon\varepsilon_1(\varepsilon)$ . The scales  $\varepsilon$  and  $\varepsilon_1(\varepsilon)$  are assumed to be well-separated, i.e.,

$$\lim_{\varepsilon \rightarrow 0} \varepsilon_1(\varepsilon) = 0, \text{ and } \lim_{\varepsilon \rightarrow 0} \frac{\varepsilon_1(\varepsilon)}{\varepsilon} = 0. \quad (2.1.149)$$

We assume also that there exists an  $\varepsilon$  such that  $\bar{Y}$  is exactly covered by a finite number of cells  $\varepsilon_1(\varepsilon)\bar{Z}$ . Therefore, we deduce that there is no intersection between the solid obstacles  $\varepsilon Y_2$  and  $\varepsilon\varepsilon_1(\varepsilon)Z_2$  in the cell  $Y$ . The domain  $D^\varepsilon$  is connected, but the union of solid obstacles is not connected (see Figure 2.7).

Such a geometry represents, for example, a porous medium in which the perforations correspond to solid impervious obstacles as in Figure 2.7. In the pore-space/fluid part of this porous medium we consider Allen-Cahn/Cahn-Hilliard dynamics, fully described by the microscopic formulation,

$$\begin{cases} \partial_t c^\varepsilon = -(1 - m \operatorname{div}(\mathbb{I}\nabla))\mu^\varepsilon & \text{in } D_T^\varepsilon, \\ \mu^\varepsilon := f_L'(c^\varepsilon) - \lambda^2 \Delta c^\varepsilon & \text{in } D_T^\varepsilon, \\ \partial_n c^\varepsilon = \partial_n \mu^\varepsilon = \partial_n \Delta c^\varepsilon = 0 & \text{on } \partial D_T^\varepsilon, \end{cases} \quad (2.1.150)$$

for which we extensively discussed the homogenization procedure by considering only on microscale, in the previous subsections.

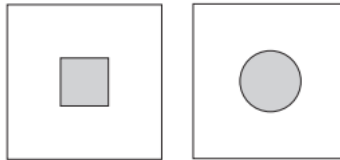


Figure 2.6: Different types of periodic reference cells involved. The figure is taken from [183].

We therefore, apart from  $\mathbf{r}$ , we introduce two additional microscale variables  $\mathbf{y} := \mathbf{r}/\varepsilon$ ,  $\mathbf{y}_1 := \mathbf{r}/\varepsilon_1(\varepsilon)\varepsilon$  and we consider  $\mathbf{r}, \mathbf{y}, \mathbf{y}_1$ , as three separated variables. In the same context we can identify the characteristic functions of the pore-phases  $Y_1, Z_1$ , which can be denoted by  $\chi_{Y_1}(\mathbf{y}), \chi_{Z_1}(\mathbf{y}_1)$  and are defined by:



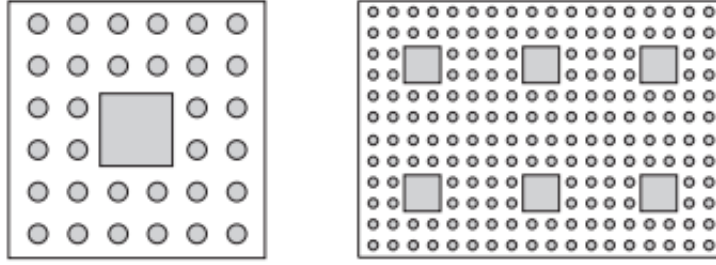


Figure 2.7: The periodic composite geometry under consideration. The figure is taken from [183].

$$\chi_{Y_1}(\mathbf{y}) = \begin{cases} 1 & \text{in } Y_1, \\ 0 & \text{in } Y \setminus Y_1. \end{cases} \quad \chi_{Z_1}(\mathbf{y}_1) = \begin{cases} 1 & \text{in } Z_1, \\ 0 & \text{in } Z \setminus Z_1. \end{cases} \quad (2.1.151)$$

Hence, the domain  $D^\varepsilon$ , can be defined in terms of the characteristic functions by:

$$D^\varepsilon := \left\{ \mathbf{r} \in D : \chi_{Y_1} \left( \frac{\mathbf{r}}{\varepsilon} \right) \chi_{Z_1} \left( \frac{\mathbf{r}}{\varepsilon \varepsilon_1(\varepsilon)} \right) = 1 \right\}. \quad (2.1.152)$$

The domain  $D^\varepsilon$  in this case can be interpreted as a structure with a double periodicity: there are small perforations of size  $\varepsilon$  and very small perforations of size  $\varepsilon \varepsilon_1(\varepsilon)$ . The boundary  $\partial D^\varepsilon$  that is composed by two parts: the boundary of  $D$  denoted  $\partial D$  and the union of the boundaries of all the obstacles, denoted  $\Gamma_\varepsilon$ . The domain  $D^\varepsilon$  is connected, but the union of solid obstacles is not connected, as in Figure 2.7. Similarly to the context of the two-scale asymptotic expansions there exist two convergence statements related to reiterated three-scale homogenization (see [151, 152, 181, 184–187] for more details).

**Definition 2.7 (Three-scale convergence).** [184, 189–191] *A sequence of functions  $\{c^\varepsilon\}_{\varepsilon>0}$  in  $L^2(D_T)$  three-scale converges to a limit  $c_0(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \in L^2(D_T \times Y \times Z)$  if*

$$\lim_{\varepsilon \rightarrow 0} \int_{D_T} c^\varepsilon(\mathbf{r}, t) \varphi \left( \mathbf{r}, \frac{\mathbf{r}}{\varepsilon}, \frac{\mathbf{r}}{\varepsilon^2}, t \right) d\mathbf{r} dt = \frac{1}{|Y||Z|} \int_{D_T \times Y \times Z} c_0(\mathbf{r}, \mathbf{y}_1, \mathbf{y}_2, t) \varphi(\mathbf{r}, \mathbf{y}_1, \mathbf{y}_2, t) d\mathbf{r} d\mathbf{y}_1 d\mathbf{y}_2 dt, \quad (2.1.153)$$

for all  $\varphi \in L^2(D_T, C_{per}^\infty(Y \times Z))$ . Note that each different reference cell  $Y, Z$  is decomposed of in terms of its own solid obstacle and pore-space parts, i.e.,  $Y := Y_1 \cup Y_2$  and  $Z := Z_1 \cup Z_2$ , as defined in Figure 2.2.

**Lemma 2.13** ([191–193]). *Let  $\{c^\varepsilon\}_{\varepsilon>0}$  be a bounded sequence in  $L^2(0, T; H_0^1(D))$  and assume that the scales are well separated. Then there exists a subsequence still denoted by  $\{c^\varepsilon\}_{\varepsilon>0}$  and a triplet  $(c_0, c_1, c_1^*) \in L^2(0, T; H_0^1(D)) \times L^2(D_T, H_{per}^1(Y)) \times L^2(D_T \times Y; H_{per}^1(Z))$  such that, as  $\varepsilon \rightarrow 0$ ,*

$$\begin{aligned} c^\varepsilon &\rightharpoonup c_0, \text{ three-scale in } L^2(0, T; H_0^1(D)), \\ \nabla_{\mathbf{r}} c^\varepsilon &\rightharpoonup \nabla_{\mathbf{r}} c_0 + \nabla_{\mathbf{y}} c_1 + \nabla_{\mathbf{y}_1} c_1^*, \text{ three-scale in } L^2(D_T). \end{aligned} \quad (2.1.154)$$

Moreover, D. Trucu et al [184] in a recent approach generalised the notion of three-scale convergence based on two distinct scaling parameters  $\varepsilon$  and  $\varepsilon_1$  that independently approach 0, i.e.,  $\varepsilon_1$  is not a function depending on  $\varepsilon$ . To this end, they introduced a notion

of three-scale convergence similar to the one by J. Lions et al (see Definition 2.7), as follows:

**Definition 2.8.** [184, Def. 3.1.] A sequence of functions is said to three-scale convergent to a function  $c_0 \in L^2(D_T \times Y \times Z)$  if for any  $\varphi \in \mathcal{D}(D_T; C_{per}^\infty(Y; C_{per}^\infty(Y)))$ , denoting

$$\lim_{\varepsilon, \varepsilon_1 \rightarrow 0} \int_{D_T} c^{\varepsilon, \varepsilon_1}(\mathbf{r}, t) \varphi\left(\mathbf{r}, \frac{\mathbf{r}}{\varepsilon}, \frac{\mathbf{r}}{\varepsilon_1 \varepsilon}, t\right) d\mathbf{r} dt = \lim_{\varepsilon \rightarrow 0} \left( \lim_{\varepsilon_1 \rightarrow 0} \int_{D_T} c^{\varepsilon, \varepsilon_1}(\mathbf{r}, t) \varphi\left(\mathbf{r}, \frac{\mathbf{r}}{\varepsilon}, \frac{\mathbf{r}}{\varepsilon_1 \varepsilon}, t\right) d\mathbf{r} dt \right), \quad (2.1.155)$$

the following relation is valid

$$\lim_{\varepsilon, \varepsilon_1 \rightarrow 0} \int_{D_T} c^{\varepsilon, \varepsilon_1}(\mathbf{r}, t) \varphi\left(\mathbf{r}, \frac{\mathbf{r}}{\varepsilon}, \frac{\mathbf{r}}{\varepsilon_1 \varepsilon}, t\right) d\mathbf{r} dt = \frac{1}{|Y||Z|} \int_{D_T \times Y \times Z} c_0(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \varphi(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt. \quad (2.1.156)$$

**Remark 2.17.** In the same context we can define the reiterated unfolding operator  $\mathcal{T}_{\varepsilon \circ \varepsilon_1} : L^2(D) \rightarrow L^2(D \times Y \times Z)$ , such that

$$\mathcal{T}_{\varepsilon \circ \varepsilon_1}(\widetilde{c^{\varepsilon, \varepsilon_1}})(\mathbf{r}, \mathbf{y}, \mathbf{y}_1) = \widetilde{c^{\varepsilon, \varepsilon_1}}\left(\varepsilon \left\lfloor \frac{\mathbf{r}}{\varepsilon} \right\rfloor_Y + \varepsilon \varepsilon_1 \left\lfloor \frac{\mathbf{y}}{\varepsilon} \right\rfloor_Z + \varepsilon \varepsilon_1 \mathbf{y}_1\right) = c_0(\mathbf{r}, \mathbf{y}, \mathbf{y}_1), \quad (2.1.157)$$

which allows to capture the oscillatory effects at both scales  $\varepsilon$  and  $\varepsilon \varepsilon_1$  and leads to an effective (but artificial) separation of the scale effects [158, 182, 185]. Moreover, we can very naturally extend this definition for both space and time-dependent functions and also the convergence of the gradient

$$\mathcal{T}_{\varepsilon \circ \varepsilon_1}(\nabla_{\mathbf{r}} \widetilde{c^{\varepsilon, \varepsilon_1}}) \rightarrow \nabla c_0 + \nabla_{\mathbf{y}} c_1 + \nabla_{\mathbf{y}_1} c_1^* \text{ in } L^2(D_T \times Y \times Z). \quad (2.1.158)$$

We also extending the integral preserving property of the unfolding operator (see 2.8) in the three-scale case as follows:

$$\|\mathcal{T}_{\varepsilon \circ \varepsilon_1}(\widetilde{c^{\varepsilon, \varepsilon_1}})\|_{L^p(D_T \times Y \times Z)} = |Y|^{1/p} |Z|^{1/p} \|\widetilde{c^{\varepsilon, \varepsilon_1}}\|_{L^p(D_T)}, \quad (2.1.159)$$

for all  $\widetilde{c^{\varepsilon, \varepsilon_1}} \in L^p(D_T)$ .

In the same context, H. Duanla and J-L. Woukeng [192] as well as N. Svansedt and J-L. Woukeng [194] recently examined a reiterated homogenization approach over two-space scales  $\mathbf{r}, \mathbf{r}/\varepsilon$  one and two-time scales  $t, t/\varepsilon^k$  of semi-linear reaction-diffusion equations of the general form

$$k\left(\frac{\mathbf{r}}{\varepsilon}\right) \partial_t c^\varepsilon(\mathbf{r}, t) = \operatorname{div}\left(A\left[\frac{\mathbf{r}}{\varepsilon}, \frac{\mathbf{r}}{\varepsilon^2}\right] \nabla c^\varepsilon(\mathbf{r}, t)\right) + \varepsilon^{-1} g\left(\frac{\mathbf{r}}{\varepsilon}, \frac{\mathbf{r}}{\varepsilon^2}, c^\varepsilon(\mathbf{r}, t)\right) \text{ in } D_T^\varepsilon, \quad (2.1.160)$$

where  $A$  is a symmetric positive definite matrix. In addition, as an extension of the classical two-space scale convergence, H. Duanla E. Tetsadjio [190] have also consider the case of three-space scales  $\mathbf{r}, \mathbf{r}/\varepsilon, \mathbf{r}/\varepsilon^2$  and two-time scales  $t, t/\varepsilon^2$  in the homogenization in porous media with tiny periodically distributed holes, of hyperbolic-parabolic equations such as for example

$$k\left(\frac{\mathbf{r}}{\varepsilon^2}\right) \partial_t^2 c^\varepsilon(\mathbf{r}, t) + k_1\left(\frac{\mathbf{r}}{\varepsilon}, \frac{t}{\varepsilon^2}\right) \partial_t c^\varepsilon(\mathbf{r}, t) = \operatorname{div}\left(A\left[\frac{\mathbf{r}}{\varepsilon}, \frac{\mathbf{r}}{\varepsilon^2}\right] \nabla c^\varepsilon(\mathbf{r}, t)\right) + f(\mathbf{r}, t) \text{ in } D_T^\varepsilon, \quad (2.1.161)$$

The models are also supplemented with homogeneous Neumann and Dirichlet boundary conditions and  $H_0^1(D^\varepsilon)$  initial data. Finally, homogenization via multiscale convergence of parabolic problems with an arbitrary number of microscopic scales in space and time, i.e,

$$\partial_t c^\varepsilon(\mathbf{r}, t) = \operatorname{div}\left(A\left[\frac{\mathbf{r}}{\varepsilon^{q_1}}, \dots, \frac{\mathbf{r}}{\varepsilon^{q_n}}, \frac{t}{\varepsilon^{r_1}}, \dots, \frac{t}{\varepsilon^{r_m}}\right] \nabla c^\varepsilon(\mathbf{r}, t)\right) + f(\mathbf{r}, t) \text{ in } D_T^\varepsilon, \quad (2.1.162)$$

as well as reiterated homogenization of heat conduction in composite media, has been recently investigated by L. Floden et al [195] and E. I. Rodrigez et al. [196].

In the sequel, motivated by the previously mentioned articles on reiterated homogenization, we will apply a similar upscaling procedure for the microscopic Allen-Cahn/Cahn-Hilliard formulation with its solution to be defined over two microscopic length scales and one time scale. Finally, our homogenization arguments are also based on a very recent rigorous three-scale convergence approach on the homogenization problem for a stationary Bingham flow in a porous medium with solid obstacles of different size, (see [183]) and we also found useful ideas and motivation in [197–199].

**Theorem 2.1.6 (Homogenized/macroscopic Allen-Cahn/Cahn-Hilliard system).**

Assuming that the extended initial condition converges, i.e.,  $\widetilde{c_{init}^\varepsilon} \xrightarrow{\varepsilon \rightarrow 0} c_{init,0}$  in  $L^2(D)$ , then there exist limiting functions  $c_0, \mu_0 \in L^2(0, T; H^1(D))$  and  $c_1, \mu_1 \in L^2(D_T; H_{per}^1(Y))$  and  $c_1^*, \mu_1^* \in L^2(D_T \times Y; H_{per}^1(Z))$ , such that the related subsequences  $c^\varepsilon$  and  $\mu^\varepsilon$  satisfy the convergence results (2.1.148), indicated in the previous lemma and also the existence and extension results of Remark 2.7 and Theorem 2.1.1 discussed in the previous subsection. In addition, the limiting functions are solutions of the following homogenized/macroscopic Allen-Cahn/Cahn-Hilliard system for isotropic mobility  $\mathbb{M} := m\mathbb{I} := m\{\delta_{ij}\}_{1 \leq i, j \leq d}$ ,  $m > 0$ , i.e.,

$$\begin{cases} p_1 \partial_t c_0(\mathbf{r}, t) = m \operatorname{div}(\mathbb{D}_1 \nabla \mu_0(\mathbf{r}, t)) - p_1 \mu_0(\mathbf{r}, t) & \text{in } D_T, \\ \mu_0(\mathbf{r}, t) = f_L'(c_0(\mathbf{r}, t)) - (p_1)^{-1} \lambda^2 \operatorname{div}(\mathbb{D}_1 \nabla c_0(\mathbf{r}, t)) & \text{in } D_T, \\ \mathbb{D}_1 \nabla_{\mathbf{n}} c_0 = \mathbb{D}_1 \nabla_{\mathbf{n}} (\operatorname{div}(\mathbb{D}_1 \nabla_{\mathbf{r}} c_0(\mathbf{r}, t))) = 0 & \text{on } \partial D_T, \\ c_0(\mathbf{r}, 0) = c_{init,0}(\mathbf{r}, 0) & \text{in } D, \end{cases} \quad (2.1.163)$$

in which we define the porosity  $p_1 := |Y_1| |Z_1| / |Y| |Z|$ . The elements of the effective tensor  $\{(\mathbb{D}_1)_{ij}\}_{1 \leq i, j \leq d}$  are defined by

$$(\mathbb{D}_1)_{ij} := \frac{1}{|Y| |Z|} \int_{Y_1 \times Z_1} \sum_{k, l=1}^d \left( \delta_{ij} - \delta_{il} \frac{\partial \xi^j(\mathbf{y})}{\partial y_l} - \delta_{ik} \frac{\partial (\xi^*)^j(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1k}} + \delta_{il} \frac{\partial (\xi^*)^k(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1l}} \cdot \frac{\partial \xi^j(\mathbf{y})}{\partial y_k} \right) d\mathbf{y} d\mathbf{y}_1, \quad (2.1.164)$$

where the correctors  $\xi^k(\mathbf{y}), (\xi^*)^k(\mathbf{y}, \mathbf{y}_1)$   $k = 1, \dots, d$  are unique, in the sense of distributions, solutions of the following reference cell problems:

$$\begin{cases} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi^k) = 0. \end{cases} \quad (2.1.165)$$

and also

$$\left\{ \begin{array}{l} \sum_{i,k,l=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ij} - \delta_{il} \frac{\partial \xi^j(\mathbf{y})}{\partial y_l} - \delta_{ik} \frac{\partial (\xi^*)^j(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1k}} + \delta_{il} \frac{\partial (\xi^*)^k(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1l}} \cdot \frac{\partial \xi^j(\mathbf{y})}{\partial y_k} \right) = 0 \quad \text{in } Y_1, \\ \sum_{i,k,l=1}^d n_i \left( \delta_{ij} - \delta_{il} \frac{\partial \xi^j(\mathbf{y})}{\partial y_l} - \delta_{ik} \frac{\partial (\xi^*)^j(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1k}} + \delta_{il} \frac{\partial (\xi^*)^k(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1l}} \cdot \frac{\partial \xi^j(\mathbf{y})}{\partial y_k} \right) = 0 \quad \text{on } \partial Y_2, \\ \xi^k(\mathbf{y}) \text{ is } Y \text{ periodic and, } (\xi^*)^k(\mathbf{y}, \mathbf{y}_1) \text{ is } Z\text{-periodic and } \mathcal{M}_{Y_1}(\xi^k) = \mathcal{M}_{Z_1}((\xi^*)^k) = 0. \end{array} \right. \quad (2.1.166)$$

For the proof we make use of the following two Lemmas at a first stage.

**Lemma 2.14 (Three-scale convergence).** *Assuming that the extended initial condition converges, i.e.,  $\widetilde{c_{init}^\varepsilon} \xrightarrow{\varepsilon \rightarrow 0} c_{init,0}$  in  $L^2(D)$ , then there exist two pairs of limiting functions  $c_0, \mu_0 \in L^2(0, T; H^1(D))$ ,  $c_1, \mu_1 \in L^2(D_T; H_{per}^1(Y))$  and  $c_1^*, \mu_1^* \in L^2(D_T \times Y; H_{per}^1(Z))$ , such that the related (not relabeled) subsequences  $\widetilde{c^\varepsilon}$  and  $\widetilde{\mu^\varepsilon}$ , satisfy the following convergence results as  $\varepsilon \rightarrow 0$ :*

- (i)  $\{\widetilde{c^\varepsilon}\}_{\varepsilon > 0}$  converges in the three-scale sense to  $c_0$ ,
  - (ii)  $\{\nabla_{\mathbf{r}} \widetilde{c^\varepsilon}\}_{\varepsilon > 0}$  is three-scale convergent to  $\nabla_{\mathbf{r}} c_0 + \nabla_{\mathbf{y}} c_1 + \nabla_{\mathbf{y}_1} c_1^*$ ,
  - (iii)  $\{\widetilde{\mu^\varepsilon}\}_{\varepsilon > 0}$  converges in the three-scale sense to  $\mu_0$ ,
  - (iv)  $\{\nabla_{\mathbf{r}} \widetilde{\mu^\varepsilon}\}_{\varepsilon > 0}$  is three-scale convergent to  $\nabla_{\mathbf{r}} \mu_0 + \nabla_{\mathbf{y}} \mu_1 + \nabla_{\mathbf{y}_1} \mu_1^*$ .
- (2.1.167)

*Proof.* The convergence in all arguments follows from the estimate (2.1.32), as a result of Lemma 2.13. □

**Lemma 2.15 (Strong convergence and nonlinear term).** *We obtain with the help of the unfolding operator discussed in Definition 2.4, the following convergence results:*

- (i)  $\{\widetilde{c^\varepsilon}\}_{\varepsilon > 0}$  converges to  $c_0$  strongly in  $L^2(D_T)$ ,
  - (ii)  $\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\widetilde{c^\varepsilon})$  to  $c_0$  strongly in  $L^2(D_T \times Y \times Z)$ ,
  - (iii)  $\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\nabla_{\mathbf{r}} \widetilde{\mu^\varepsilon})$  converges weakly to  $\nabla_{\mathbf{r}} \mu_0 + \nabla_{\mathbf{y}} \mu_1 + \nabla_{\mathbf{y}_1} \mu_1^*$  in  $L^2(D_T \times Y \times Z)$ ,
  - (iv)  $f_L'(\widetilde{c^\varepsilon})$  is three-scale convergent to  $f_L'(c)$ .
- (2.1.168)

*Proof.* (i) In light of Remark 2.7 and the estimates (2.1.43), (2.1.113), there exists a subsequence (not relabeled and still denoted by the same index) of the extension  $\{\widetilde{c^\varepsilon}\}_{\varepsilon > 0}$  such that  $\{\widetilde{c^\varepsilon}\}_{\varepsilon > 0} \xrightarrow{\varepsilon \rightarrow 0} c_0$ , strongly in  $L^2(D_T)$ , by Theorem 2.1.3. The convergence in (ii) and (iii) holds straightforwardly by Remark 2.17 due to the estimates (2.1.43) and (2.1.49).

In order to show the argument (iv), we note that the weak two-scale convergence of  $f_L'(\widetilde{c^\varepsilon})$  to  $f_L'(c_0)$  is equivalent to the weak convergence  $\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(f_L'(\widetilde{c^\varepsilon})) := f_L'(\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\widetilde{c^\varepsilon})) \rightharpoonup f_L'(c_0)$ . Then, by the integral conservation property of the unfolding operator (2.1.159), we obtain with the help of the estimate (2.1.116) that there exists a constant  $C_{D,Y,Z}'' > 0$  independent of  $\varepsilon$  that depends on the volumes of the reference cells of type  $Z$  and  $Y$ , such that the following inequality holds

$$\|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\widetilde{c^\varepsilon})\|_{L^4(D_T \times Y \times Z)} = (|Y||Z|)^{1/4} \|\widetilde{c^\varepsilon}\|_{L^4(D_T)} = C_{Y,Z} \|\widetilde{c^\varepsilon}\|_{L^4(D_T)} \leq C_{D,Y,Z}'' \quad (2.1.169)$$

since we assumed that the porous medium consists of periodically distributed reference cells of unit volume, i.e.,  $Y := (0, \ell_1)^d$ ,  $Z := (0, \ell_2)^d$ ,  $d = 2, 3$  and hence  $|Y| = \ell_1^d$  and  $|Z| = \ell_2^d$ ,  $d = 2, 3$ , see Figure 2.7. Furthermore, since  $f_L(c) := (c^2 - 1)^2/4$  and also  $f'_L(c) = c^3 - c$  then, pointwise convergence and the generalized Lebesgue dominated convergence theorem in  $L^p$ -spaces[176] due to the bound (2.1.169), imply that for all test functions  $\varphi \in C_0(D_T; C_{per}^\infty(Y \times Z))$ :

$$\begin{aligned}
 & \left| \int_{D_T \times Y \times Z} f'_L(\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)) \varphi \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt - \int_{D_T \times Y \times Z} f'_L(c_0) \varphi \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt \right| \\
 & \stackrel{\text{Triangle}}{\leq} \int_{D_T \times Y \times Z} \left| (f'_L(\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)) - f'_L(c_0)) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt \\
 & = \int_{D_T \times Y \times Z} \left| ([\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)]^3 - \mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) - c_0^3 + c_0) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt \\
 & \stackrel{\text{Triangle}}{\leq} \int_{D_T \times Y \times Z} \left| ([\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)]^3 - c_0^3) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt + \int_{D_T \times Y \times Z} \left| (\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) - c_0) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt \\
 & \stackrel{\text{Hölder's}}{\leq} \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) - c_0\|_{L^2(D_T \times Y \times Z)} \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)^2 + \mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)c_0 + c_0^2\|_{L^2(D_T \times Y \times Z)} \|\varphi\|_{L^\infty(D_T \times Y \times Z)} \\
 & \quad + \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) - c_0\|_{L^2(D_T \times Y \times Z)} \|\varphi\|_{L^2(D_T \times Y \times Z)}, \tag{2.1.170}
 \end{aligned}$$

Hence, the strong convergence  $\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) \xrightarrow{\varepsilon \rightarrow 0} c_0$  in  $L^2(D_T \times Y \times Z)$  implies

$$\begin{aligned}
 & \lim_{\varepsilon \rightarrow 0} \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) - c_0\|_{L^2(D_T \times Y \times Z)} \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)^2 + \mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)c_0 + c_0^2\|_{L^2(D_T \times Y \times Z)} \|\varphi\|_{L^\infty(D_T \times Y \times Z)} \\
 & \quad + \lim_{\varepsilon \rightarrow 0} \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) - c_0\|_{L^2(D_T \times Y \times Z)} \|\varphi\|_{L^2(D_T \times Y \times Z)} = 0, \tag{2.1.171}
 \end{aligned}$$

since

$$\begin{aligned}
 & \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) (\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) + c_0) + c_0^2\|_{L^2(D_T \times Y \times Z)}^2 = \int_{D_T \times Y \times Z} [\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)]^2 (\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) + c_0)^2 \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt \\
 & \quad + 2 \int_{D_T \times Y \times Z} \mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) (\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon) + c_0) c_0^2 \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt \\
 & \quad + \int_{D_T \times Y \times Z} |c_0|^4 \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt \\
 & \leq C_1 \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)\|_{L^4(D_T \times Y \times Z)}^4 + C_2 |Y| |Z| \|c_0\|_{L^4(D_T)}^4 \\
 & \quad + 2|Y| |Z| \|\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)\|_{L^2(D_T \times Y \times Z)} \|c_0\|_{L^2(D_T)} \\
 & \leq C_D''', \tag{2.1.172}
 \end{aligned}$$

which follows by Hölder's and Young's inequality and also the bound (2.1.169). As a result

$$\lim_{\varepsilon \rightarrow 0} \int_{D_T \times Y \times Z} f'_L(\mathcal{T}_{\varepsilon_1 \circ \varepsilon}(\tilde{c}^\varepsilon)) \varphi \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt = \int_{D_T \times Y \times Z} f'_L(c_0) \varphi \, d\mathbf{r} \, d\mathbf{y} \, d\mathbf{y}_1 \, dt. \tag{2.1.173}$$

□

*Proof of Theorem 2.1.6.* Since we have so far verified the three-scale convergence of the related terms we are now able to continue with the homogenization procedure under similar arguments as for the two-scale case. To capture all the microscopic and mesoscopic behaviours of the phenomenon modelled by problem (2.1.24), we choose functions  $\phi_0 \in C_0^\infty(D_T)$  and  $\phi_1 \in C_0^\infty(D_T; C_{per}^\infty(Y))$ ,  $\tilde{\phi}_1 \in C_0^\infty(D_T; C_{per}^\infty(Y \times Z))$  and we plug the test function

$$\phi^{\varepsilon, \varepsilon_1}(\mathbf{r}, t) = \phi_0(\mathbf{r}, t) + \varepsilon \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \varepsilon \varepsilon_1 \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t), \tag{2.1.174}$$

in the weak Allen-Cahn/Cahn-Hilliard microscopic formulation (2.1.24). We will also make use of the three-scale spatial differential property, i.e.,

$$\nabla \rightarrow \nabla_{\mathbf{r}} + \varepsilon^{-1} \nabla_{\mathbf{y}} + (\varepsilon_1 \varepsilon)^{-1} \nabla_{\mathbf{y}_1} \tag{2.1.175}$$

and we additionally assume that the flow is taking place inside the intersections of all the pore-phase parts  $Y_1, Z_1$  of each type of reference reference cells  $Y, Z$ . Thus, we obtain

$$\begin{aligned}
 & - \int_{D_T^\varepsilon} c^\varepsilon(\mathbf{r}, t) \left( \partial_t \phi_0(\mathbf{r}, t) + \varepsilon \partial_t \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \varepsilon_1 \varepsilon \partial_t \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 & - \int_{D_T^\varepsilon} \mu^\varepsilon(\mathbf{r}, t) \left( \phi_0(\mathbf{r}, t) + \varepsilon \partial_t \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \varepsilon_1 \varepsilon \partial_t \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 = & -\mathbb{M} \int_{D_T^\varepsilon} \nabla_{\mathbf{r}} \mu^\varepsilon(\mathbf{r}, t) \cdot \left( \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) + \varepsilon \nabla_{\mathbf{r}} \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 & -\mathbb{M} \int_{D_T^\varepsilon} \nabla_{\mathbf{r}} \mu^\varepsilon(\mathbf{r}, t) \cdot \left( \varepsilon_1 \varepsilon \nabla_{\mathbf{r}} \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) + \varepsilon_1 \nabla_{\mathbf{y}} \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt. \quad (2.1.176)
 \end{aligned}$$

Equivalently we obtain the extension to the macroscopic domain  $D$  with the help of the characteristic function which can be defined by  $\chi_{D^\varepsilon}(\mathbf{r}) := \chi_{Y_1}\left(\frac{\mathbf{r}}{\varepsilon}\right) \chi_{Z_1}\left(\frac{\mathbf{r}}{\varepsilon \varepsilon_1}\right)$ ,  $\mathbf{r} \in D$ , and we can pass to the limit  $\varepsilon \rightarrow 0$  in the three-scale sense using the property (2.1.145), i.e.,  $\lim_{\varepsilon \rightarrow 0} \varepsilon_1(\varepsilon)/\varepsilon = 0$ . Hence, we deduce

$$\begin{aligned}
 & |Y_1||Z_1| \int_{D_T} c_0(\mathbf{r}, t) \partial_t \phi_0(\mathbf{r}, t) d\mathbf{r} dt + |Y_1||Z_1| \int_{D_T} \mu_0(\mathbf{r}, t) \phi_0(\mathbf{r}, t) d\mathbf{r} dt \\
 = & \mathbb{M} \int_{D_T \times Y_1 \times Z_1} \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) \cdot \left( \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt \\
 & + \mathbb{M} \int_{D_T \times Y_1 \times Z_1} \left( \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \mu_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) \cdot \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt \\
 & + \mathbb{M} \int_{D_T \times Y_1 \times Z_1} \left( \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \mu_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) \cdot \left( \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt. \quad (2.1.177)
 \end{aligned}$$

Therefore, if we choose  $\phi_0 = 0$  and  $\phi_1, \tilde{\phi}_1 \neq 0$ , we deduce that

$$\begin{aligned}
 & -\mathbb{M} \int_{D_T \times Y_1 \times Z_1} \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) \cdot \left( \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt \\
 = & \mathbb{M} \int_{D_T \times Y_1 \times Z_1} \left( \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \mu_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) \cdot \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt \\
 & + \mathbb{M} \int_{D_T \times Y_1 \times Z_1} \left( \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \mu_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) \cdot \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt, \quad (2.1.178)
 \end{aligned}$$

which implies after integration by parts, that

$$\begin{cases} -\nabla_{\mathbf{y}} \cdot \left( \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \mu_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) = \nabla_{\mathbf{y}} \cdot \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t), \\ -\nabla_{\mathbf{y}_1} \cdot \left( \nabla_{\mathbf{y}_1} \mu_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) + \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) \right) = \nabla_{\mathbf{y}_1} \cdot \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t). \end{cases} \quad (2.1.179)$$

In the same way, if we choose  $\phi_1 = \tilde{\phi}_1 = 0$  and  $\phi_0 \neq 0$ , we deduce from (2.1.177) that,

$$\begin{aligned}
 & |Y_1||Z_1| \int_{D_T} c_0(\mathbf{r}, t) \partial_t \phi_0(\mathbf{r}, t) d\mathbf{r} dt + \int_{D_T} |Y_1||Z_1| \mu_0(\mathbf{r}, t) \phi_0(\mathbf{r}, t) d\mathbf{r} dt \\
 = & \mathbb{M} \int_{D_T \times Y_1 \times Z_1} \left( \nabla_{\mathbf{r}} \mu_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \mu_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) \cdot \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt. \quad (2.1.180)
 \end{aligned}$$

This yields the following homogenized equation

$$\partial_t c_0(\mathbf{r}, t) + \mu_0(\mathbf{r}, t) + \mathbb{M} \Delta_{\mathbf{r}} \mu_0(\mathbf{r}, t) = -\mathbb{M} \nabla_{\mathbf{r}} \cdot \left( \frac{1}{|Y_1||Z_1|} \int_{Y_1 \times Z_1} \left( \nabla_{\mathbf{y}} \mu_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \mu_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) d\mathbf{y} d\mathbf{y}_1 \right). \quad (2.1.181)$$

In the same way, the weak formulation for the chemical potential reads

$$\begin{aligned}
 & \int_{D_T^\varepsilon} \mu^\varepsilon(\mathbf{r}, t) \left( \partial_t \phi_0(\mathbf{r}, t) + \varepsilon \partial_t \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \varepsilon_1 \varepsilon \partial_t \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 &= \int_{D_T^\varepsilon} f_L'(c^\varepsilon) \left( \phi_0(\mathbf{r}, t) + \varepsilon \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \varepsilon_1 \varepsilon \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 &+ \lambda^2 \int_{D_T^\varepsilon} \nabla c^\varepsilon(\mathbf{r}, t) \left( \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) + \varepsilon \nabla_{\mathbf{r}} \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 &+ \lambda^2 \int_{D_T^\varepsilon} \nabla c^\varepsilon(\mathbf{r}, t) \left( \varepsilon_1 \varepsilon \nabla_{\mathbf{r}} \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) + \varepsilon_1 \nabla_{\mathbf{y}} \tilde{\phi}_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, (\varepsilon \varepsilon_1)^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \quad (2.1.182)
 \end{aligned}$$

and we obtain after taking the upscaling limit  $\varepsilon \rightarrow 0$  with the help of the characteristic function  $\mathcal{X}_{D^\varepsilon}(\mathbf{r})$  similarly as above, that

$$\begin{aligned}
 & |Y_1| |Z_1| \int_{D_T} \mu_0(\mathbf{r}, t) \phi_0(\mathbf{r}, t) d\mathbf{r} dt - |Y_1| |Z_1| \int_{D_T} f_L'(c(\mathbf{r}, t)) \phi_0(\mathbf{r}, t) d\mathbf{r} dt \\
 &= \lambda^2 |Y_1| |Z_1| \int_{D_T} \nabla_{\mathbf{r}} c_0(\mathbf{r}, t) \cdot \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) d\mathbf{r} dt \\
 &+ \lambda^2 \int_{D_T} \left( \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} c_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) \cdot \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt \\
 &+ \lambda^2 \int_{D_T \times Y_1 \times Z_1} \left( \nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \left( \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) \right) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt \\
 &+ \lambda^2 \int_{D_T \times Y_1 \times Z_1} \nabla_{\mathbf{y}_1} c_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \cdot \left( \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) \right) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt \quad (2.1.183)
 \end{aligned}$$

Hence, for  $\phi_0 = 0$  (2.1.183) can be simplified further to

$$\left( \nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} c_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) \cdot \left( \nabla_{\mathbf{y}_1} \tilde{\phi}_1(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) + \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) \right) = 0, \quad (2.1.184)$$

which additionally yields

$$\begin{cases} -\nabla_{\mathbf{y}} \cdot \left( \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} c_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) = \nabla_{\mathbf{y}} \cdot \nabla_{\mathbf{r}} c_0(\mathbf{r}, t), \\ -\nabla_{\mathbf{y}_1} \cdot \left( \nabla_{\mathbf{y}_1} c_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) \right) = \nabla_{\mathbf{y}_1} \cdot \nabla_{\mathbf{r}} c_0(\mathbf{r}, t). \end{cases} \quad (2.1.185)$$

The combination of the relationships in (2.1.179), (2.1.185) separately and by setting  $\xi_z^*(\mathbf{y}, \mathbf{y}_1) := (\xi_z^*)_i(\mathbf{y}, \mathbf{y}_1)$ ,  $1 \leq i \leq d$ ,  $z = \{\mu, c\}$ , leads by virtue of linearity and for almost everywhere in  $D_T \times Y \times Z$ , the following decoupling of variables:

$$\tilde{z}_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) = - \sum_{j=1}^d (\xi_z^*)^j(\mathbf{y}, \mathbf{y}_1) \left( \frac{\partial z_0(\mathbf{r}, t)}{\partial r_j} + \frac{\partial z_1(\mathbf{r}, \mathbf{y}, t)}{\partial y_j} \right), \quad z = \{\mu, c\}. \quad (2.1.186)$$

Hence, on setting  $(\nabla_{\mathbf{y}_1} \xi_z^*)_{ij} = \frac{\partial (\xi_z^*)^i}{\partial y_{1j}}$ , ( $1 \leq i, j \leq d$ ), we deduce for either  $z = \mu$  or  $z = c$  from (2.1.186) that

$$\nabla_{\mathbf{y}_1} \tilde{z}_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) = - \nabla_{\mathbf{y}_1}^T \xi_z^*(\mathbf{y}, \mathbf{y}_1) \cdot \left( \nabla_{\mathbf{r}} z_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} z_1(\mathbf{r}, \mathbf{y}, t) \right). \quad (2.1.187)$$

Moreover, choosing  $\phi_0 = \tilde{\phi}_1 = 0$  in (2.1.183) and by the weak form of the second equation in (2.1.179), provides that

$$\int_{D_T \times Y_1 \times Z_1} \left( \nabla_{\mathbf{r}} z_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} z_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} \tilde{z}_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \right) \cdot \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} d\mathbf{y}_1 dt = 0, \quad z = \{\mu, c\}, \quad (2.1.188)$$

which in view of (2.1.187) can be further simplified to

$$\begin{aligned} & \int_{D_T \times Y_1} \left( \int_{Z_1} (\mathbb{I} - \nabla_{\mathbf{y}_1}^T \xi_z^*(\mathbf{y}, \mathbf{y}_1)) d\mathbf{y}_1 \right) \nabla_{\mathbf{r}z_0}(\mathbf{r}, t) \cdot \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} dt \\ &= - \int_{D_T \times Y_1} \left( \int_{Z_1} (\mathbb{I} - \nabla_{\mathbf{y}_1}^T \xi_z^*(\mathbf{y}, \mathbf{y}_1)) d\mathbf{y}_1 \right) \nabla_{\mathbf{y}z_1}(\mathbf{r}, \mathbf{y}, t) \cdot \nabla_{\mathbf{y}} \phi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} dt, \quad z = \{\mu, c\}. \end{aligned} \quad (2.1.189)$$

Taking  $\phi_1 = \varphi \otimes \psi$  where  $\varphi \in C_0^\infty(D_T)$  and  $\psi \in C_{per}^\infty(Y)$  arbitrary functions and hence for almost every  $(\mathbf{r}, t) \in D_T$ , the functions  $z_1(\mathbf{r}, t) \in H_{per}^1(Y)$ ,  $z = \{\mu, c\}$  are unique solutions to the following variational problems (one for  $z = c$  and one other for  $z = \mu$ ):

$$\begin{aligned} & \int_{Y_1} \left( \int_{Z_1} (\mathbb{I} - \nabla_{\mathbf{y}_1}^T \xi_z^*(\mathbf{y}, \mathbf{y}_1)) d\mathbf{y}_1 \right) \nabla_{\mathbf{r}z_0}(\mathbf{r}, t) \cdot \nabla_{\mathbf{y}} \psi(\mathbf{y}) d\mathbf{y} \\ &= - \int_{Y_1} \left( \int_{Z_1} (\mathbb{I} - \nabla_{\mathbf{y}_1}^T \xi_z^*(\mathbf{y}, \mathbf{y}_1)) d\mathbf{y}_1 \right) \nabla_{\mathbf{y}z_1}(\mathbf{r}, t) \cdot \nabla_{\mathbf{y}} \psi(\mathbf{y}) d\mathbf{y}, \quad \forall \psi \in H_{per}^1(Y). \end{aligned} \quad (2.1.190)$$

Moreover, setting  $I_{\xi_z^*}(\mathbf{y}) := \int_{Z_1} (\mathbb{I} - \nabla_{\mathbf{y}_1}^T \xi_z^*(\mathbf{y}, \mathbf{y}_1)) d\mathbf{y}_1$ ,  $\mathbf{y} \in Y$  in (2.1.190), we recall that there exist unique solutions  $\xi_z := (\xi_z^i)_{1 \leq i \leq d} \in (H_{per}^1(Y))_d$  of the following local variational formulations:

$$\begin{cases} \xi_z^i(\mathbf{y}) \in H_{per}^1(Y), \\ \int_{Y_1} I_{\xi_z^*}(\mathbf{y}) \nabla_{\mathbf{y}} \xi_z^i(\mathbf{y}) \cdot \nabla_{\mathbf{y}} v(\mathbf{y}) d\mathbf{y} = \int_{Y_1} \sum_k (I_{\xi_z^*}(\mathbf{y}))_{ik} \frac{\partial v(\mathbf{y})}{\partial y_k} d\mathbf{y}, \quad i = 1, \dots, d, \end{cases} \quad (2.1.191)$$

for all  $v \in H_{per}^1(Y)$ . We can easily deduce that the functions  $(\mathbf{r}, \mathbf{y}, t) \mapsto \xi_z(\mathbf{y}) \cdot \nabla_{\mathbf{r}z_0}(\mathbf{r}, t)$ ,  $z = \{\mu, c\}$  are also a solution to (2.1.190) and hence by uniqueness (see [192, Prop. 4.4], [190, Part 5.3] and Remark 2.12), we can deduce for  $z = \{c, \mu\}$  that

$$z_1(\mathbf{r}, \mathbf{y}, t) = - \sum_{i=1}^d \xi_z^i(\mathbf{y}) \frac{\partial z_0(\mathbf{r}, t)}{\partial r_i} \quad \text{for a.e. } (\mathbf{y}, \mathbf{r}, t) \in Y \times D_T \quad (2.1.192)$$

and consequently we can also define its gradients by

$$\nabla_{\mathbf{y}z_1}(\mathbf{r}, \mathbf{y}, t) = - \nabla_{\mathbf{y}} \xi_z(\mathbf{y}) \cdot \nabla_{\mathbf{r}z_0}(\mathbf{r}, t). \quad (2.1.193)$$

In light of the ansatz (2.1.192) the above relation implies that the the correctors  $\xi_z^k(\mathbf{y})$ ,  $k = 1, \dots, d$  are solutions of the following reference cell problems for  $z = \{c, \mu\}$ :

$$\begin{cases} - \sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial \xi_z^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi_z^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ \xi_z^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi_z^k) = 0. \end{cases} \quad (2.1.194)$$

Moreover, in view of (2.1.186) and (2.1.192) the relations (2.1.187), (2.1.191) and (2.1.188), we can identify the following cell problems

$$\begin{cases} \sum_{i,k,l=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ij} - \delta_{il} \frac{\partial \xi_z^j(\mathbf{y})}{\partial y_l} - \delta_{ik} \frac{\partial (\xi_z^*)^j(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1k}} + \delta_{il} \frac{\partial (\xi_z^*)^k(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1l}} \cdot \frac{\partial \xi_z^j(\mathbf{y})}{\partial y_k} \right) = 0 & \text{in } Y_1, \\ \sum_{i,k,l=1}^d n_i \left( \delta_{ij} - \delta_{il} \frac{\partial \xi_z^j(\mathbf{y})}{\partial y_l} - \delta_{ik} \frac{\partial (\xi_z^*)^j(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1k}} + \delta_{il} \frac{\partial (\xi_z^*)^k(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1l}} \cdot \frac{\partial \xi_z^j(\mathbf{y})}{\partial y_k} \right) = 0 & \text{on } \partial Y_2, \\ \xi_z^k(\mathbf{y}) \text{ is } Y \text{ periodic and, } (\xi_z^*)^k(\mathbf{y}, \mathbf{y}_1) \text{ is } Z\text{-periodic and } \mathcal{M}_{Y_1}(\xi_z^k) = \mathcal{M}_{Z_1}((\xi_z^*)^k) = 0. \end{cases} \quad (2.1.195)$$



As a result, in light of (2.1.194) and (2.1.195), we can identify the equivalence between the different families of correctors, i.e.,  $(\xi^*)^k := (\xi_c^*)^k = (\xi_\mu^*)^k$ ,  $k = 1, \dots, d$  and also  $\xi^k := \xi_c^k = \xi_\mu^k$ ,  $k = 1, \dots, d$ . Analogously for  $\phi_1 = \tilde{\phi}_1 = 0$  and  $\phi_0 \neq 0$ , we obtain the weak formulation

$$\begin{aligned} \int_{\tilde{D}_{1T}} \mu_0(\mathbf{r}, t) \phi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dy_1 \, dt &= \int_{\tilde{D}_{1T}} f'_L(c(\mathbf{r}, t)) \phi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dy_1 \, dt \\ &+ \lambda^2 \int_{\tilde{D}_{1T}} (\nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} c_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t)) \cdot \nabla_{\mathbf{r}} \phi_0(\mathbf{r}, t) \, d\mathbf{r} \, dy \, dy_1 \, dt, \end{aligned} \quad (2.1.196)$$

which subsequently implies the upscaled chemical potential

$$\mu_0(\mathbf{r}, t) = f'_L(c(\mathbf{r}, t)) - \frac{\lambda^2}{p_1} \nabla_{\mathbf{r}} \left( \nabla_{\mathbf{r}} c_0(\mathbf{r}, t) + \frac{1}{|Y||Z|} \int_{Y_1 \times Z_1} \nabla_{\mathbf{y}} c_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} c_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t) \, dy \, dy_1 \right), \quad (2.1.197)$$

where  $p_1 := |Y_1||Z_1|/|Y||Z|$  denotes the porosity of the composite medium. As a result, in view of (2.1.193) and (2.1.187), we can rewrite (2.1.197), as follows:

$$\mu_0(\mathbf{r}, t) = f'_L(c_0(\mathbf{r}, t)) - \frac{\lambda^2}{p_1} \operatorname{div}(\mathbb{D}_1 \nabla_{\mathbf{r}} c_0(\mathbf{r}, t)), \quad (2.1.198)$$

where we defined the elements of the effective tensor by

$$(\mathbb{D}_1)_{ij} := \frac{1}{|Y||Z|} \int_{Y_1 \times Z_1} \sum_{k, l=1}^d \left( \delta_{ij} - \delta_{il} \frac{\partial \xi^j(\mathbf{y})}{\partial y_l} - \delta_{ik} \frac{\partial (\xi^*)^j(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1k}} + \delta_{il} \frac{\partial (\xi^*)^k(\mathbf{y}, \mathbf{y}_1)}{\partial y_{1l}} \cdot \frac{\partial \xi^j(\mathbf{y})}{\partial y_k} \right) dy \, dy_1. \quad (2.1.199)$$

Finally in view of the related boundary conditions

$$[\nabla_{\mathbf{r}} z_0(\mathbf{r}, t) + z_1^{av}(\mathbf{r}, t)] \cdot \mathbf{n} = 0, \quad z = \{\mu, c\} \text{ on } \partial D_T, \quad (2.1.200)$$

where we defined

$$z_1^{av}(\mathbf{r}, t) := \frac{1}{|Y_1||Z_1|} \int_{Y_1 \times Z_1} (\nabla_{\mathbf{y}} z_1(\mathbf{r}, \mathbf{y}, t) + \nabla_{\mathbf{y}_1} z_1^*(\mathbf{r}, \mathbf{y}, \mathbf{y}_1, t)) \, dy \, dy_1, \quad z = \{\mu, c\}, \quad (2.1.201)$$

we further obtain with the help of (2.1.186), (2.1.192) and the definition of the effective tensor (2.1.199), that

$$\mathbb{D}_1 \nabla_{\mathbf{n}} c_0 = 0 \text{ on } \partial D_T. \quad (2.1.202)$$

Similarly we also deduce the no-flux condition

$$\begin{aligned} \mathbb{D}_1 \nabla_{\mathbf{n}} \mu_0 &:= \mathbf{n} \cdot \mathbb{D}_1 f''_L(c_0(\mathbf{r}, t)) \nabla c_0 - \frac{\lambda^2}{p_1} \mathbb{D}_1 \nabla_{\mathbf{n}} (\operatorname{div}(\mathbb{D}_1 \nabla_{\mathbf{r}} c_0(\mathbf{r}, t))) \\ &= -\frac{\lambda^2}{p_1} \mathbb{D}_1 \nabla_{\mathbf{n}} (\operatorname{div}(\mathbb{D}_1 \nabla_{\mathbf{r}} c_0(\mathbf{r}, t))) = 0 \text{ on } \partial D_T \end{aligned} \quad (2.1.203)$$

and since by assumption  $\lambda^2, p \neq 0$ , we end up with the following simplified form of the boundary conditions

$$\mathbb{D}_1 \nabla_{\mathbf{n}} c_0 = \mathbb{D}_1 \nabla_{\mathbf{n}} (\operatorname{div}(\mathbb{D}_1 \nabla_{\mathbf{r}} c_0(\mathbf{r}, t))) = 0 \text{ on } \partial D_T \quad (2.1.204)$$

and the proof of Theorem 2.1.6 is completed.  $\square$

**Remark 2.18.** *An interesting fact is that the homogenization limit formulation obtained for the three-scale case in Theorem 2.1.6 has many similarities with the one in Theorem 2.1.5, especially in the general form of the upscaled equations. The influence of the presence of the*

extra microscale, provides different results in more precisely the expression for the effective tensor (2.1.263, (2.1.164), the corresponding correctors and of course the definition of the porosity, which in the two-scale case is defined by  $p := |Y_1|/|Y|$  and in the three-scale is obviously more involved, i.e.,  $p_1 := |Y_1||Z_1|/|Y||Z|$ .

### 2.1.5 Multiphase-ternary mixtures and homogenization.

We extend our previous considerations to the study of mixtures with more than two substances [200–202], which also involve the presence of more than two phases. To the best of our knowledge there are a various attempts to model and investigate the properties and existence-regularity of solutions to multicomponent flows. Moreover, C. M. Elliott and H. Garcke [203] extended their study on well-posedness for the classical Cahn-Hilliard equation (see Theorem 1.2.4 and [7]) and verified global existence of solutions for a model of fourth-order degenerate parabolic partial differential equations with concentration dependent mobility matrix. The particular system can be derived by the Onsager Principle or gradient flow formulations, as an extension of the classical Cahn-Hilliard formulation of  $M$ -component conserved order parameters  $\mathbf{c} := [c_1, \dots, c_M]$ , based on a generalised Ginzburg-Landau free energy of the form:

$$F_{GM}(\mathbf{c}) := \int_D K(\Theta) \sum_{i=1}^M \alpha_i c_i \ln(c_i) + \frac{1}{2} \mathbf{c} \cdot \mathbb{A} \mathbf{c} + \frac{1}{2} \nabla \mathbf{c} \cdot \mathbb{B} \nabla \mathbf{c} \, dr, \quad (2.1.205)$$

where the elements of the symmetric  $M \times M$  matrix  $\mathbb{A}$  are the interaction parameters and those of the symmetric and positive definite  $\mathbb{B}$  are gradient energy parameters.

As a continuation of the coupling with Navier-Stokes, reactive flow models in the context of combustion in complex chemistry and nonlinear multicomponent reaction-diffusion equations are also being considered, such as the one in [207], in which the authors are dealing with a system of Navier-Stokes coupled with a Cahn-Hilliard with advection type of evolution for the different mass fractions of the components and a nonlinear convection diffusion equation, for the evolution of the temperature field. In addition, a comprehensive survey of global existence of solutions and regularity arguments for systems of reaction-diffusion systems arising in population dynamics, chemistry and theory of electromigration is provided in [208].

A similar study related to the global existence of solutions, has been carried out in [209], where the model under investigation consists of the classical momentum balance coupled with mass and total energy balances and a Cahn-Hilliard with advection type balance for the species mass fractions. Another interesting thermodynamic approach on modelling multiphase multicomponent flows can be found in [210], where the authors are just dealing with a general overview of the constitutive equations in this case, their variational structure and properties. Finally the corresponding sharp interface limits using the method of matched asymptotic expansions, for multicomponent alloys, have been examined by H. Garcke and B. Stinner in [211], analogously as the approximation of the Mullins-Sekerka flow by the classical one component Cahn-Hilliard model discussed in [19, 212, 213]. Furthermore, multicomponent reactive flows for a number of diluted

chemical species in a saturated periodically varying media and homogenization, have been also investigated more recently by G. Allaire and H. Hutridurga in [214, 215].

Finally, A. Jüngel and M. Ptashnyk in a very recent work [161] combine a rigorous two-scale convergence approach and the boundedness-by-entropy method [174], for homogenization of strongly coupled cross-diffusion  $M$ -component  $\mathbf{c}^\varepsilon := [c_1^\varepsilon, \dots, c_M^\varepsilon]$  flows with a formal gradient flow or entropy structure and reactions  $R_i(\mathbf{c}^\varepsilon) : \mathbb{R}^M \rightarrow \mathbb{R}$  in a periodically structured porous domain  $D^\varepsilon$ , such as, e.g,

$$\partial_t c_i^\varepsilon = \operatorname{div} \left( \sum_{j=1}^M \mathbb{M}_{ij}(\mathbf{c}^\varepsilon) \nabla c_j^\varepsilon \right) + R_i(\mathbf{c}^\varepsilon) \text{ in } D_T^\varepsilon, \quad i, j = 1, \dots, M, \quad (2.1.206)$$

where the tensor  $\mathbb{M}(\mathbf{c}^\varepsilon) = \{\mathbb{M}_{ij}(\mathbf{c}^\varepsilon)\}_{i,j=1,\dots,M}$  admits the non-local degeneracy structure  $\mathbb{M}_{ij}(\mathbf{c}^\varepsilon) = D_i(\delta_{ij}c_{M+1}^\varepsilon + c_i^\varepsilon)$ ,  $i, j = 1, \dots, M$ , with  $D_i > 0$  and the constraint  $c_{M+1}^\varepsilon = 1 - \sum_{i=1}^M c_i^\varepsilon$ . In our case, we will focus on the study of multiphase ternary alloys in the periodic porous media setting, however we will not consider coupling with fluid flow (Navier-Stokes). For a model like this we subsequently derive effective/homogenized evolution equations, using formal two-scale convergence arguments.

**Derivation of the model.** As an extension to the C. M. Elliott and H. Garcke multi-component free energy density approach (2.1.205), the modelling of dynamic behaviour in multiphase-ternary flows is based on an abstract free energy functional initially introduced by Wheeler-Boettinger-McFadden (WBM) in [216, 217] in the context of binary mixtures, who apart from the composition variable  $c$  imposed an extra non-conserved order parameter  $\phi$  (phase function) to indicate which regions of the system are solid ( $\phi = 1$ ) and which are liquid ( $\phi = 0$ ). To this end, they adapt the classical binary Cahn-Hilliard free energy

$$\mathcal{F}(c) = \int_D f_L(c) + \frac{\lambda^2}{2} |\nabla c|^2 \, d\mathbf{r}, \quad (2.1.207)$$

which accounts only for the composition function  $c$ , to a formulation for again a binary mixture involving the extra order phase parameter  $\phi$  apart from  $c$  and the corresponding extra gradient penalty term, namely

$$\mathcal{F}_{WBM}(\phi, c) := \int_D F_{WBM}(\phi, c) \, d\mathbf{r} := \int_D f_0(c, \phi, \Theta) + \frac{\lambda_c^2}{2} |\nabla c|^2 + \frac{\lambda_\phi^2}{2} |\nabla \phi|^2 \, d\mathbf{r}, \quad (2.1.208)$$

where the homogeneous free energy density  $f_0(c, \phi, \Theta)$  (with  $\Theta$  denoting the temperature) advances phase separation in the absence of interfacial energies. The physical interpretation of the functional  $\mathcal{F}_{WBM}(\phi, c)$  is that it actually models a diffuse interface as an interpolation between phases in which the compositions of phases at the interface are equal and therefore the phase and composition gradients are considered to cross each other in the state of equilibrium in order to form an interface, and the gradient squared terms flatten this interface and introduce interfacial energy. The evolution of the phase function was proposed to be modelled by Allen-Cahn dynamics ensuring that the total amount of solute is conserved, i.e.,

$$\partial_t \phi = -\tilde{M}_\phi \partial_\phi F_{WBM}(\phi, c) \quad (2.1.209)$$

and the composition evolution by the Cahn-Hilliard dynamics with a degenerate type of diffusion coefficient, that is,

$$\partial_t c = \tilde{M}_c \operatorname{div} [c(1-c) \nabla \partial_c F_{WBM}(\phi, c)], \quad (2.1.210)$$

for scalar constants  $\tilde{M}_\phi, \tilde{M}_c > 0$  (see also [216]). This idea was later extended by D. A. Gogswell and W. C. Carter to  $M$ -component mixtures with compositions  $c_i, i = 1, \dots, M$  under the assumption of the presence of  $N$  different phases  $\phi_\alpha, \alpha = 1, \dots, N$  [15]. In comparison to the two-phase binary systems that has been already studied in the previous subsections, the extension to multiphase and multicomponent systems with the additional degrees of freedom, imply a more complex situation. Hence, we restrict ourselves to the simplest case of a three-component/multiphase mixture in the periodic porous media setting and we will extensively discuss a rigorous two-scale convergence homogenization approach similar to the proof of Theorem 2.1.5, after formally deriving the model in the homogeneous setting via gradient flows (see Theorem 2.1.7). These type of ternary-multiphase systems were introduced for simulation of problems such as for example solidification via nucleation, pre-melting at phase boundaries with triple junctions and other applications (see [14–16]). The free energy of such a system was proposed to be given by

$$\mathcal{F}_m(c_1, c_2, \phi_\alpha) := \int_D F(c_1, c_2, \phi_\alpha) d\mathbf{r} := \int_D \left[ f_0(c_1, c_2, \phi_\alpha, \Theta) + \sum_{\alpha, \beta=1}^{N-1} \frac{1}{2} k_{\alpha\beta} \nabla \phi_\alpha \cdot \nabla \phi_\beta + \sum_{i,j=1}^2 \frac{1}{2} \lambda_{ij}^2 \nabla c_i \cdot \nabla c_j \right] d\mathbf{r} dt, \quad (2.1.211)$$

where we denoted the chemical components by  $c_i, i = 1 : 3$  which obey by the constraint  $c_3 = 1 - c_2 - c_1$ . Moreover, the parameters  $\{\lambda_{ij}\}_{i,j=1,2}$  stand for the elements of a symmetric matrix of gradient energy coefficients and  $k_{\alpha\beta}$ . In addition, the multiphase homogeneous free energy contribution  $f_0(c_1, c_2, \phi_\alpha, \Theta)$  can be defined as a combination of the bulk multiphase double well potential and an additional summation of the interaction terms between all the present phases in the mixture, as follows:

$$f_0(c_1, c_2, \phi_\alpha, \Theta) := \sum_{\alpha=1}^N \phi_\alpha f_\alpha(c_1, c_2, \Theta) + \sum_{\beta \neq \alpha} W_{\alpha\beta} \phi_\alpha \phi_\beta, \quad (2.1.212)$$

with  $W_{\alpha\beta} > 0$  being a mean field interaction potential between phases and the variable  $\phi_\alpha$  can be interpreted as phase fraction that corresponds to each phase  $\alpha$  and varies between the values 0 and 1. The potential  $f_\alpha(c_1, c_2, \Theta)$  satisfies the following Assumption 2.2.

**Assumption 2.2.** *There exist some constants  $C_{0,i}, C_{1,i}, C_2, C_3, C_4, C_5 > 0, i = 1, 2$  that may depend on  $\Theta$  such that*

$$\begin{aligned} C_2 \sum_{i=1}^2 |c_i|^{q+1} - C_3 &\leq f_\alpha(c_1, c_2, \Theta) \leq C_4 \sum_{i=1}^2 |c_i|^{q+1} + C_5, \\ |\partial_{c_i} f_\alpha(c_1, c_2, \Theta)| &\leq C_{0,i} |c_i|^q + C_{1,i}, \quad i = 1, 2, \end{aligned} \quad (2.1.213)$$

for  $q = d/(d-2)$ , if  $d \geq 3$  or  $q \in \mathbb{R}^+$  and arbitrary when  $d = 1, 2$ .

Therefore a natural choice of a free energy density that satisfies Assumption 2.2 is a

double well potential of the form , e.g.,

$$f_\alpha(c_1, c_2, \Theta) = K(\Theta) \sum_{i=1}^2 \frac{1}{4} (c_i - 1)^2 c_i^2, \quad (2.1.214)$$

where  $K(\Theta) > 0$  a temperature dependent constant.

**Remark 2.19 (Interpretation of the phase variables  $\phi_\alpha$ 's).** Phases can be considered as regions which are usually differ in composition and/or crystal structure and having certain microstructure with homogeneous properties that are physically distinct from other regions of the mixture, excluding geometric transformations that map one region onto another. Each of these regions is characterized by a homogeneous free energy density denoted by  $f_\alpha$ , that differs from the free energy densities of the other regions. Each phase is assigned a phase fraction  $\phi_\alpha$  that varies between 0 and 1. For a system with  $N$  phases, the phase fractions obey a phase fraction constraint:  $\sum_{\alpha=1}^N \phi_\alpha = 1$ . Obviously if we assign the value  $\phi_\alpha = 0$ , we nominate areas where no  $\alpha$ -phase is present, and the value  $\phi_\alpha = 1$  corresponds to single-phase regions of phase  $\alpha$ .

In order to obtain a thermodynamically consistent dynamic description for the molar fractions  $c_1, c_2$  and  $c_3$ , subject to the following constraint  $\sum_{i=1}^3 c_i = 1$ , we recruit the related gradient flow formulation for minimizing the free energy (2.1.211), in order to approach the equilibrium state. The result can be summarised in the theorem below (see [15, 218] for more details).

**Theorem 2.1.7 (Gradient flow equations).** We consider the abstract  $L^2$ -gradient flow formulation for the minimization of the free energy (2.1.211) adapted to the case of ternary mixtures, i.e.,

$$\langle \partial_t c_i, v \rangle_{L^2(D)} = -\langle \nabla_{c_i}^{L^2} \mathcal{F}_m(c_1, c_2, \phi_\alpha), v \rangle_{L^2(D)}, \quad i = 1, 2, \quad (2.1.215)$$

for all  $v \in L^2(D)$ . We subsequently consider the variation with respect to the following semi-inner products (see (1.2.27), [20, 84]):

$$\begin{aligned} \langle u_1, v \rangle_{H^1(D)} &:= \langle \hat{M}_1 \nabla u_1 - \hat{M}_2 \nabla u_2, \nabla v \rangle_{L^2(D)} \text{ and} \\ \langle u_2, v \rangle_{H^1(D)} &:= \langle \hat{M}_1 \nabla u_2 - \hat{M}_2 \nabla u_1, \nabla v \rangle_{L^2(D)}, \quad \forall u_1, u_2, v \in H^1(D), \end{aligned} \quad (2.1.216)$$

where the mobility coefficients  $\hat{M}_1, \hat{M}_2$ , can be defined as functions of the related compositions, i.e.,  $\hat{M}_1 := \hat{M}_1(c_i) := \mathbb{M}_i c_i (1 - c_i)$  or  $\hat{M}_2 := \hat{M}_2(c_i) := \mathbb{M}_i c_1 c_2$ ,  $i = 1, 2$ , where  $\mathbb{M}_i := \mathbb{D}_i / R\Theta$  (Nernst-Einstein relation for the diffusivity  $\mathbb{D}_i$ ,  $\Theta$  the temperature and  $R$  is the universal gas constant). The three components are connected subject to the following constraint  $c_3 = 1 - c_1 - c_2$ . Note that below and over the rest of this subsection we make use of the following simplified notation  $F_z := \partial_z F$ ,  $z \in \{c_1, c_2, \phi_\alpha\}$ . Therefore (2.1.215) and afterwards (2.1.216), applied to the functional (2.1.211) imply the following evolution equations for  $i = 1, 2$ :

$$\begin{cases} \partial_t c_i = -\text{div}(\mathbf{J}_i(c_i, \phi_\alpha)) := \text{div} \left( \mathbb{M}_i \sum_{j=1}^2 \hat{\mathbb{M}}_{ij}(\mathbf{c}) \nabla F_{c_j} \right) & \text{in } D_T, \\ \partial_{\mathbf{n}} \mathbf{J}_i = \partial_{\mathbf{n}} c_i = 0 & \text{on } \partial D_T, \end{cases} \quad (2.1.217)$$

where  $\hat{M}_{ij}(\mathbf{c}) := c_i(\delta_{ij} - c_j)$ ,  $i, j = 1, 2$  with  $\mathbf{c} := [c_1, c_2]$ . The related potentials  $F_{c_i}$ , for  $i = 1, 2$  are defined by

$$F_{c_i}(c_i, \phi_\alpha) := \sum_{\alpha=1}^N \phi_\alpha \frac{\partial f_\alpha(c_i, \phi_\alpha)}{\partial c_i} - \sum_{j=1}^2 \lambda_{ij}^2 \Delta c_j \quad \text{in } D_T. \quad (2.1.218)$$

Independently we consider the evolution of the phase field, following the Allen-Cahn dynamics with  $\partial_n \phi_\alpha = 0$ , i.e.,

$$\partial_t \phi_\alpha = -k_\alpha F_{\phi_\alpha} \quad \text{in } D_T, \quad (2.1.219)$$

with the evolution of the potential term to be defined by:

$$F_{\phi_\alpha}(c_1, c_2, \phi_\alpha) := \frac{\partial f_0}{\partial \phi_\alpha} - \sum_{\beta=1}^{N-1} k_{\alpha\beta} \Delta \phi_\beta \quad \text{in } D_T, \quad (2.1.220)$$

where the parameter  $k_\alpha > 0$  stands for a kinetic coefficient associated with the speed of transformation of phase  $\alpha$  to another phase, at constant composition.

*Proof.* As a natural extension of the already derived  $L^2$ -gradient flow of the Cahn-Hilliard free energy in (1.2.20), the Gâteaux differential of  $\mathcal{F}_m(c_i, \phi_\alpha)$  at each of  $c_i$ ,  $i = 1, 2$  in the direction of  $v \in L^2(D)$  ( $L^2$ -gradient), can be formally derived as follows (for simplicity as the variation is considered with respect to  $c_1$  this time, we denote by  $\tilde{\mathcal{F}}_m(c_1) := \mathcal{F}_m(c_1, c_2, \phi_\alpha)$  and also  $\tilde{f}_0(c_1) := f_0(c_i, \phi_\alpha, T)$ ):

$$\begin{aligned} \delta_{c_1}^{L^2} \mathcal{F}_m(c_1, c_2, \phi_\alpha) &:= \langle \nabla_{c_1}^{L^2} \mathcal{F}_m(c_1, c_2, \phi_\alpha), v \rangle_{L^2} \\ &= \lim_{k \rightarrow 0} \frac{\tilde{\mathcal{F}}_m(c_1 + kv) - \tilde{\mathcal{F}}_m(c_1)}{k} \\ &= \int_D \left( \lim_{k \rightarrow 0} \frac{\tilde{f}_0(c_1 + \varepsilon v) - \tilde{f}_0(c_1)}{k} + \frac{\lambda_{11}^2}{2} \nabla c_1 \cdot \nabla v + \frac{\lambda_{12}^2}{2} \nabla c_2 \cdot \nabla v \right) d\mathbf{r} \\ &= \int_D \lim_{k \rightarrow 0} \frac{\tilde{f}_0(c_1 + kv) - \tilde{f}_0(c_1)}{k} d\mathbf{r} - \lambda_{11}^2 \int_D v \Delta c_1 d\mathbf{r} - \lambda_{12}^2 \int_D v \Delta c_2 d\mathbf{r}, \end{aligned} \quad (2.1.221)$$

where we used integration by parts and homogeneous Neumann boundary conditions. Furthermore by plugging the Taylor expansion around  $c_1$ , namely  $\tilde{f}_0(c_1 + kv) = \tilde{f}_0(c_1) + kv \tilde{f}_0'(c_1) + \dots$ , into the first term of the integrand we deduce that

$$\delta_{c_1}^{L^2} \mathcal{F}_m(c_1, c_2, \phi_\alpha) = \langle \partial_{c_1} f_0(c_1, c_2, \phi_\alpha) - \lambda_{11}^2 \Delta c_1 - \lambda_{12}^2 \Delta c_2, v \rangle_{L^2(D)}. \quad (2.1.222)$$

Being motivated by exactly the same procedure with respect to  $c_2$  this time, we obtain the following variation

$$\delta_{c_2}^{L^2} \mathcal{F}_m(c_1, c_2, \phi_\alpha) = \langle \partial_{c_2} f_0(c_1, c_2, \phi_\alpha) - \lambda_{21}^2 \Delta c_1 - \lambda_{22}^2 \Delta c_2, v \rangle_{L^2(D)}. \quad (2.1.223)$$

As a result, the semi-inner products (2.1.216) for  $u_2 := \partial_{c_2} f_0(c_1, c_2, \phi_\alpha) - \lambda_{21}^2 \Delta c_1 - \lambda_{22}^2 \Delta c_2$  and  $u_1 := \partial_{c_1} f_0(c_1, c_2, \phi_\alpha) - \lambda_{11}^2 \Delta c_1 - \lambda_{12}^2 \Delta c_2$ , imply the system of evolution equations (2.1.217). Finally, regarding the evolution of the phase-field, we simply evaluate the first variation of  $\mathcal{F}_m(c_1, c_2, \phi_\alpha)$  with respect to  $\phi_\alpha$ , following the same procedure for  $\tilde{\mathcal{F}}_m(\phi_\alpha) := \mathcal{F}_m(c_1, c_2, \phi_\alpha)$  and  $\forall v \in L^2(D)$ , we obtain

$$\begin{aligned}
 \delta_{\phi_\alpha}^{L^2} \mathcal{F}_m(c_1, c_2, \phi_\alpha) &:= \langle \nabla_{\phi_\alpha}^{L^2} \hat{\mathcal{F}}_m(\phi_\alpha), v \rangle_{L^2(D)} \\
 &= \lim_{k \rightarrow 0} \frac{\tilde{\mathcal{F}}_m(\phi_\alpha + kv) - \tilde{\mathcal{F}}_m(\phi_\alpha)}{k} \\
 &= \int_D \left( \lim_{k \rightarrow 0} \frac{\tilde{f}_0(\phi_\alpha + \varepsilon v) - \tilde{f}_0(\phi_\alpha)}{k} + \sum_{\alpha, \beta=1}^{N-1} k_{\alpha\beta} \nabla v \cdot \nabla \phi_\beta \right) d\mathbf{r} \\
 &= \int_D \lim_{k \rightarrow 0} \frac{\tilde{f}_0(\phi_\alpha + kv) - \tilde{f}_0(\phi_\alpha)}{k} d\mathbf{r} - \int_D \sum_{\beta=1}^{N-1} k_{\alpha\beta} v \Delta \phi_\beta d\mathbf{r}, \\
 &= \langle \partial_{\phi_\alpha} f_0 - \sum_{\beta=1}^{N-1} k_{\alpha\beta} \Delta \phi_\beta, v \rangle_{L^2(D)}, \tag{2.1.224}
 \end{aligned}$$

which implies the coupled Allen-Cahn system (2.1.219), (2.1.220), for the  $L^2$ -gradient flow, i.e.,

$$\langle \partial_t c, v \rangle_{L^2(D)} = \langle \partial_{\phi_\alpha} f_0 - \sum_{\beta=1}^{N-1} k_{\alpha\beta} \Delta \phi_\beta, v \rangle_{L^2(D)}. \tag{2.1.225}$$

□

**Remark 2.20.** We assume that there is no coupling between the first system of the evolution of the components and the second system of the phase field dynamics, due the fact that phases are not conserved quantities since they can not be created or destroyed during phase transitions [218].

**Remark 2.21.** It has been rigorously shown by C. M. Elliott and H. Garcke in [203, Section 2], that for an  $M$ -component mixture with degenerate mobility given by  $\hat{\mathbb{M}}_{ij}(\mathbf{c}) := c_i(\delta_{ij} - c_j)$ ,  $i, j = 1, \dots, M$  where  $\mathbf{c} := [c_1, \dots, c_M]$ ,  $\hat{\mathbb{M}}_{ij}(\mathbf{c})$  is positive semi-definite on the Gibbs-simplex  $\mathcal{Q}^M := \{\mathbf{u} \in \mathbb{R}^M \mid \sum_{i=1}^M u_i = 1 \text{ and } u_i \geq 0, \text{ for } i = 1, \dots, M\}$ .

In our case, since the mole fractions by definition obey the constraints  $c_i \geq 0, i = 1 : 3$  and  $\sum_{i=1}^3 c_i = 1$  for all times, by remark 2.21 we have for  $M = 2$  that the  $2 \times 2$  matrix

$$\hat{\mathbb{M}}_{ij=\{1,2\}} = \begin{pmatrix} c_1(1-c_1) & -c_1c_2 \\ -c_1c_2 & c_2(1-c_2) \end{pmatrix}, \tag{2.1.226}$$

is positive semi-definite and hence by definition, the following scalar quantity (with constants  $\mathbb{M}_1, \mathbb{M}_2 > 0$ ),

$$(\nabla F_{c_1}, \nabla F_{c_2}) \cdot \begin{pmatrix} c_1(1-c_1) & -c_1c_2 \\ -c_1c_2 & c_2(1-c_2) \end{pmatrix} \cdot \begin{pmatrix} \mathbb{M}_1 \nabla F_{c_1} \\ \mathbb{M}_2 \nabla F_{c_2} \end{pmatrix}, \tag{2.1.227}$$

is positive or zero. The relation (2.1.227) is equivalent to

$$\mathbb{M}_1 c_1 (1 - c_1) |\nabla F_{c_1}|^2 - (\mathbb{M}_1 + \mathbb{M}_2) c_1 c_2 \nabla F_{c_1} \cdot \nabla F_{c_2} + \mathbb{M}_2 c_2 (1 - c_2) |\nabla F_{c_2}|^2 \geq 0. \tag{2.1.228}$$

**Porous media setting and homogenization.** We can further introduce the same problem in the porous media setting, i.e.,

$$\left\{ \begin{array}{l} \partial_t c_i^\varepsilon = \operatorname{div} \left( \mathbb{M}_i \sum_{j=1}^2 \hat{\mathbb{M}}_{ij}(\mathbf{c}^\varepsilon) \nabla F_{c_j}^\varepsilon \right) \quad \text{in } D_T^\varepsilon, \\ F_{c_i}^\varepsilon(c_i^\varepsilon, \phi_\alpha^\varepsilon) := \sum_{\alpha=1}^N \phi_\alpha^\varepsilon \frac{\partial f_\alpha^\varepsilon(c_i^\varepsilon, \phi_\alpha^\varepsilon)}{\partial c_i^\varepsilon} - \sum_{j=1}^2 \lambda_{ij}^2 \Delta c_j^\varepsilon \quad \text{in } D_T^\varepsilon, \\ \partial_{\mathbf{n}} \mathbf{J}_i(\mathbf{c}^\varepsilon) = \partial_{\mathbf{n}} c_i^\varepsilon = 0 \quad \text{on } \partial D_T^\varepsilon, \end{array} \right. \quad (2.1.229)$$

where  $\hat{\mathbb{M}}_{ij}(\mathbf{c}^\varepsilon) := c_i^\varepsilon (\delta_{ij} - c_j^\varepsilon)$ ,  $i, j = 1, 2$  with  $\mathbf{c}^\varepsilon := [c_1^\varepsilon, c_2^\varepsilon]$  and initial conditions  $c_{i,init}^\varepsilon(\mathbf{r}) := c_i^\varepsilon(\mathbf{r}, 0) \in H^1(D^\varepsilon)$ . Here as noted also earlier, we defined  $D_T^\varepsilon := D^\varepsilon \times (0, T) \subset \mathbb{R}^3 \times (0, +\infty)$  as usual the perforated domain of length  $\Lambda$  and heterogeneity  $\varepsilon := \ell/\Lambda$  by

$$D^\varepsilon := \cup_{\mathbf{z} \in \mathbf{Z}^d} \varepsilon(Y + \mathbf{z}), \quad (2.1.230)$$

which is assumed to be exactly covered by a finite number of single periodic reference cells  $Y := (0, \ell)^d \subset \mathbb{R}^d$  such that  $Y := Y_1 \cup Y_2$ , with  $Y_1$  being the pore phase of each cell (e.g. liquid or gas phase in wetting problems) and  $Y_2$  the corresponding solid phase (see Figure 2.2).

Moreover, we can identify the related evolution of the phase field variables, by the Allen-Cahn equation, i.e.,

$$\left\{ \begin{array}{l} \partial_t \phi_\alpha^\varepsilon = -k_\alpha F_{\phi_\alpha}^\varepsilon \quad \text{in } D_T^\varepsilon, \\ F_{\phi_\alpha}^\varepsilon(c_1^\varepsilon, c_2^\varepsilon, \phi_\alpha^\varepsilon) := \frac{\partial f_0^\varepsilon}{\partial \phi_\alpha^\varepsilon} - \sum_{\beta=1}^{N-1} k_{\alpha\beta} \Delta \phi_\beta^\varepsilon \quad \text{in } D_T^\varepsilon. \end{array} \right. \quad (2.1.231)$$

In order to proceed further with the homogenization procedure, we will make use of the following assumption.

**Assumption 2.3.** *We assume that there exist strictly positive constants  $C_z$  independent of  $\varepsilon$ , such that, one can verify the following bounds:  $\|\phi_\alpha^\varepsilon\|_{L^2(0,T;H^1(D^\varepsilon))} \leq C$ ,  $\alpha = 1, \dots, N$ ,  $\|c_i^\varepsilon\|_{L^2(0,T;H^1(D^\varepsilon))} \leq C'$ ,  $i = 1, 2$  and  $\|F_z^\varepsilon\|_{L^2(0,T;H^1(D^\varepsilon))} \leq C_z$ ,  $z \in \{c_1, c_2, \phi_\alpha\}$ ,  $\alpha = 1, \dots, N$ , provided that we have the same regularity properties for the corresponding initial data. Moreover, we also claim that the positive definite mobility matrix defined in Remark 2.21 is bounded from above in the  $L^\infty$ -norm, i.e.,  $\|\mathbb{M}_{ij}(\mathbf{c}^\varepsilon)\|_{L^\infty(D^\varepsilon)} \leq C_M$ . A reader may verify these bounds following the approach discussed in the proof of (2.1.1), i.e., to obtain an energy type estimate with the help of Remark 2.21 and proceed further by verifying the additional estimates needed, or the boundness-by-entropy method extensively discussed in [161, 174, 204–206].*

Furthermore, since we note that estimates for the time derivative  $\partial_t c_i^\varepsilon$ ,  $i = 1, 2$  of the type  $L^2(0, T; H^{-1}(D^\varepsilon))$  do not ensure a priori estimates uniform in  $\varepsilon$  for the discrete time derivative for an extension of  $c_i^\varepsilon$ ,  $i = 1, 2$  to the macroscopic domain  $D$ , we recruit the Riesz-Fréchet-Kolmogorov theorem (see Theorem 2.1.3) in order to derive an upper bound for the discrete forward difference of the time derivative of each of the  $c_i^\varepsilon$ 's, i.e., the quantity  $\partial_\tau c_i^\varepsilon(\mathbf{r}, t) - c_i^\varepsilon(\mathbf{r}, t)$ , where we defined  $\partial_\tau c_i^\varepsilon(\mathbf{r}, t) = c_i^\varepsilon(\mathbf{r}, t + \tau)$  for  $\mathbf{r} \in D^\varepsilon$  and  $t \in (0, T - \tau)$ . To do this, we adapt some of the ideas presented in [161, 174] as well as in the proof of Theorem 2.1.5



and we replace the test functions  $\varphi$  appearing in the weak formulations for the time derivatives of  $c_1, c_2$  (2.1.229) by

$$\begin{cases} \varphi_i(\mathbf{r}, t) = \int_{t-\tau}^t \left( \partial_\tau c_i^\varepsilon(\mathbf{r}, s) - c_i^\varepsilon(\mathbf{r}, s) \right) k(s) ds, \quad \forall \tau \in (0, T) \text{ and } i = 1, 2, \\ \varphi_i(\mathbf{r}, 0) = \varphi_i(\mathbf{r}, T) = 0, \quad i = 1, 2 \end{cases} \quad (2.1.232)$$

and in which we defined  $k(s) = 1$ , for  $s \in (0, T - \tau)$ ,  $k(s) = 0$ , for  $s \in [-\tau, 0] \cup [T - \tau, T]$ . Hence, we obtain by examining the boundedness of each term separately in

$$-\sum_{i=1}^2 \int_{D_T^\varepsilon} c_i^\varepsilon \partial_t \varphi_i \, d\mathbf{r} \, dt = - \int_{D_T^\varepsilon} \sum_{i,j=1}^2 \mathbb{M}_{ij}(\mathbf{c}^\varepsilon) \nabla F_{c_j}^\varepsilon(\mathbf{c}^\varepsilon) \cdot \nabla \varphi_i \, d\mathbf{r} \, dt, \quad (2.1.233)$$

that is

$$\begin{aligned} - \int_{D_T^\varepsilon} c_1^\varepsilon \partial_t \varphi_1 \, d\mathbf{r} \, dt &= - \int_0^{T-\tau} \int_{D^\varepsilon} c_1^\varepsilon (\partial_\tau c_1^\varepsilon - c_1^\varepsilon) \, d\mathbf{r} \, dt + \int_\tau^T \int_{D^\varepsilon} c_1^\varepsilon (c_1^\varepsilon - \partial_{-\tau} c_1^\varepsilon) \, d\mathbf{r} \, dt \\ &= - \int_0^{T-\tau} \int_{D^\varepsilon} c_1^\varepsilon (\partial_\tau c_1^\varepsilon - c_1^\varepsilon) \, d\mathbf{r} \, dt + \int_0^{T-\tau} \int_{D^\varepsilon} \partial_\tau c_1^\varepsilon (\partial_\tau c_1^\varepsilon - c_1^\varepsilon) \, d\mathbf{r} \, dt \\ &= \int_0^{T-\tau} \int_{D^\varepsilon} (\partial_\tau c_1^\varepsilon - c_1^\varepsilon)^2 \, d\mathbf{r} \, dt \end{aligned} \quad (2.1.234)$$

and the same for  $-\int_{D_T^\varepsilon} c_2^\varepsilon \partial_t \varphi_2 \, d\mathbf{r} \, dt$  and therefore  $\sum_{i=1}^2 \int_{D_T^\varepsilon} \partial_t c_i^\varepsilon \varphi_i \, d\mathbf{r} \, dt \geq \sum_{i=1}^2 \int_0^{T-\tau} \int_{D^\varepsilon} (\partial_\tau c_i^\varepsilon - c_i^\varepsilon)^2 \, d\mathbf{r} \, dt$ . Moreover, in light of the identity (2.1.110), we obtain for the right-hand side of (2.1.233),

$$\begin{aligned} & - \int_{D_T^\varepsilon} \sum_{i,j=1}^2 \mathbb{M}_{ij}(\mathbf{c}^\varepsilon) \nabla F_{c_j}^\varepsilon(\mathbf{c}^\varepsilon) \cdot \nabla \varphi_i \, d\mathbf{r} \, dt \\ &= - \int_{D_T^\varepsilon} \int_{t-\tau}^t \sum_{i,j=1}^2 \mathbb{M}_{ij}(\mathbf{c}^\varepsilon(\mathbf{r}, t)) \nabla F_{c_j}^\varepsilon(\mathbf{c}^\varepsilon(\mathbf{r}, t)) \cdot \nabla (\partial_\tau c_i^\varepsilon(\mathbf{r}, s + \tau) - c_i^\varepsilon(\mathbf{r}, s)) \, ds \, d\mathbf{r} \, dt \\ &= - \int_{D_{T-\tau}^\varepsilon} \sum_{i,j=1}^2 \nabla (\partial_\tau c_i^\varepsilon(\mathbf{r}, t + \tau) - c_i^\varepsilon(\mathbf{r}, t)) \cdot \int_t^{t+\tau} \mathbb{M}_{ij}(\mathbf{c}^\varepsilon(\mathbf{r}, s)) \nabla F_{c_j}^\varepsilon(\mathbf{c}^\varepsilon(\mathbf{r}, s)) \, ds \, d\mathbf{r} \, dt \end{aligned} \quad (2.1.235)$$

and therefore by Hölder's inequality and the bounds for  $c_i^\varepsilon$  and  $F_{c_i}^\varepsilon$  stated in Assumption 2.3 we deduce that,

$$\begin{aligned} & \left| \int_{D_T^\varepsilon} \sum_{i,j=1}^2 \mathbb{M}_{ij}(\mathbf{c}^\varepsilon) \nabla F_{c_j}^\varepsilon(\mathbf{c}^\varepsilon) \cdot \nabla \varphi_i \, d\mathbf{r} \, dt \right| \\ & \leq \int_0^{T-\tau} \sum_{i,j=1}^2 \left( \|\nabla \partial_\tau c_i^\varepsilon\|_{L^2(D^\varepsilon)} + \|\nabla c_i^\varepsilon\|_{L^2(D^\varepsilon)} \right) \int_t^{t+\tau} \|\mathbb{M}_{ij}(\mathbf{c}^\varepsilon)\|_{L^\infty(D^\varepsilon)} \|\nabla F_{c_j}^\varepsilon(\mathbf{c}^\varepsilon)\|_{L^2(D^\varepsilon)} \, ds \, dt \\ & \leq C'_G \tau^{1/2}, \end{aligned} \quad (2.1.236)$$

where  $C'_G > 0$  is a combination of the constants from the bounds stated in Assumption 2.3 and independent of  $\varepsilon$ . As a result, putting the bounds (2.1.236), (2.1.234) provides the following estimates for  $i = 1, 2$ :

$$\|\partial_\tau c_i^\varepsilon(\mathbf{r}, t) - c_i^\varepsilon(\mathbf{r}, t)\|_{L^2(D_{T-\tau}^\varepsilon)} \leq C'_G \tau^{1/4}. \quad (2.1.237)$$

Consequently Theorem 2.1.3 implies the strong integral equicontinuity

$$\lim_{\tau \rightarrow 0^+} \|\partial_\tau c_i^\varepsilon(\mathbf{r}, t) - c_i^\varepsilon(\mathbf{r}, t)\|_{L^2(D_{T-\tau}^\varepsilon)} = 0 \quad (2.1.238)$$

and the boundedness in  $L^2(D_T^\varepsilon)$ . Moreover, following the same procedure in terms of the weak formulation of the time evolution  $\phi_\alpha^\varepsilon$ 's in (2.1.231), we obtain for test functions

$$\begin{cases} \varphi_\alpha(\mathbf{r}, t) = \int_{t-\tau}^t (\partial_\tau \phi_\alpha^\varepsilon(\mathbf{r}, s) - \phi_\alpha^\varepsilon(\mathbf{r}, s)) k(s) ds, \quad \forall \tau \in (0, T) \text{ and } \alpha = 1, \dots, N, \\ \varphi_\alpha(\mathbf{r}, 0) = \varphi_\alpha(\mathbf{r}, T) = 0 \end{cases} \quad (2.1.239)$$

and in which we defined  $k(s) = 1$ , for  $s \in (0, T - \tau)$ ,  $k(s) = 0$ , for  $s \in [-\tau, 0] \cup [T - \tau, T]$ . Hence, we obtain by examining the boundness of each term separately in

$$\int_{D_T^\varepsilon} \phi_\alpha^\varepsilon \partial_t \varphi_\alpha d\mathbf{r} dt = \int_{D_T^\varepsilon} p_\alpha F_{\phi_\alpha}^\varepsilon \varphi_\alpha d\mathbf{r} dt, \quad (2.1.240)$$

where  $\varphi_\alpha$  are given in (2.1.239), that

$$\begin{aligned} & \int_{D_{T-\tau}^\varepsilon} (\partial_\tau \phi_\alpha^\varepsilon(\mathbf{r}, s) - \phi_\alpha^\varepsilon(\mathbf{r}, s))^2 d\mathbf{r} dt \\ & \leq k\alpha \int_t^{t+\tau} \|F_{\phi_\alpha}^\varepsilon\|_{L^2(D^\varepsilon)} ds \int_0^{T-\tau} (\|\partial_\tau \phi_\alpha^\varepsilon\|_{L^2(D^\varepsilon)} + \|\phi_\alpha^\varepsilon\|_{L^2(D^\varepsilon)}) dt, \end{aligned} \quad (2.1.241)$$

or equivalently due to the bounds stated in Assumption 2.3, we deduce the estimates

$$\|\partial_\tau \phi_\alpha^\varepsilon(\mathbf{r}, t) - \phi_\alpha^\varepsilon(\mathbf{r}, t)\|_{L^2(D_{T-\tau}^\varepsilon)} \leq C_G'' \tau^{1/4}, \quad \text{for all } \alpha = 1, \dots, N, \quad (2.1.242)$$

where  $C_G'' > 0$  is a combination of the constants from the bounds stated in Assumption 2.3 and independent of  $\varepsilon$ .

**Remark 2.22.** *From the assumptions on the microscopic structure of  $D^\varepsilon$  and the fact that  $c_i^\varepsilon \in H^1(D^\varepsilon)$ ,  $i = 1, 2$  and  $\phi_\alpha^\varepsilon \in H^1(D^\varepsilon)$ ,  $\alpha = 1, \dots, N$ , we can guarantee from Lemma 2.2 the existence of extensions  $\widetilde{c}_i^\varepsilon$  of  $c_i^\varepsilon$  for  $i = 1, 2$  and  $\widetilde{\phi}_\alpha^\varepsilon$  of  $\phi_\alpha^\varepsilon$ ,  $\widetilde{F}_{c_i}^\varepsilon$  to  $F_{c_i}^\varepsilon$  and also  $\widetilde{F}_{\phi_\alpha}^\varepsilon$  to  $F_{\phi_\alpha}^\varepsilon$  from  $D^\varepsilon$  to  $D$ , such that*

$$\|\widetilde{c}_i^\varepsilon\|_{L^2(D)} \leq k \|c_i^\varepsilon\|_{L^2(D^\varepsilon)} \text{ and } \|\nabla \widetilde{c}_i^\varepsilon\|_{L^2(D)} \leq k \|\nabla c_i^\varepsilon\|_{L^2(D^\varepsilon)}, \quad i = 1, 2 \quad (2.1.243)$$

and also

$$\|\widetilde{\phi}_\alpha^\varepsilon\|_{L^2(D)} \leq k' \|\phi_\alpha^\varepsilon\|_{L^2(D^\varepsilon)} \text{ and } \|\nabla \widetilde{\phi}_\alpha^\varepsilon\|_{L^2(D)} \leq k' \|\nabla \phi_\alpha^\varepsilon\|_{L^2(D^\varepsilon)}, \quad \text{for all } \alpha = 1, \dots, N. \quad (2.1.244)$$

Similarly we obtain,

$$\|\widetilde{F}_{c_i}^\varepsilon\|_{L^2(D)} \leq k'' \|F_{c_i}^\varepsilon\|_{L^2(D^\varepsilon)} \text{ and } \|\nabla \widetilde{F}_{c_i}^\varepsilon\|_{L^2(D)} \leq k'' \|\nabla F_{c_i}^\varepsilon\|_{L^2(D^\varepsilon)}, \quad i = 1, 2, \quad (2.1.245)$$

and also

$$\|\widetilde{F}_{\phi_\alpha}^\varepsilon\|_{L^2(D)} \leq k''' \|F_{\phi_\alpha}^\varepsilon\|_{L^2(D^\varepsilon)} \text{ and } \|\nabla \widetilde{F}_{\phi_\alpha}^\varepsilon\|_{L^2(D)} \leq k''' \|\nabla F_{\phi_\alpha}^\varepsilon\|_{L^2(D^\varepsilon)}, \quad \text{for all } \alpha = 1, \dots, N, \quad (2.1.246)$$

where  $k, k', k''$  and  $k'''$  are generic positive constants independent of  $\varepsilon$ , (see also [153, 154] for more details).

**Lemma 2.16 (Two-scale convergence).** *Assuming that the extended initial condition converges, i.e.,  $\widetilde{c}_{init}^\varepsilon \xrightarrow{\varepsilon \rightarrow 0} c_{init,0}$  and  $(\widetilde{\phi}_\alpha^{init})^\varepsilon \xrightarrow{\varepsilon \rightarrow 0} \phi_\alpha^{init,0}$  in  $L^2(D)$ . Then, there exist subsequences of the extensions defined in Remark 2.22, that can be denoted by  $\{\widetilde{c}_i^\varepsilon\}_{\varepsilon > 0}$ ,  $\{\widetilde{\phi}_\alpha^\varepsilon\}_{\varepsilon > 0}$  and  $\{\widetilde{F}_{c_i}^\varepsilon\}_{\varepsilon > 0}$ ,  $\{\widetilde{F}_{\phi_\alpha}^\varepsilon\}_{\varepsilon > 0}$  for  $i = 1, 2$  such that there exist two pairs of limiting functions  $c_i^0, \phi_\alpha^0, F_{c_i}^0, F_{\phi_\alpha}^0 \in L^2(0, T; H^1(D)) = 1, 2$  and  $c_i^1, \phi_\alpha^1, F_{c_i}^1, F_{\phi_\alpha}^1 \in L^2(D_T; H_{per}^1(Y))$ ,  $= 1, 2$ , such that the related (not relabeled) subsequences  $\widetilde{c}_i^\varepsilon$ ,  $\widetilde{\phi}_\alpha^\varepsilon$  and  $\widetilde{F}_{c_i}^\varepsilon, \widetilde{F}_{\phi_\alpha}^\varepsilon$  satisfy the following convergence results as  $\varepsilon \rightarrow 0$ :*

- (i)  $\{\tilde{c}_i^\varepsilon\}_{\varepsilon>0}$  is two-scale convergent to  $c_i^0$ ,  $i = 1, 2$ ,
- (ii)  $\{\nabla_{\mathbf{r}}\tilde{c}_i^\varepsilon\}_{\varepsilon>0}$  is two-scale convergent to  $\nabla_{\mathbf{r}}c_i^0 + \nabla_{\mathbf{y}}c_i^1$ ,  $i = 1, 2$ ,
- (iii)  $\{\tilde{F}_{c_i}^\varepsilon\}_{\varepsilon>0}$  is two-scale convergent to  $F_{c_i}^0$ ,  $i = 1, 2$ ,
- (iv)  $\{\nabla_{\mathbf{r}}\tilde{F}_{c_i}^\varepsilon\}_{\varepsilon>0}$  is two-scale convergent to  $\nabla_{\mathbf{r}}F_{c_i}^0 + \nabla_{\mathbf{y}}F_{c_i}^1$ ,  $i = 1, 2$ ,
- (v)  $\{\tilde{F}_{\phi_\alpha}^\varepsilon\}_{\varepsilon>0}$  is two-scale convergent to  $F_{\phi_\alpha}^0$ ,  $\alpha = 1, \dots, N$ ,
- (vi)  $\{\nabla_{\mathbf{r}}\tilde{F}_{\phi_\alpha}^\varepsilon\}_{\varepsilon>0}$  is two-scale convergent to  $\nabla_{\mathbf{r}}F_{\phi_\alpha}^0 + \nabla_{\mathbf{y}}F_{\phi_\alpha}^1$ ,  $\alpha = 1, \dots, N$ . (2.1.247)

*Proof.* The result is a direct consequence of the estimates for provided in Assumption 2.3 and the related convergence Lemmas 2.3 and 2.5.  $\square$

**Lemma 2.17 (Strong convergence and nonlinear terms).** *We obtain with the help of the unfolding operator discussed in Definition 2.4 the following convergence results*

- (i)  $\{\tilde{c}_1^\varepsilon, \tilde{c}_2^\varepsilon\}_{\varepsilon>0}$  and  $\sum_{\alpha=1}^N \tilde{\phi}_\alpha^\varepsilon$  converge to  $(c_1^0, c_2^0)$ ,  $\sum_{\alpha=1}^N \phi_\alpha^0$  strongly in  $L^2(D_T)$ ,
- (ii)  $\mathcal{T}_\varepsilon\{\tilde{c}_1^\varepsilon, \tilde{c}_2^\varepsilon\}_{\varepsilon>0}$  converges to  $(c_1^0, c_2^0)$  and  $\mathcal{T}_\varepsilon(\tilde{\phi}_\alpha^\varepsilon) \rightarrow \phi_\alpha^0$ , strongly in  $L^2(D_T \times Y)$ ,
- (iii) In addition  $\mathcal{T}_\varepsilon(\nabla_{\mathbf{r}}\tilde{F}_{c_i}^\varepsilon)_{(i=1,2)}$  converges weakly to  $(\nabla_{\mathbf{r}}F_{c_i}^0 + \nabla_{\mathbf{y}}F_{c_i}^1)$  in  $L^2(D_T \times Y)$ ,
- (iv) The nonlinear terms  $\sum_{\alpha=1}^N \tilde{\phi}_\alpha^\varepsilon \frac{\partial \tilde{f}_\alpha^\varepsilon(c_i^\varepsilon)}{\partial c_i^\varepsilon}$  are two-scale convergent to  $\sum_{\alpha=1}^N \phi_\alpha^0 \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0}$ ,  $i = 1, 2$ ,
- (v) The terms  $\mathbb{M}_i \tilde{c}_1^\varepsilon \tilde{c}_2^\varepsilon \nabla_{\mathbf{r}}\tilde{F}_{c_i}^\varepsilon$  and  $\mathbb{M}_i \tilde{c}_i^\varepsilon (1 - \tilde{c}_i^\varepsilon) \nabla_{\mathbf{r}}\tilde{F}_{c_i}^\varepsilon$  for  $i = 1, 2$ ,  
are two-scale convergent to  $\mathbb{M}_i c_1^0 c_2^0 (\nabla_{\mathbf{r}}F_{c_i}^0 + \nabla_{\mathbf{y}}F_{c_i}^1)$  and  $\mathbb{M}_i c_i^0 (1 - c_i^0) (\nabla_{\mathbf{r}}F_{c_i}^0 + \nabla_{\mathbf{y}}F_{c_i}^1)$ . (2.1.248)

*Proof.* (i) In light of Remark 2.7, (Assumption 2.3), (2.1.237) and (2.1.242), there exists a subsequence (not relabeled and still denoted by the same symbol) of the extension  $\{\tilde{c}_1^\varepsilon, \tilde{c}_2^\varepsilon\}_{\varepsilon>0}$  such that  $\{\tilde{c}_1^\varepsilon, \tilde{c}_2^\varepsilon\}_{\varepsilon>0} \xrightarrow{\varepsilon \rightarrow 0} (c_1^0, c_2^0)$  strongly in  $L^2(D_T)$ , by Theorem 2.1.3. The convergence in (ii) and (iii) holds straightforwardly by Lemma 2.6 and Lemma 2.7 due to the estimate stated in Assumption 2.3, e.g.,  $\|F_{c_i}^\varepsilon\|_{L^2(0,T;H^1(D^\varepsilon))} \leq C_{c_i}$ . The same strong convergence result holds for  $\sum_{\alpha=1}^N \phi_\alpha^\varepsilon$  and the estimate (2.1.242), Assumption 2.3 for the  $H^1$ -boundness of  $\phi_\alpha$ 's and lemma 2.3. More details can be found in [158, Lemma 5.1, 6.1]. Moreover, in order to show part (iv), we note that the two-scale convergence of the quantity

$$\sum_{\alpha=1}^N \tilde{\phi}_\alpha^\varepsilon \frac{\partial \tilde{f}_\alpha^\varepsilon(c_i^\varepsilon)}{\partial c_i^\varepsilon} \text{ to } \sum_{\alpha=1}^N \phi_\alpha^0 \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0}, \quad (2.1.249)$$

is equivalent to the following weak convergence,

$$\mathcal{T}_\varepsilon \left( \sum_{\alpha=1}^N \tilde{\phi}_\alpha^\varepsilon \frac{\partial \tilde{f}_\alpha^\varepsilon(c_i^\varepsilon)}{\partial c_i^\varepsilon} \right) := \sum_{\alpha=1}^N \mathcal{T}_\varepsilon(\tilde{\phi}_\alpha^\varepsilon) \frac{\partial \tilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon c_i^\varepsilon)}{\partial c_i^\varepsilon} \rightharpoonup \sum_{\alpha=1}^N \phi_\alpha^0 \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0}, \quad i = 1, 2. \quad (2.1.250)$$

Therefore, by applying the integral conservation property of the unfolding operator (2.1.159), we obtain with the help of Assumption 2.3, the embedding lemma 2.1 and Poincaré inequality, the following bounds:

$$\|\mathcal{T}_\varepsilon \tilde{c}_i^\varepsilon\|_{L^2(D_T \times Y)} = |Y|^{1/2} \|\tilde{c}_i^\varepsilon\|_{L^2(D_T)} \leq C'' \text{ and } \sum_{\alpha=1}^N \|\mathcal{T}_\varepsilon \tilde{\phi}_\alpha^\varepsilon\|_{L^2(D_T \times Y)} = |Y|^{1/2} \sum_{\alpha=1}^N \|\tilde{\phi}_\alpha^\varepsilon\|_{L^2(D_T)} \leq C'. \quad (2.1.251)$$

Furthermore since  $\partial_{c_1} f_\alpha(c_1) = K(\Theta)(2c_1^3 - 3c_1^2 + c_1)/2$  and  $\partial_{c_2} f_\alpha(c_2) = K(\Theta)(2c_2^3 - 3c_2^2 + c_2)/2$ , then point-wise convergence and the generalized Lebesgue dominated convergence theorem (see [176]) due to the bound (2.1.251), imply that for all test functions  $\varphi \in C^\infty(D_T; C_{per}^\infty(Y))$  and for  $i = 1, 2$ :

$$\begin{aligned} & \int_{D_T \times Y} \sum_{\alpha=1}^N \mathcal{T}_\varepsilon(\widetilde{\phi}_\alpha^\varepsilon) \frac{\partial \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon \widetilde{c}_i^\varepsilon)}{\partial c_i^\varepsilon} \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt - \int_{D_T \times Y} \sum_{\alpha=1}^N \phi_\alpha^0 \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0} \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \\ & \leq \left| \int_{D_T \times Y} \sum_{\alpha=1}^N (\mathcal{T}_\varepsilon(\widetilde{\phi}_\alpha^\varepsilon) - \phi_\alpha^0) \frac{\partial \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon \widetilde{c}_i^\varepsilon)}{\partial c_i^\varepsilon} \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \right| \\ & \quad + \left| \int_{D_T \times Y} \sum_{\alpha=1}^N \phi_\alpha^0 \left( \frac{\partial \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon \widetilde{c}_i^\varepsilon)}{\partial c_i^\varepsilon} - \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0} \right) \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \right|, \end{aligned} \quad (2.1.252)$$

in which we applied the triangle inequality. The first absolute value in the above sum and in light of Hölder's inequality, we obtain

$$\begin{aligned} & \left| \int_{D_T \times Y} \sum_{\alpha=1}^N (\mathcal{T}_\varepsilon(\widetilde{\phi}_\alpha^\varepsilon) - \phi_\alpha^0) \frac{\partial \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon \widetilde{c}_i^\varepsilon)}{\partial c_i^\varepsilon} \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \right| \\ & \leq \sum_{\alpha=1}^N \|\mathcal{T}_\varepsilon(\widetilde{\phi}_\alpha^\varepsilon) - \phi_\alpha^0\|_{L^2(D_T \times Y)} \|\partial_{c_i^\varepsilon} \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon \widetilde{c}_i^\varepsilon)\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)} \xrightarrow{\varepsilon \rightarrow 0} 0, \end{aligned} \quad (2.1.253)$$

due to the strong convergence  $\mathcal{T}_\varepsilon(\widetilde{\phi}_\alpha^\varepsilon) \rightarrow \phi_\alpha^0$  in  $L^2(D_T \times Y)$  and the fact that from the integral preserving property (2.1.159) of the unfolding operator and the related bound from (2.1.251), it follows that  $\|\partial_{c_i^\varepsilon} \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon \widetilde{c}_i^\varepsilon)\|_{L^2(D_T \times Y)} = |Y|^{1/2} \|\partial_{c_i^\varepsilon} \widetilde{f}_\alpha^\varepsilon(\widetilde{c}_i^\varepsilon)\|_{L^2(D_T)} \leq C$ . We can finally deduce for the second integral in (2.1.259) that,

$$\left| \int_{D_T \times Y} \sum_{\alpha=1}^N \phi_\alpha^0 \left( \frac{\partial \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon \widetilde{c}_i^\varepsilon)}{\partial c_i^\varepsilon} - \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0} \right) \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \right| \xrightarrow{\varepsilon \rightarrow 0} 0. \quad (2.1.254)$$

The property (2.1.254) can be verified, as follows:

$$\begin{aligned} & \int_{D_T \times Y} \sum_{\alpha=1}^N \phi_\alpha^0 \frac{\partial \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon))}{\partial c_i^\varepsilon} \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt - \int_{D_T \times Y} \sum_{\alpha=1}^N \phi_\alpha^0 \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0} \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \\ & \stackrel{\text{Triangle}}{\leq} \int_{D_T \times Y} \left| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \frac{\partial \widetilde{f}_\alpha^\varepsilon(\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon))}{\partial c_i^\varepsilon} - \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0} \right) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, dt \\ & = \frac{K(\Theta)}{2} \int_{D_T \times Y} \left| \sum_{\alpha=1}^N \phi_\alpha^0 \left( 2[\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon)]^3 - 3[\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon)]^2 + \mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon) - 2(c_i^0)^3 + 3(c_i^0)^2 - c_i^0 \right) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, dt \\ & \stackrel{\text{Triangle}}{\leq} K(\Theta) \int_{D_T \times Y} \left| \sum_{\alpha=1}^N \phi_\alpha^0 \left( [\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon)]^3 - (c_i^0)^3 \right) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, dt \\ & \quad + \frac{K(\Theta)}{2} \int_{D_T \times Y} \left| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon) - c_i^0 \right) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, dt \\ & \quad + 3K(\Theta) \int_{D_T \times Y} \left| \sum_{\alpha=1}^N \phi_\alpha^0 \left( [\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon)]^2 - (c_i^0)^2 \right) \varphi \right| \, d\mathbf{r} \, d\mathbf{y} \, dt \\ & \stackrel{\text{Hölder's}}{\leq} K(\Theta) \|\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon) - c_i^0\|_{L^2(D_T \times Y)} \left\| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon)^2 + \mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon)c_i^0 + (c_i^0)^2 \right) \right\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)} \\ & \quad + \frac{K(\Theta)}{2} \|\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon) - c_i^0\|_{L^2(D_T \times Y)} \left\| \sum_{\alpha=1}^N \phi_\alpha^0 \right\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)} \\ & \quad + 3K(\Theta) \|\mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon) - c_i^0\|_{L^2(D_T \times Y)} \left\| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\widetilde{c}_i^\varepsilon) + c_i^0 \right) \right\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)}. \end{aligned} \quad (2.1.255)$$

Hence, the strong convergence  $\mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) \xrightarrow{\varepsilon \rightarrow 0} c_i^0$  in  $L^2(D_T \times Y)$  implies

$$\begin{aligned} & K(\Theta) \lim_{\varepsilon \rightarrow 0} \|\mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) - c_i^0\|_{L^2(D_T \times Y)} \left\| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon)^2 + \mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) c_i^0 + (c_i^0)^2 \right) \right\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)} \\ & + \frac{K(\Theta)}{2} \lim_{\varepsilon \rightarrow 0} \|\mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) - c_i^0\|_{L^2(D_T \times Y)} \left\| \sum_{\alpha=1}^N \phi_\alpha^0 \right\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)} \\ & + 3K(\Theta) \lim_{\varepsilon \rightarrow 0} \|\mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) - c_i^0\|_{L^2(D_T \times Y)} \left\| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) + c_i^0 \right) \right\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)}, \end{aligned} \quad (2.1.256)$$

since

$$\begin{aligned} \left\| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) + c_i^0 \right) \right\|_{L^2(D_T \times Y)}^2 & := \int_{D_T \times Y} \left| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) + c_i^0 \right) \right|^2 d\mathbf{r} dy dt \\ & \leq \sum_{\alpha=1}^N \int_{D_T \times Y} |\phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) + c_i^0 \right)|^2 d\mathbf{r} dy dt \\ & \leq \sum_{\alpha=1}^N \int_{D_T \times Y} \left( C_1 |\phi_\alpha^0|^4 + C_2 |\mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon)|^4 + C_3 |\phi_\alpha^0|^2 \right) d\mathbf{r} dy dt \\ & \leq C'_1 \sum_{\alpha=1}^N |Y| \|\phi_\alpha^0\|_{L^2(D_T)} \|\nabla \phi_\alpha^0\|_{L^2(D_T)}^3 + C_2 |Y| \|\tilde{c}_i^\varepsilon\|_{L^4(D_T)}^4 + C'_3 \\ & \leq C''_G + C'_2 |Y| \|\tilde{c}_i^\varepsilon\|_{L^2(D_T)} \|\nabla \tilde{c}_i^\varepsilon\|_{L^2(D_T)} \\ & \leq C'''_G, \end{aligned} \quad (2.1.257)$$

in which we made use of Young's and Ladyzhenskaya's [224] inequalities for  $d = 3$  and also the integral preserving property of the unfolding operator (see Definition 2.4) and the estimates stated in Assumption 2.3, (2.1.237). Analogously we can verify the boundedness of the term  $\left\| \sum_{\alpha=1}^N \phi_\alpha^0 \left( \mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon)^2 + \mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon) c_i^0 + (c_i^0)^2 \right) \right\|_{L^2(D_T \times Y)}$ . As a result, the limit  $\varepsilon \rightarrow 0$  of (2.1.256) leads to

$$\int_{D_T \times Y} \frac{\partial f_\alpha^\varepsilon(\mathcal{T}_\varepsilon(\tilde{c}_i^\varepsilon))}{\partial c_i^\varepsilon} \varphi d\mathbf{r} dy dt = \int_{D_T \times Y} \frac{\partial f_\alpha(c_i^0)}{\partial c_i^0} \varphi d\mathbf{r} dy dt. \quad (2.1.258)$$

For the proof of argument (v), we shall use the same technique as above and start by first investigating the nonlinear terms  $\mathbb{M}_i \tilde{c}_1^\varepsilon \tilde{c}_2^\varepsilon \nabla_{\mathbf{r}} \tilde{F}_{c_i}^\varepsilon$ ,  $i = 1, 2$ , as follows,

$$\begin{aligned} & \int_{D_T \times Y} \mathcal{T}_\varepsilon(\tilde{c}_1^\varepsilon \tilde{c}_2^\varepsilon) \mathcal{T}_\varepsilon(\nabla_{\mathbf{r}} \tilde{F}_{c_i}^\varepsilon) \varphi d\mathbf{r} dy dt - \int_{D_T \times Y} c_1^0 c_2^0 (\nabla_{\mathbf{r}} F_{c_i}^0 + \nabla_{\mathbf{y}} F_{c_i}^1) \varphi d\mathbf{r} dy dt \\ & \stackrel{\text{Triangle}}{\leq} \left| \int_{D_T \times Y} [\mathcal{T}_\varepsilon(\tilde{c}_1^\varepsilon \tilde{c}_2^\varepsilon) - c_1^0 c_2^0] \mathcal{T}_\varepsilon(\nabla_{\mathbf{r}} \tilde{F}_{c_i}^\varepsilon) \varphi d\mathbf{r} dy dt \right| \\ & + \left| \int_{D_T \times Y} c_1^0 c_2^0 [\mathcal{T}_\varepsilon(\nabla_{\mathbf{r}} \tilde{F}_{c_i}^\varepsilon) - \nabla_{\mathbf{r}} F_{c_i}^0 - \nabla_{\mathbf{y}} F_{c_i}^1] \varphi d\mathbf{r} dy dt \right|. \end{aligned} \quad (2.1.259)$$

Therefore, since  $\|\mathcal{T}_\varepsilon(\nabla_{\mathbf{r}} \tilde{F}_{c_i}^\varepsilon)\|_{L^2(D_T \times Y)} = |Y|^{1/2} \|\nabla_{\mathbf{r}} \tilde{F}_{c_i}^\varepsilon\|_{L^2(D_T)} \leq C''$  due to the integral preserving property (2.1.159) and in view of Assumption 2.3, we obtain that

$$\begin{aligned} & \left| \int_{D_T \times Y} [\mathcal{T}_\varepsilon(\tilde{c}_1^\varepsilon \tilde{c}_2^\varepsilon) - c_1^0 c_2^0] \mathcal{T}_\varepsilon(\nabla_{\mathbf{r}} \tilde{F}_{c_i}^\varepsilon) \varphi d\mathbf{r} dy dt \right| \\ & \stackrel{\text{H\"older's}}{\leq} \|\mathcal{T}_\varepsilon(\tilde{c}_1^\varepsilon \tilde{c}_2^\varepsilon) - c_1^0 c_2^0\|_{L^2(D_T \times Y)} \|\mathcal{T}_\varepsilon(\nabla_{\mathbf{r}} \tilde{F}_{c_i}^\varepsilon)\|_{L^2(D_T \times Y)} \|\varphi\|_{L^\infty(D_T \times Y)} \xrightarrow{\varepsilon \rightarrow 0} 0, \end{aligned} \quad (2.1.260)$$

due to the strong convergence  $\mathcal{T}_\varepsilon(\tilde{c}_1^\varepsilon \tilde{c}_2^\varepsilon) = \mathcal{T}_\varepsilon(\tilde{c}_1^\varepsilon) \mathcal{T}_\varepsilon(\tilde{c}_2^\varepsilon) \rightarrow c_1^0 c_2^0$  in  $L^2(D_T \times Y)$  by (Lemma 2.6).

Moreover the second integral convergences to zero as well, i.e.,

$$\left| \int_{D_T \times Y} c_1^0 c_2^0 \left[ \mathcal{T}_\varepsilon \left( \nabla_{\mathbf{r}} \widetilde{F}_{c_i}^\varepsilon \right) - \nabla_{\mathbf{r}} F_{c_i}^0 - \nabla_{\mathbf{y}} F_{c_i}^1 \right] \varphi \, d\mathbf{r} \, d\mathbf{y} \, dt \right| \xrightarrow{\varepsilon \rightarrow 0} 0, \quad (2.1.261)$$

since it has been already verified that  $\nabla_{\mathbf{r}} \widetilde{F}_{c_i}^\varepsilon \xrightarrow{\varepsilon \rightarrow 0} \nabla_{\mathbf{r}} F_{c_i}^0 + \nabla_{\mathbf{y}} F_{c_i}^1$ . The two-scale convergence of the term  $\mathbb{M}_i \widetilde{c}_i^\varepsilon (1 - \widetilde{c}_i^\varepsilon) \nabla_{\mathbf{r}} \widetilde{F}_{c_i}^\varepsilon$  for  $i = 1, 2$ , can be verified in the same way.  $\square$

**Theorem 2.1.8 (Homogenized equations).** *The limit functions  $c_i^0, \phi_\alpha^0, F_{c_i}^0, F_{\phi_\alpha}^0 \in L^2(0, T; H^1(D))$  and  $c_i^1, \phi_\alpha^1, F_{c_i}^1, F_{\phi_\alpha}^1 \in L^2(D_T; H_{per}^1(Y))$  for  $i = 1, 2$  from Lemma 2.16, satisfy the following homogenized/macroscopic system*

$$\begin{aligned} \partial_t c_i^0(\mathbf{r}, t) &= \sum_{k,m=1}^d \sum_{l=1}^2 \frac{\partial}{\partial r_m} \left( \mathbb{K}_{mk}^{il}(\mathbf{c}^0) \frac{\partial}{\partial r_k} \left[ \sum_{\alpha=1}^N \left( \phi_\alpha \frac{\partial f_\alpha}{\partial c_l} \right)^0(\mathbf{r}, t) - \sum_{s,j=1}^2 \lambda_{lj}^2 \operatorname{div}(\mathbb{D}^{js} \nabla c_j^0(\mathbf{r}, t)) \right] \right), \quad i = 1, 2, \quad \text{in } D_T, \\ \sum_{k,m=1}^d \sum_{l=1}^2 n_m \mathbb{K}_{mk}^{il}(\mathbf{c}^0) \frac{\partial}{\partial r_k} \left[ \sum_{\alpha=1}^N \left( \phi_\alpha \frac{\partial f_\alpha}{\partial c_l} \right)^0(\mathbf{r}, t) - \sum_{s,j=1}^2 \lambda_{lj}^2 \operatorname{div}(\mathbb{D}^{js} \nabla c_j^0(\mathbf{r}, t)) \right] &= 0 \quad \text{on } \partial D_T, \\ \text{also } \sum_{k,m=1}^d \sum_{l=1}^2 n_k \mathbb{D}_{mk}^{sl} \frac{\partial}{\partial r_k} c_l^0(\mathbf{r}, t) &= 0 \quad \text{on } \partial D_T, \quad \text{and } \lim_{\varepsilon \rightarrow 0} c_i^\varepsilon(\mathbf{r}, 0)_{(i=1,2)} = c_i^0(\mathbf{r}, 0) \in H^1(D). \end{aligned} \quad (2.1.262)$$

In the above  $\mathbb{K}_{mk}^{il}(\mathbf{c}^0)$ , where  $\mathbf{c}^0 := [c_1^0, c_2^0]$ , stands for the homogenized cross-diffusion tensor defined by

$$\mathbb{K}_{mk}^{il}(\mathbf{c}^0) := \sum_{s=1}^2 \widehat{\mathbb{M}}_{is}(\mathbf{c}^0) \mathbb{D}_{mk}^{sl}, \quad (2.1.263)$$

in which the elements of  $\widehat{\mathbb{M}}(\mathbf{c}^0)$  are given by  $\widehat{\mathbb{M}}_{is}(\mathbf{c}^0) := \mathbb{M}_i c_i^0 (\delta_{is} - c_s^0)$ ,  $i, s = 1, 2$  and we also defined the effective tensors

$$\mathbb{D}_{mk}^{sl} := \sum_{j=1}^2 \left( \delta_{km} \delta_{jl} - \frac{1}{|Y_1|} \int_{Y_1} \frac{\partial W_j^{k,l}(\mathbf{y})}{\partial y_m} \right) d\mathbf{y} \quad \text{for all } k = 1, \dots, d \text{ and } l = 1, 2. \quad (2.1.264)$$

The correctors  $W_j^{kl}(\mathbf{y})$  are  $Y$ -periodic functions solving the following elliptic cell problems:

$$\begin{cases} \sum_{m=1}^d \sum_{j=1}^2 \frac{\partial}{\partial y_m} \left( \delta_{jl} \delta_{km} - \frac{\partial W_j^{k,l}(\mathbf{y})}{\partial y_m} \right) = 0 & \text{in } Y_1, \\ \sum_{m=1}^d \sum_{j=1}^2 \left( \delta_{jl} \delta_{km} - \frac{\partial W_j^{k,l}(\mathbf{y})}{\partial y_m} \right) \cdot \mathbf{n} = 0 & \text{on } \partial Y_2, \\ \mathcal{M}_{Y_1}(W_j^{k,l}) = 0, \quad j = 1, 2. \end{cases}$$

*Proof.* Following the same procedure as in the previous subsections, we choose test functions  $\varphi_0 \in C_0^\infty(D_T)$  and  $\varphi_1 \in C_0^\infty(D_T; C_{per}^\infty(Y))$  and we take  $\varphi^\varepsilon(\mathbf{r}, t) = \varphi_0(\mathbf{r}, t) + \varepsilon \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t)$  in the weak microscopic formulation. Therefore, we obtain for all test functions  $\varphi^\varepsilon \in L^2(0, T; H^1(D^\varepsilon))$ , in the weak formulation for the evolution of  $c_i^\varepsilon$ ,  $i = 1, 2$  in (2.1.229) that for all  $i \neq j = 1, 2$ ,

$$\begin{aligned} & \int_0^T \langle \partial_t c_i^\varepsilon(\mathbf{r}, t), \varphi^\varepsilon(\mathbf{r}, t) \rangle_{H^{-1}(D^\varepsilon) \times H^1(D^\varepsilon)} \, dt \\ &= -\mathbb{M}_i \int_{D_T^\varepsilon} \operatorname{div} \left( (c_i^\varepsilon c_j^\varepsilon)(\mathbf{r}, t) \nabla_{\mathbf{r}} F_{c_j}^\varepsilon(\mathbf{r}, t) \right) \varphi^\varepsilon(\mathbf{r}, t) \, d\mathbf{r} \, dt \\ & \quad + \mathbb{M}_i \int_{D_T^\varepsilon} \operatorname{div} \left( c_i^\varepsilon(\mathbf{r}, t) (1 - c_i^\varepsilon(\mathbf{r}, t)) \nabla_{\mathbf{r}} F_{c_i}^\varepsilon(\mathbf{r}, t) \right) \varphi^\varepsilon(\mathbf{r}, t) \, d\mathbf{r} \, dt, \end{aligned} \quad (2.1.265)$$

Hence, integration by parts over space and time implies

$$\begin{aligned}
 & - \int_{D_T^\varepsilon} c_i^\varepsilon(\mathbf{r}, t) \left( \partial_t \varphi_0(\mathbf{r}, t) + \varepsilon \partial_t \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 = & \mathbb{M}_i \int_{D_T^\varepsilon} (c_i^\varepsilon c_j^\varepsilon)(\mathbf{r}, t) \nabla_{\mathbf{r}} F_{c_j}^\varepsilon(\mathbf{r}, t) \cdot \left( \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) + \varepsilon \nabla_{\mathbf{r}} \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 & - \mathbb{M}_i \int_{D_T^\varepsilon} c_i^\varepsilon(\mathbf{r}, t) (1 - c_i^\varepsilon(\mathbf{r}, t)) \nabla_{\mathbf{r}} F_{c_i}^\varepsilon(\mathbf{r}, t) \cdot \left( \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) + \varepsilon \nabla_{\mathbf{r}} \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\
 & - \mathbb{M}_i \int_{D_T^\varepsilon} c_i^\varepsilon(\mathbf{r}, t) (1 - c_i^\varepsilon(\mathbf{r}, t)) \nabla_{\mathbf{r}} F_{c_i}^\varepsilon(\mathbf{r}, t) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) d\mathbf{r} dt. \tag{2.1.266}
 \end{aligned}$$

Following the same procedure as in the proof of Theorem 2.1.5, we can obtain the corresponding extension to the macroscopic domain  $D$  with the help of the characteristic function over the pore-phase  $Y_1$ , i.e.,  $\chi_{Y_1}(\varepsilon^{-1} \mathbf{r})$ ,  $\mathbf{r} \in D^\varepsilon$ . Consequently by passing to the limit  $\varepsilon \rightarrow 0$  in the two-scale sense in (2.1.266), we obtain:

$$\begin{aligned}
 & |Y_1| \int_{D_T \times Y_1} c_i^0(\mathbf{r}, t) \partial_t \varphi_0(\mathbf{r}, t) d\mathbf{r} dt \\
 = & - \mathbb{M}_i \int_{D_T \times Y_1} (c_i^0 c_j^0)(\mathbf{r}, t) \left( \nabla_{\mathbf{r}} F_{c_j}^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} F_{c_j}^1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \left( \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) \right) d\mathbf{r} d\mathbf{y} dt \\
 & + \mathbb{M}_i \int_{D_T \times Y_1} c_i^0(\mathbf{r}, t) (1 - c_i^0(\mathbf{r}, t)) \nabla_{\mathbf{r}} F_{c_i}^0(\mathbf{r}, t) \cdot \left( \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) \right) d\mathbf{r} d\mathbf{y} dt \\
 & + \mathbb{M}_i \int_{D_T \times Y_1} c_i^0(\mathbf{r}, t) (1 - c_i^0(\mathbf{r}, t)) \nabla_{\mathbf{y}} F_{c_i}^1(\mathbf{r}, \mathbf{y}, t) \cdot \left( \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) \right) d\mathbf{r} d\mathbf{y} dt \tag{2.1.267}
 \end{aligned}$$

Hence, the choice  $\varphi_0 = 0$ , implies immediately, that

$$\begin{aligned}
 & \mathbb{M}_i \int_{D_T \times Y_1} (c_i^0 c_j^0)(\mathbf{r}, t) \left( \nabla_{\mathbf{r}} F_{c_j}^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} F_{c_j}^1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} dt \\
 = & \mathbb{M}_i \int_{D_T \times Y_1} c_i^0(\mathbf{r}, t) (1 - c_i^0(\mathbf{r}, t)) \nabla_{\mathbf{r}} F_{c_i}^0(\mathbf{r}, t) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} dt \\
 & + \mathbb{M}_i \int_{D_T \times Y_1} c_i^0(\mathbf{r}, t) (1 - c_i^0(\mathbf{r}, t)) \nabla_{\mathbf{y}} F_{c_i}^1(\mathbf{r}, \mathbf{y}, t) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} dt \tag{2.1.268}
 \end{aligned}$$

Moreover, we plug into (2.1.268) the following well-accepted scale separation ansatz

$$F_{c_j}^1(\mathbf{r}, \mathbf{y}, t) = - \sum_{k=1}^d \sum_{l=1}^2 \frac{\partial}{\partial \mathbf{r}_k} F_{c_i}^0(\mathbf{r}, t) \xi_{F_j}^{k,l}(\mathbf{y}) + \beta(\mathbf{r}), \quad j = 1, 2, \text{ in } L^2(D_T, H_{per}^1(Y)/\mathbb{R}), \tag{2.1.269}$$

where  $\beta(\mathbf{r})$  is arbitrary and can be chosen to be equal to zero for simplicity. Hence, we obtain:

$$\begin{aligned}
 0 = & \int_{D_T \times Y_1} \sum_{i,j=1}^2 \hat{\mathbb{M}}_{ij}(\mathbf{c}^0) \sum_{m=1}^d \left( \frac{\partial F_{c_j}^0(\mathbf{r}, t)}{\partial r_m} - \sum_{k=1}^d \sum_{l=1}^2 \frac{\partial F_{c_i}^0(\mathbf{r}, t)}{\partial r_k} \frac{\partial \xi_{F_j}^{k,l}(\mathbf{y})}{\partial y_m} \right) \frac{\partial \varphi_1^1(\mathbf{r}, \mathbf{y}, t)}{\partial y_m} d\mathbf{y} d\mathbf{r} dt \\
 = & \int_{D_T \times Y_1} \sum_{k=1}^d \sum_{l=1}^2 \frac{\partial F_{c_i}^0(\mathbf{r}, t)}{\partial r_k} \sum_{i,j=1}^2 \sum_{m=1}^d \hat{\mathbb{M}}_{ij}(\mathbf{c}^0) \left( \delta_{km} \delta_{jl} - \frac{\partial \xi_{F_j}^{k,l}(\mathbf{y})}{\partial y_m} \right) \frac{\partial \varphi_1^1(\mathbf{r}, \mathbf{y}, t)}{\partial y_m} d\mathbf{y} d\mathbf{r} dt, \tag{2.1.270}
 \end{aligned}$$

where  $\hat{\mathbb{M}}_{ij}(\mathbf{c}^0) := \mathbb{M}_i c_i^0 (\delta_{ij} - c_j^0)$ ,  $i \neq j = 1, 2$  and  $\mathbf{c}^0 = [c_1^0, c_2^0]$ . As a result, by the linear independence of  $(\partial F_{c_i}^0(\mathbf{r}, t) / \partial r_k)_{kl}$  we infer that the corrector  $Y$ -periodic functions  $\xi_{F_j}^{k,l}(\mathbf{y})$ 's are solutions of

the following linear elliptic cross-diffusion reference cell problems for  $l = 1, 2$ :

$$\begin{cases} \sum_{m=1}^d \sum_{j=1}^2 \frac{\partial}{\partial y_m} \left[ \hat{\mathbb{M}}_{ij}(\mathbf{c}^0(\mathbf{r}, t)) \left( \delta_{jl} \delta_{km} - \frac{\partial \xi_{F_j}^{k,l}(\mathbf{y})}{\partial y_m} \right) \right] = 0 & \text{in } D_T \times Y_1, \\ \sum_{m=1}^d \sum_{j=1}^2 \hat{\mathbb{M}}_{ij}(\mathbf{c}^0(\mathbf{r}, t)) \left( \delta_{jl} \delta_{km} - \frac{\partial \xi_{F_j}^{k,l}(\mathbf{y})}{\partial y_m} \right) \cdot \mathbf{n} = 0 & \text{on } D_T \times \partial Y_2, \\ \mathcal{M}_{Y_1}(\xi_{F_j}^{k,l}) = 0, \quad j = 1, 2, \end{cases}$$

for which solvability arguments have been discussed in [161]. Moreover, since  $c_1^0, c_2^0 \neq 0$  or 1, the cell problems simplify further to

$$\begin{cases} \sum_{m=1}^d \sum_{j=1}^2 \frac{\partial}{\partial y_m} \left( \delta_{jl} \delta_{km} - \frac{\partial \xi_{F_j}^{k,l}(\mathbf{y})}{\partial y_m} \right) = 0 & \text{in } Y_1, \\ \sum_{m=1}^d \sum_{j=1}^2 \left( \delta_{jl} \delta_{km} - \frac{\partial \xi_{F_j}^{k,l}(\mathbf{y})}{\partial y_m} \right) \cdot \mathbf{n} = 0 & \text{on } \partial Y_2, \\ \mathcal{M}_{Y_1}(\xi_{F_j}^{k,l}) = 0, \quad j = 1, 2. \end{cases}$$

In the same way, setting  $\varphi_1 = 0$  provides for all  $i \neq j = 1, 2$  that

$$\begin{aligned} & |Y_1| \int_{D_T} \partial_t c_i^0(\mathbf{r}, t) \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dt \\ &= -\mathbb{M}_i \int_{D_T \times Y_1} \nabla_{\mathbf{r}} \left[ (c_i^0 c_j^0)(\mathbf{r}, t) (\nabla_{\mathbf{r}} F_{c_j}^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} F_{c_j}^1(\mathbf{r}, \mathbf{y}, t)) \right] \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, d\mathbf{y} \, dt \\ &+ |Y_1| \mathbb{M}_i \int_{D_T} \nabla_{\mathbf{r}} \left[ c_i^0(\mathbf{r}, t) (1 - c_i^0(\mathbf{r}, t)) \nabla_{\mathbf{r}} F_{c_i}^0(\mathbf{r}, t) \right] \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dt \\ &+ \mathbb{M}_i \int_{D_T \times Y_1} \nabla_{\mathbf{r}} \left[ c_i^0(\mathbf{r}, t) (1 - c_i^0(\mathbf{r}, t)) \nabla_{\mathbf{y}} F_{c_i}^1(\mathbf{r}, \mathbf{y}, t) \right] \varphi_0(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{r} \, d\mathbf{y} \, dt. \end{aligned} \quad (2.1.271)$$

This consequently implies for the integrands, the homogenized equations below:

$$\begin{aligned} \partial_t c_i^0(\mathbf{r}, t) &= \mathbb{M}_i \nabla_{\mathbf{r}} \left( c_i^0(\mathbf{r}, t) (1 - c_i^0(\mathbf{r}, t)) \nabla_{\mathbf{r}} F_{c_i}^0(\mathbf{r}, t) \right) \\ &+ \mathbb{M}_i \nabla_{\mathbf{r}} \left( c_i^0(\mathbf{r}, t) (1 - c_i^0(\mathbf{r}, t)) |Y_1|^{-1} \int_{Y_1} \nabla_{\mathbf{y}} F_{c_i}^1(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{y} \right) \\ &- \mathbb{M}_i \nabla_{\mathbf{r}} \left( (c_i^0 c_j^0)(\mathbf{r}, t) \nabla_{\mathbf{r}} F_{c_j}^0(\mathbf{r}, t) + (c_i^0 c_j^0) |Y_1|^{-1} \int_{Y_1} \nabla_{\mathbf{y}} F_{c_j}^1(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{y} \right), \quad i \neq j = 1, 2. \end{aligned} \quad (2.1.272)$$

Hence, in light of the ansatz (2.1.269) and for  $i = 1$  we obtain from (2.1.272) that,

$$\begin{aligned} \partial_t c_1^0(\mathbf{r}, t) &= \mathbb{M}_1 \operatorname{div} \left( c_1^0(\mathbf{r}, t) (1 - c_1^0(\mathbf{r}, t)) \left( \sum_{k,i=1}^d \sum_{l=1}^2 \delta_{ik} - |Y_1|^{-1} \int_{Y_1} \frac{\partial \xi_{F_1}^{k,l}(\mathbf{y})}{\partial y_i} \, d\mathbf{y} \right) \nabla_{\mathbf{r}} F_{c_1}^0(\mathbf{r}, t) \right) \\ &- \mathbb{M}_1 \operatorname{div} \left( (c_1^0 c_2^0)(\mathbf{r}, t) \left( \sum_{k,i=1}^d \sum_{l=1}^2 \delta_{ik} - |Y_1|^{-1} \int_{Y_1} \frac{\partial \xi_{F_2}^{k,l}(\mathbf{y})}{\partial y_i} \, d\mathbf{y} \right) \nabla_{\mathbf{r}} F_{c_2}^0(\mathbf{r}, t) \right) \end{aligned} \quad (2.1.273)$$

and similarly for  $i = 2$

$$\begin{aligned} \partial_t c_2^0(\mathbf{r}, t) &= \mathbb{M}_2 \operatorname{div} \left( c_2^0(\mathbf{r}, t) (1 - c_2^0(\mathbf{r}, t)) \left( \sum_{k,i=1}^d \sum_{l=1}^2 \delta_{ik} - |Y_1|^{-1} \int_{Y_1} \frac{\partial \xi_{F_2}^{k,l}(\mathbf{y})}{\partial y_i} \, d\mathbf{y} \right) \nabla_{\mathbf{r}} F_{c_2}^0(\mathbf{r}, t) \right) \\ &- \mathbb{M}_2 \operatorname{div} \left( (c_1^0 c_2^0)(\mathbf{r}, t) \left( \sum_{k,i=1}^d \sum_{l=1}^2 \delta_{ik} - |Y_1|^{-1} \int_{Y_1} \frac{\partial \xi_{F_1}^{k,l}(\mathbf{y})}{\partial y_i} \, d\mathbf{y} \right) \nabla_{\mathbf{r}} F_{c_1}^0(\mathbf{r}, t) \right). \end{aligned} \quad (2.1.274)$$



The above system (2.1.273), (2.1.274) can be rewritten as follows:

$$\partial_t c_i^0(\mathbf{r}, t) = \sum_{k,m=1}^d \sum_{l=1}^2 \frac{\partial}{\partial r_m} \left( \mathbb{K}_{mk}^{il}(\mathbf{c}^0) \frac{\partial F_{c_l}^0(\mathbf{r}, t)}{\partial r_k} \right), \quad i = 1, 2, \quad \text{in } D_T, \quad (2.1.275)$$

where we defined the homogenized cross-diffusion tensor

$$\mathbb{K}_{mk}^{il}(\mathbf{c}^0) := \sum_{j=1}^2 \hat{\mathbb{M}}_{ij}(\mathbf{c}^0) \left( \delta_{km} \delta_{jl} - |Y_1|^{-1} \int_{Y_1} \frac{\partial \xi_{F_j}^{k,l}(\mathbf{y})}{\partial y_m} d\mathbf{y} \right), \quad (2.1.276)$$

where  $\hat{\mathbb{M}}_{ij}(\mathbf{c}^0) := \mathbb{M}_i c_j^0 (\delta_{ij} - c_j^0)$ ,  $i \neq j = 1, 2$  and  $\mathbf{c}^0 = [c_1^0, c_2^0]$ . and also the correctors  $\xi_{F_j}^{k,l}(\mathbf{y})$  are solutions of (2.1.271). Analogously for the corresponding potentials, we follow similar homogenization arguments and therefore we obtain for  $i = 1, 2$  that

$$\begin{aligned} & \int_{D_T^\varepsilon} F_{c_i}^\varepsilon(\mathbf{r}, t) \left( \varphi_0(\mathbf{r}, t) + \varepsilon \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\ &= \int_{D_T^\varepsilon} \left( \sum_{\alpha=1}^N \left( \phi_\alpha^\varepsilon \frac{\partial f_\alpha}{\partial c_i^\varepsilon} \right) (\mathbf{r}, t) [\varphi_0(\mathbf{r}, t) + \varepsilon \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t)] \right) d\mathbf{r} dt \\ & \quad + \lambda_{i1}^2 \int_{D_T^\varepsilon} \nabla_{\mathbf{r}} c_1^\varepsilon(\mathbf{r}, t) \cdot \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) d\mathbf{r} dt \\ & \quad + \lambda_{i1}^2 \int_{D_T^\varepsilon} \nabla_{\mathbf{r}} c_1^\varepsilon(\mathbf{r}, t) \cdot \left( \varepsilon \nabla_{\mathbf{r}} \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt \\ & \quad + \lambda_{i2}^2 \int_{D_T^\varepsilon} \nabla_{\mathbf{r}} c_2^\varepsilon(\mathbf{r}, t) \cdot \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) d\mathbf{r} dt \\ & \quad + \lambda_{i2}^2 \int_{D_T^\varepsilon} \nabla_{\mathbf{r}} c_2^\varepsilon(\mathbf{r}, t) \cdot \left( \varepsilon \nabla_{\mathbf{r}} \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) + \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) \right) d\mathbf{r} dt, \end{aligned} \quad (2.1.277)$$

where we simplified appropriately the notation by  $F_{c_i}^\varepsilon(c_1^\varepsilon, c_2^\varepsilon, \phi_\alpha^\varepsilon)(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t) := F_{c_i}^\varepsilon(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t)$ , in the first line. Hence, by passing to the limit  $\varepsilon \rightarrow 0$  with the help of the characteristic function over the pore phase, i.e., implies for each  $i = 1, 2$  that,

$$\begin{aligned} \int_{D_T \times Y_1} F_{c_i}^0(\mathbf{r}, t) \varphi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} dt &= \int_{D_T \times Y_1} \sum_{\alpha=1}^N \left( \phi_\alpha \frac{\partial f_\alpha}{\partial c_i} \right)^0(\mathbf{r}, t) \varphi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} dt \\ & \quad + \lambda_{i1}^2 \int_{D_T \times Y_1} \left( \nabla_{\mathbf{r}} c_1^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1^1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} dt \\ & \quad + \lambda_{i1}^2 \int_{D_T \times Y_1} \left( \nabla_{\mathbf{r}} c_1^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1^1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} dt \\ & \quad + \lambda_{i2}^2 \int_{D_T \times Y_1} \left( \nabla_{\mathbf{r}} c_2^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_2^1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) d\mathbf{r} d\mathbf{y} dt \\ & \quad + \lambda_{i2}^2 \int_{D_T \times Y_1} \left( \nabla_{\mathbf{r}} c_2^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_2^1(\mathbf{r}, \mathbf{y}, t) \right) \cdot \nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) d\mathbf{r} d\mathbf{y} dt. \end{aligned} \quad (2.1.278)$$

Similarly as in the applications discussed earlier, the initial choice of  $\varphi_0 = 0$  in this case provides the following homogenized relations

$$\lambda_{i1}^2 \nabla_{\mathbf{y}} \cdot \left( \nabla_{\mathbf{r}} c_1^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_1^1(\mathbf{r}, \mathbf{y}, t) \right) = -\lambda_{i2}^2 \nabla_{\mathbf{y}} \cdot \left( \nabla_{\mathbf{r}} c_2^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} c_2^1(\mathbf{r}, \mathbf{y}, t) \right), \quad i = 1, 2. \quad (2.1.279)$$

Moreover, the consideration of the following well-accepted scale separation ansatz

$$c_j^1(\mathbf{r}, \mathbf{y}, t) = - \sum_{k=1}^d \sum_{l=1}^2 \frac{\partial}{\partial \mathbf{r}_k} c_j^0(\mathbf{r}, t) \xi_{c_j}^{k,l}(\mathbf{y}), \quad j = 1, 2, \quad \text{in } L^2(D_T, H_{per}^1(Y)/\mathbb{R}) \quad (2.1.280)$$

in (2.1.279), implies that the corrector  $Y$ -periodic functions  $\xi_{c_j}^{k,l}(\mathbf{y})$ 's are solutions of the

following reference cell problems for all  $l = 1, 2$ ,

$$\left\{ \begin{array}{l} \mathbb{L}^2 \left[ \sum_{l=1}^2 \sum_{i=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \frac{\partial \xi_{c_1}^{k,l}(\mathbf{y})}{\partial y_i} \right), \sum_{i=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \frac{\partial \xi_{c_2}^{k,l}(\mathbf{y})}{\partial y_i} \right) \right]^T = [0, 0]^T \quad \text{in } Y_1, \\ \sum_{l=1}^2 \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi_{c_1}^{k,l}(\mathbf{y}))}{\partial y_j} \right) = \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - \xi_{c_2}^{k,l}(\mathbf{y}))}{\partial y_j} \right) = 0 \quad \text{on } \partial Y_2, \\ \xi_{c_1}^{k,l}(\mathbf{y}), \xi_{c_2}^{k,l}(\mathbf{y}) \text{ are } Y \text{ periodic and } \mathcal{M}_{Y_1}(\xi_{c_1}^{k,l}) = \mathcal{M}_{Y_1}(\xi_{c_2}^{k,l}) = 0, \end{array} \right. \quad (2.1.281)$$

where  $\mathbb{L}^2 := \begin{bmatrix} \lambda_{11}^2 & \lambda_{12}^2 \\ \lambda_{21}^2 & \lambda_{22}^2 \end{bmatrix}$ . In order to compare it with the cell problems (2.1.271) and since the coefficients  $\lambda_{ij}^2$  are different from zero, we can rewrite (2.1.281) in the following equivalent form

$$\sum_{j=1}^2 \sum_{m=1}^d \frac{\partial}{\partial y_m} \left( \delta_{jl} \delta_{mk} - \frac{\partial \xi_{c_j}^{k,l}(\mathbf{y})}{\partial y_m} \right) = 0, \text{ for all } l = 1, 2 \text{ in } Y_1 \quad (2.1.282)$$

and analogously the boundary conditions

$$\sum_{m=1}^d \sum_{j=1}^2 \left( \delta_{jl} \delta_{km} - \frac{\partial \xi_{c_j}^{k,l}(\mathbf{y})}{\partial y_m} \right) \cdot \mathbf{n} = 0 \quad \text{on } \partial Y_2. \quad (2.1.283)$$

Hence, from (2.1.282), (2.1.283) and the cell problems (2.1.271) we can identify the equivalence of the different types of correctors, i.e.,  $W_j^{k,l}(\mathbf{y}) := \xi_{c_j}^{k,l}(\mathbf{y}) = \xi_{F_j}^{k,l}(\mathbf{y})$ . In comparison, setting  $\phi_1 = 0$ , yields for  $i = 1, 2$ :

$$\begin{aligned} F_{c_i}^0(\mathbf{r}, t) - \sum_{\alpha=1}^N \left( \phi_\alpha \frac{\partial f_\alpha}{\partial c_i} \right)^0(\mathbf{r}, t) &= - \sum_{j=1}^2 \lambda_{ij}^2 \nabla_{\mathbf{r}} \cdot \left( \nabla_{\mathbf{r}} c_j^0(\mathbf{r}, t) + |Y_1|^{-1} \int_{Y_1} \nabla_{\mathbf{y}} c_j^1(\mathbf{r}, \mathbf{y}, t) d\mathbf{y} \right) \\ &= - \sum_{m,j=1}^2 \lambda_{ij}^2 \operatorname{div} \left( \mathbb{D}^{j,m} \nabla c_j^0(\mathbf{r}, t) \right), \end{aligned} \quad (2.1.284)$$

where we defined the effective tensors

$$\mathbb{D}_{mk}^{i,l} := \sum_{j=1}^2 \left( \delta_{km} \delta_{jl} - \frac{1}{|Y_1|} \int_{Y_1} \frac{\partial W_j^{k,l}(\mathbf{y})}{\partial y_m} d\mathbf{y} \right) \text{ for all } k = 1, \dots, d \text{ and } l = 1, 2. \quad (2.1.285)$$

This completes the proof of Theorem 2.1.8.  $\square$

**Lemma 2.18.** *The phase-field microscopic evolution system (2.1.231), in view of the convergence of the extension of the initial conditions  $\lim_{\varepsilon \rightarrow 0} \widehat{\phi}_\alpha^\varepsilon(\mathbf{r}, 0)_{(\alpha=1, \dots, N)} = \phi_\alpha(\mathbf{r}, 0) \in H^1(D)$  and the convergence results (2.16) and (2.17), admits the following homogenized representation in the macroscopic setting,*

$$\left\{ \begin{array}{l} \partial_t \phi_\alpha^0(\mathbf{r}, t) = -k_\alpha F_{\phi_\alpha}^0(\mathbf{r}, t) \quad \text{in } D_T, \\ F_{\phi_\alpha}^0(\mathbf{r}, t) = \frac{\partial f_\alpha^0(\mathbf{r}, t)}{\partial \phi_\alpha} - p^{-1} \sum_{\beta=1}^{N-1} k_{\alpha\beta} \operatorname{div}(\mathbb{S} \nabla \phi_\beta^0) \quad \text{in } D_T, \\ \mathbf{n} \cdot \mathbb{S} \nabla \phi_\beta^0(\mathbf{r}, t) = 0 \quad \text{on } \partial D_T, \end{array} \right. \quad (2.1.286)$$

where we defined the porosity  $p := \frac{|Y_1|}{|Y|}$  and the elements of the effective tensor  $\mathbb{S} := \{\mathbb{S}_{ij}\}_{1 \leq i, j \leq d}$  by

$$\mathbb{S}_{ij} := \frac{1}{|Y|} \int_{Y_1} \left( \delta_{ij} - \frac{\partial w_\beta^j(\mathbf{y})}{\partial y_i} \right) d\mathbf{y} \text{ for all } i, j = 1, \dots, d. \quad (2.1.287)$$

The correctors  $w_\beta^k(\mathbf{y}) \in H_{per}^1(Y_1)$  are unique solutions of the following reference cell problems:

$$\begin{cases} -\sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial w_\beta^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - w_\beta^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ w_\beta^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(w_\beta^k) = 0. \end{cases} \quad (2.1.288)$$

*Proof.* From the Allen-Cahn type evolution for the phase-field (2.1.231), we obtain with the help of a test function as previously that,

$$\begin{aligned} -\int_{D_T^\varepsilon} \phi_\alpha^\varepsilon(\mathbf{r}, t) (\partial_t \varphi_0(\mathbf{r}, t) + \varepsilon \partial_t \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t)) \, d\mathbf{r} \, dt \\ = -\int_{D_T^\varepsilon} k_\alpha F_{\phi_\alpha}^\varepsilon(\mathbf{r}, t) (\varphi_0(\mathbf{r}, t) + \varepsilon \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t)) \, d\mathbf{r} \, dt \end{aligned} \quad (2.1.289)$$

Therefore again with the help of the characteristic function  $\chi_{Y_1}(\varepsilon^{-1} \mathbf{r})$ , we can pass to the limit  $\varepsilon \rightarrow 0$ , in the two-scale sense and obtain subsequently,

$$-\int_{D_T} \phi_\alpha^0(\mathbf{r}, t) \partial_t \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dt = -\int_{D_T} k_\alpha F_{\phi_\alpha}^0(\mathbf{r}, t) \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dt, \quad (2.1.290)$$

or equivalently this implies (2.1.286). The derivation of the homogenized potential term, is slightly more involved and hence if we substitute a test function  $\varphi^\varepsilon(\mathbf{r}, t) = \varphi_0(\mathbf{r}, t) + \varepsilon \varphi_1(\mathbf{r}, \varepsilon^{-1} \mathbf{r}, t)$  to a weak formulation for the definition potential  $F_{\phi_\alpha}^\varepsilon$  (2.1.231) and subsequently passing to the limit  $\varepsilon \rightarrow 0$  in the two-scale sense as earlier, we can deduce that

$$\begin{aligned} \int_{D_T \times Y_1} F_{\phi_\alpha}^0(\mathbf{r}, \mathbf{y}, t) \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, d\mathbf{y} \, dt - \int_{D_T} \frac{\partial f_0^0(\mathbf{r}, t)}{\partial \phi_\alpha} \varphi_0(\mathbf{r}, t) \, d\mathbf{r} \, dt \\ = \int_{D_T \times Y_1} \sum_{\beta=1}^{N-1} k_{\alpha\beta} (\nabla_{\mathbf{r}} \phi_\beta^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \phi_\beta^1(\mathbf{r}, \mathbf{y}, t)) \cdot (\nabla_{\mathbf{r}} \varphi_0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t)) \, d\mathbf{r} \, d\mathbf{y} \, dt. \end{aligned} \quad (2.1.291)$$

Hence, the choice of  $\varphi_0 = 0$  implies

$$0 = \int_{D_T \times Y_1} \sum_{\beta=1}^{N-1} k_{\alpha\beta} (\nabla_{\mathbf{r}} \phi_\beta^0(\mathbf{r}, t) + \nabla_{\mathbf{y}} \phi_\beta^1(\mathbf{r}, \mathbf{y}, t)) \cdot \nabla_{\mathbf{y}} \varphi_1(\mathbf{r}, \mathbf{y}, t) \, d\mathbf{r} \, d\mathbf{y} \, dt, \quad (2.1.292)$$

or equivalently

$$-\sum_{\beta=1}^{N-1} k_{\alpha\beta} \Delta_{\mathbf{y}} \phi_\beta^1(\mathbf{r}, \mathbf{y}, t) = \sum_{\beta=1}^{N-1} k_{\alpha\beta} \nabla_{\mathbf{y}} \nabla_{\mathbf{r}} \phi_\beta^0(\mathbf{r}, t). \quad (2.1.293)$$

This relation indicates that  $\phi_\beta^1$  depends linearly on  $\nabla_{\mathbf{r}} \phi_\beta^0$  and it can be expressed by the following scale separation ansatz,

$$\phi_\beta^1(\mathbf{r}, \mathbf{y}, t) = -\sum_{k=1}^d w_\beta^k(\mathbf{y}) \frac{\partial \phi_\beta^0(\mathbf{r}, t)}{\partial r_k} + h(\mathbf{r}), \quad \beta = 1, \dots, N-1 \text{ in } L^2(D_T, H_{per}^1(Y)/\mathbb{R}), \quad (2.1.294)$$

where  $h(\mathbf{r})$  is arbitrary and for simplicity can be chosen to be zero, i.e.,  $(c(\mathbf{r}) = 0)$ . The correctors  $w_\beta^k(\mathbf{y})$  are solutions of the following reference cell problem (if one takes into

account the related boundary conditions):

$$\begin{cases} -\sum_{i,j=1}^d \frac{\partial}{\partial y_i} \left( \delta_{ik} - \delta_{ij} \frac{\partial w_{\beta}^k(\mathbf{y})}{\partial y_j} \right) = 0 & \text{in } Y_1, \\ \sum_{i,j=1}^d n_i \left( \delta_{ij} \frac{\partial (y_k - w_{\beta}^k(\mathbf{y}))}{\partial y_j} \right) = 0 & \text{on } \partial Y_2, \\ w_{\beta}^k(\mathbf{y}) \text{ is } Y \text{ periodic and } \mathcal{M}_{Y_1}(w_{\beta}^k) = 0, \end{cases} \quad (2.1.295)$$

for which Fredholm alternative (see Remark 2.12) ensures that there exists a unique solution in  $H_{per}^1(Y)$  (up to an additive constant) to the problem (2.1.295). Finally, the choice of  $\varphi_1 = 0$  in view of the ansatz (2.1.294) consequently leads to

$$\begin{aligned} F_{\phi_{\alpha}}^0(\mathbf{r}, t) - \frac{\partial f_0^0(\mathbf{r}, t)}{\partial \phi_{\alpha}} &= -\sum_{\beta=1}^{N-1} k_{\alpha\beta} \nabla_{\mathbf{r}} \cdot \left( \nabla_{\mathbf{r}} \phi_{\beta}^0(\mathbf{r}, t) + |Y_1|^{-1} \int_{Y_1} \nabla_{\mathbf{y}} \phi_{\beta}^1(\mathbf{r}, \mathbf{y}, t) d\mathbf{y} \right) \\ &= -p^{-1} \sum_{\beta=1}^{N-1} k_{\alpha\beta} \operatorname{div}(\mathbb{S} \nabla \phi_{\beta}^0(\mathbf{r}, t)), \quad p := \frac{|Y_1|}{|Y|}, \end{aligned} \quad (2.1.296)$$

in which we defined the effective tensor  $\mathbb{S} := \{\mathbb{S}_{ij}\}_{1 \leq i, j \leq d}$  in terms of the correctors  $w_{\beta}^j(\mathbf{y}) \in H_{per}^1(Y_1)$  that solve the cell problems (2.1.295), as follows:

$$\mathbb{S}_{ij} := \frac{1}{|Y|} \int_{Y_1} \left( \delta_{ij} - \frac{\partial w_{\beta}^j(\mathbf{y})}{\partial y_i} \right) d\mathbf{y} \text{ for all } i, j = 1, \dots, d \quad (2.1.297)$$

and the proof of Lemma 2.18 is completed.  $\square$

## 2.2 Physical interpretation and numerical experiments for binary mixtures.

### 2.2.1 An overview of coarsening dynamics for the Cahn-Hilliard Equation.

Coarsening is a curvature driven process that follows phase separation, with many similarities to grain (crystallites) growth [225–227]. During the procedure, the larger characteristic domains grow at the cost of smaller ones, under constant overall volume and the initial fine-grained structure is gradually disappearing. The geometric shape of the phase regions becomes gradually simpler, and since the domain sizes are larger, their separation is also larger which finally lead to degradation of material properties. In

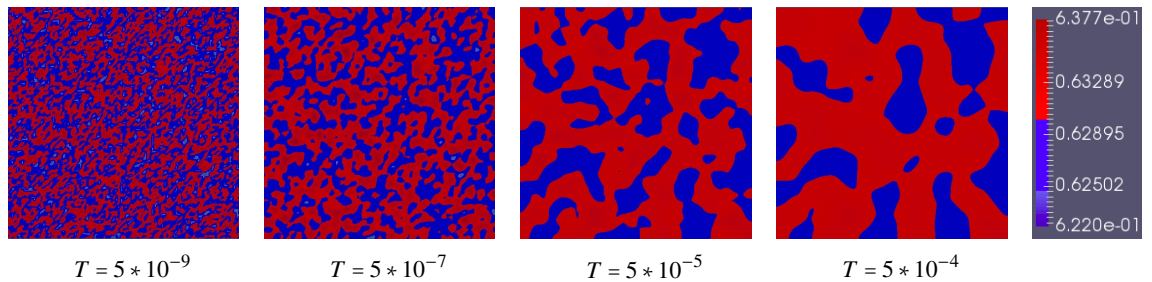


Figure 2.8: Coarsening; growth of characteristic morphological patterns under the Cahn-Hilliard equation  $\partial_t c = \Delta \mu(c)$  with  $\mu(c) := f_L^c(c) - \lambda^2 \Delta c$  with random initial conditions of the form (2.2.2), in a homogeneous medium. As one can observe, starting from a random configuration, the red and blue regions clearly separate from one another. We additionally consider a timestep size  $\Delta t = 10^{-10}$  for the computations and a double-well potential of the form  $f_L = (c^2 - 1)^2/4$ . Both the blue and red colour represent positive values of the composition and more precisely  $c_{blue} < c_{red}$ .

the case of binary alloys, the system is cooled through the transition temperature and separated into two phases and the interconnected domains of the two equilibrium phases, form specific patterns and grow with time ("coarsen") so as the interface moves and eventually tends to minimize its surface area (the region enclosed by the interface, has a fixed volume, though). The morphological patterns show an interesting scaling dynamics, in which the formations at later times are statistically similar to those at earlier times except a change of scale. It has been shown that the characteristic length scale of the patterns, let us denote it by  $L(t)$ , typically grows as a power of time  $t$ . The characteristic length can be defined by  $L(t) := 1/\mathcal{F}_N$ , where  $\mathcal{F}_N := |D|^{-1}\mathcal{F}$  (normalised free energy) represents the interfacial area per unit volume (perimeter per unit volume). It is straightforward that  $L$  has units of length. More precisely in the case of two equilibrium phases,  $L(t)$  grows as  $t^{1/3}$  or  $t^{1/4}$ , depending on the two different types of the mobility  $\mathbb{M}$  (constant or degenerate respectively). A power law like this, is experimentally validated and therefore coarsening cannot proceed faster than these rates, independently from the particular form of the initial conditions.

However, R. Kohn and F. Otto in 2002 [25] made a progress towards the rigorous understanding, by showing (for constant mobility  $\mathbb{M}$ ), the inequality:

$$T^{-1} \int_0^T \mathcal{F}_N^2 dt \geq C_d^{-1} T^{-2/3}, \quad T \geq C_d L_0^3 \text{ and } C_d^{-1} \geq \mathcal{F}_N^0, \quad (2.2.1)$$

where the constant  $C_d$  depends only on the dimension of the space,  $L_0$  and  $\mathcal{F}_N^0$  stand for an initial length scale and energy, respectively. It is worth pointing out that the universality rate of  $\mathcal{O}(t^{1/3})$  from homogeneous domains (although it lacks a rigorous argument), is recently computationally validated in the periodic porous media setting of the Cahn-Hilliard equation [20]. In particular, we study the phenomenon by imposing random initial conditions of the form:

$$c(\mathbf{r}, 0) = 0.63 + w(0.5 + l_{\mathbf{r}}), \quad (2.2.2)$$

where  $l_{\mathbf{r}} \in [0, 1]$  plays the role of random fluctuations with mean value zero, imposed on each point  $\mathbf{r} \in D$  and the parameter  $w = 0.02$  weights the influence of noise.

Finally, by observing the time shots in Figure 2.9, we are not able to deduce an influence of the heterogeneity on the coarsening rate, since for both the two values of the heterogeneity and the homogeneous formulation Figure 2.8, we obtain characteristic domains of almost the same size at the same time. For more details and numerical simulations of coarsening dynamics, the interested reader is referred to [228–232].

### **Influence of the pore geometry and porosity to the coarsening rate.**

The subsequent numerical results are devoted to the investigation of the influence of pore geometries on the coarsening rate [25] under fixed porosity  $p = 0.5$  and heterogeneity  $\varepsilon = 0.165$ . The results in Figure 2.10 are obtained by applying the scheme (2.1.8) providing time  $k$  and space  $h$  discrete solutions of the microscopic phase field problem (2.1.6) and the scheme (2.1.17) corresponding to the homogenized/upscaled Cahn-Hilliard formulation (2.1.11), respectively. We illustrated the results in for a circular (left) a square (right) pore geometry. The two different numerical schemes show qualitatively the same coarsening

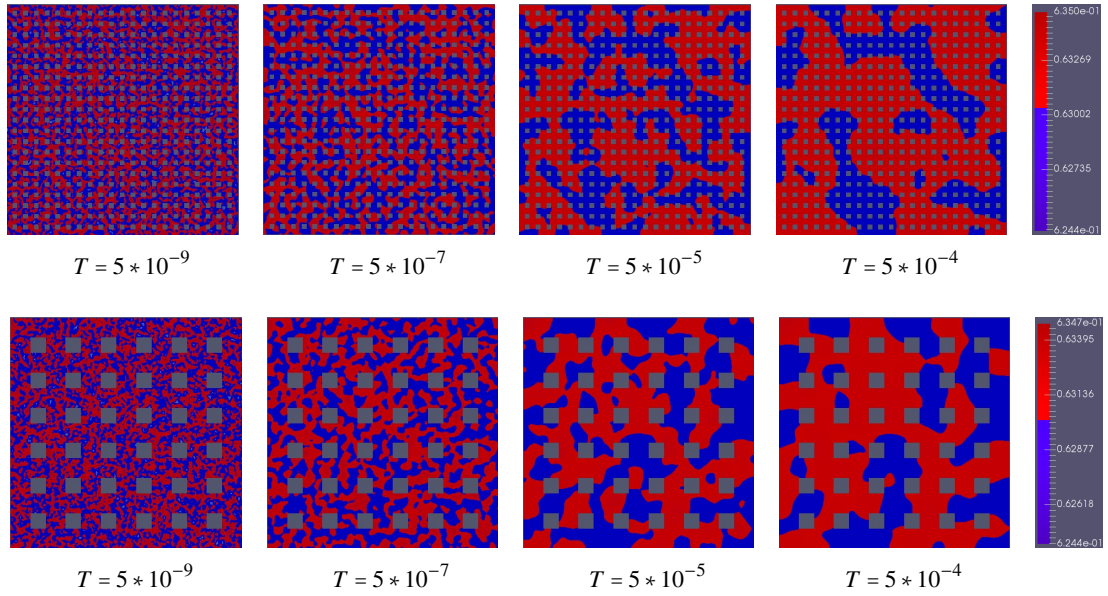


Figure 2.9: Coarsening: growth of characteristic morphological patterns under the Cahn-Hilliard equation  $\partial_t c = \Delta \mu(c)$  with  $\mu(c) := f'_1(c) - \lambda^2 \Delta c$  for the same parameters as in Figure 2.8, in a periodic porous medium with square-shaped perforations for heterogeneities  $\varepsilon \approx 0.05$  (first row) and  $\varepsilon \approx 0.167$  (second row). Both the blue and red colour represent positive values of the composition and more precisely  $c_{blue} < c_{red}$ , i.e. the values of the composition represented by the blue region are generally smaller than the ones with the red colour. A very similar evolution can be obtained for circular shaped perforations for which again we are not able to deduce a general pattern of evolution, with respect to the heterogeneity.

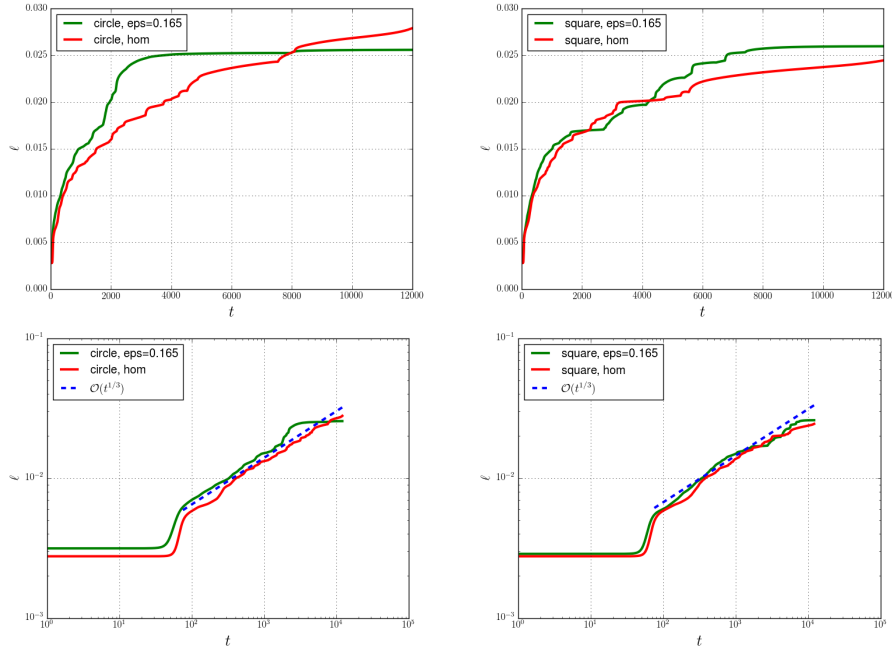


Figure 2.10: Influence of porosity on the coarsening rate (where  $\ell$  stands for the characteristic length  $L = 1/\mathcal{F}(c)$  in the figures above). The universal growth rate  $\mathcal{O}(\varepsilon^{1/3})$  is recovered in the porous media setting. The specific figures are taken from [20], under the permission of the first author of the article A. Ververis.

rate for both geometries. The slightly better approximation of the upscaled solution for square shaped pores is in part due to the more complex mesh generation of domains with curved boundaries and due to the difficulty to control the number of degrees of freedom with the FEniCs mesh generator mshr (see also [233] and [20] for more details.)

**2.2.2 The concept of curve shortening flows and the relation to the Cahn-Hilliard dynamics.**

The concept of curve shortening is clearly illustrated in the series of snapshots Figure 2.12 and Figure 2.13, in which by starting with the mass concentrated within the two different non-convex shaped (initial conditions), the interface first diffuses from the arbitrary width specified in the initial shape to the equilibrium interfacial width. The minimization of the free energy procedure additionally acts to reduce the length of the interface, but maintains its area. The minimum value of the free energy in equilibrium, is achieved by a circle in both cases. The same result is expected for any convex curve according to the Gage-Hamilton and Grayson Theorem, a statement which was initially established in the paper by R. Hamilton and M. Gage in 1986 [134] for the heat equation and can be summarized in the following sentence:

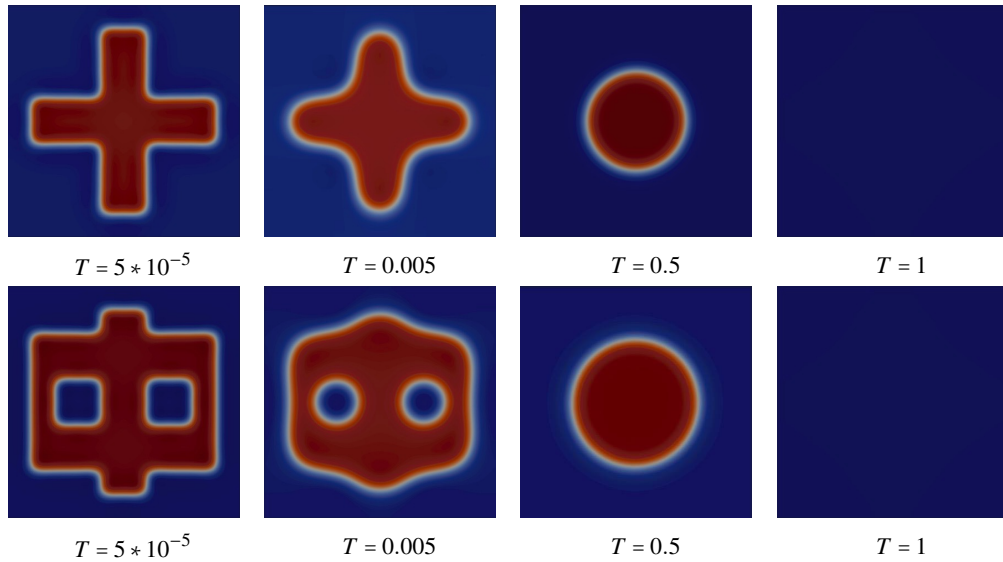


Figure 2.11: Time evolution of a cross-shaped and a more complex shape initial condition under the Allen-Cahn/Cahn-Hilliard equation  $\partial_t c = \Delta \mu(c) - \mu(c)$  with  $\mu(c) := f_L'(c) - \lambda^2 \Delta c$ , in a homogeneous domain [9]. The computations are performed for a homogeneous free energy of the form  $f_L(c) = 100c^2(1-c)^2$  (see Figure 1.3), time-step size  $\Delta t = 10^{-6}$  an surface parameter  $\lambda = 10^{-2}$ . As one can point out the Gage-Hamilton and Grayson fully holds in this case, with the convergence to a circle (with less mass) happens faster (at  $T = 0.5$ ) than the classical Cahn-Hilliard flow and immediately afterwards we observe total loss of mass at  $T = 1$  (collapsing to a point) for the Allen-Cahn/Cahn-Hilliard flow in contrast to the Cahn-Hilliard, in which we do not observe any loss of mass even for larger times.

**Theorem 2.2.1 (Gage-Hamilton and Grayson).** *"If  $\gamma_0$  is a convex curve embedded in the plane  $\mathbb{R}^2$ , the heat equation shrinks  $\gamma_0$  to a point. The curve remains convex and becomes circular as it shrinks". Followed by the later extension for non-convex curves, by M. Grayson [135]: "After some time the evolving curve becomes convex".*

It is straightforward that a smooth embedded simple closed curve remains, simple and smooth, but it reduces its initial area  $\mathcal{A}_0$  (enclosed by  $\gamma_0$ ) at a constant rate. Its perimeter decreases as quickly as possible for any continuous curve evolution over the time interval  $I := (0, \mathcal{A}_0/2\pi)$ .

**Definition 2.9 (Curve shortening flow).** *Such an evolution equation (Euclidean curve shortening geometric heat flow [234–236]), can be expressed in the following form:*

$$\partial_t \gamma(\mathbf{r}, t) = K(\mathbf{r}, t) \mathbf{N}(\mathbf{r}, t), \text{ in } \mathbb{S}^1 \times I, \tag{2.2.3}$$

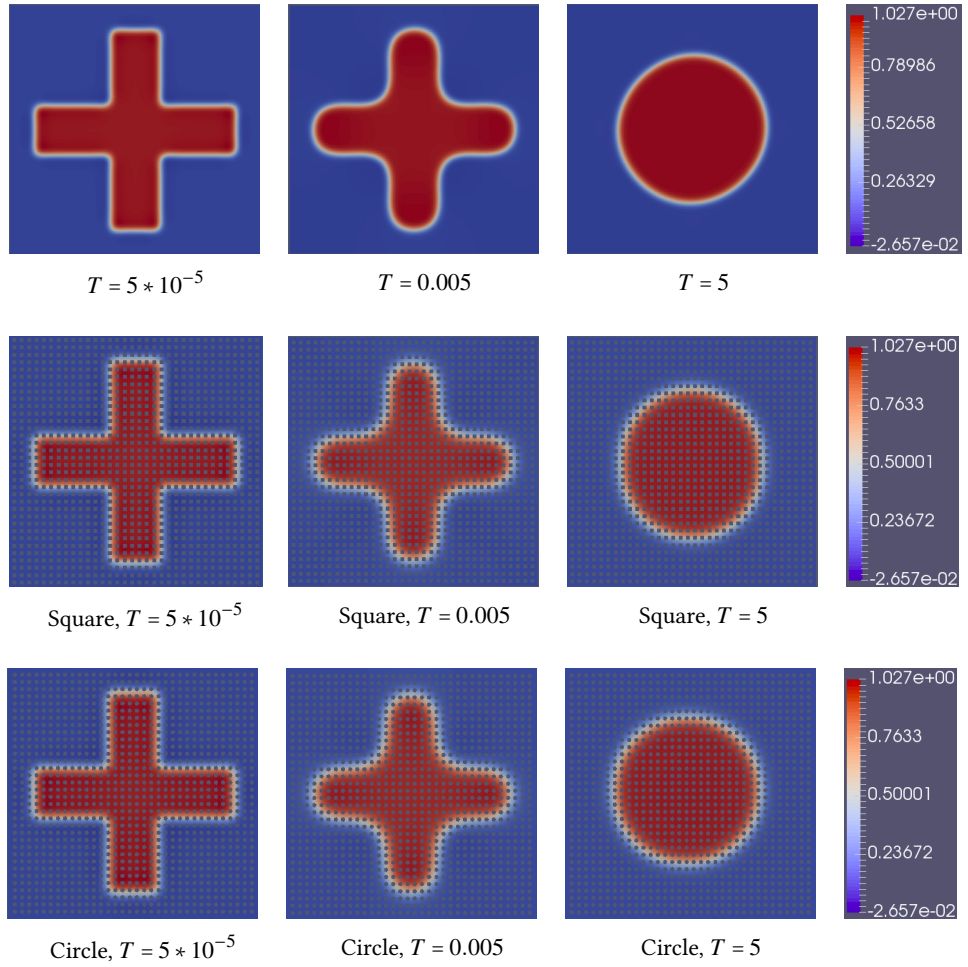


Figure 2.12: Time evolution of a cross-shaped initial condition under the classical Cahn-Hilliard equation (1.2.21), in a homogeneous domain and in a porous medium with square-shaped (middle row) and circular perforations (last row). The computations are performed for a homogeneous free energy of the form  $f_L(c) = 100c^2(1-c)^2$  (see Figure 1.3) and time-step size  $\Delta t = 10^{-6}$ . As the heterogeneity  $\varepsilon$  becomes sufficiently small of order  $10^{-2}$  ( $\varepsilon \approx 0.03$ ) and lower, the porous medium tends to become homogeneous and then the properties of the evolution in a homogeneous domain (the (almost) circular equilibrium shape for the minimum free energy) are recovered. The red colour represents positive values of the composition  $c$  and the blue stands for negative. Finally, inside the white region, the values of  $c$  are very close to zero.

in which  $K(\mathbf{r}, t)$  denotes the Euclidean curvature of  $\gamma$  and  $\mathbf{N}(\mathbf{r}, t)$ , the inward unit normal vector. This evolution relation is simply the fastest way to shrink the length of the curve  $\gamma$  [237].

**Remark 2.23 (Properties of the flow).** The area  $\mathcal{A}_{\Gamma_t}(t)$  of the domain enclosed by  $\Gamma_t := \gamma(\mathbb{S}^1, t)$  is decreasing over time by the relation

$$\mathcal{A}_{\Gamma_t}(t) = \mathcal{A}_0 - 2\pi t, \quad (2.2.4)$$

which simply indicates that the area enclosed by the curve decreases at a constant rate, namely:

$$\frac{d}{dt} \mathcal{A}_{\Gamma_t}(t) = - \int_{\Gamma_t} \langle \partial_t \gamma, \mathbf{N} \rangle ds = - \int_{\Gamma_t} \langle \mathbf{K} \mathbf{N}, \mathbf{N} \rangle ds = - \int_{\Gamma_t} K ds = -2\pi. \quad (2.2.5)$$

In addition, for the evolution of the length  $\mathcal{L}(t)$  we obtain similarly

$$\frac{d}{dt} \mathcal{L}_{\Gamma_t}(t) = - \int_{\Gamma_t} \langle \partial_t \gamma, \mathbf{K} \mathbf{N} \rangle ds = - \int_{\Gamma_t} \langle \mathbf{K} \mathbf{N}, \mathbf{K} \mathbf{N} \rangle ds = - \int_{\Gamma_t} K^2 ds < 0, \quad (2.2.6)$$

which means that curve shortening flow is the gradient flow of arc-length.



**Remark 2.24.** *M. Gage and R. Hamilton [134, 236], proved that the normalised curve*

$$\tilde{\gamma}(\mathbf{r}, t) = \pi^{1/2} (\mathcal{A}(t))^{-1/2} (\gamma(\mathbf{r}, t) - \gamma(\mathbf{r}, \mathcal{A}_0/2\pi)), \quad (2.2.7)$$

*of constant enclosed area  $\pi$ , converges to the unit circle centered at the origin, smoothly and exponentially as  $\tau := -\log(\mathcal{A}(t))/2$  goes to infinity. The total absolute curvature of an arbitrary smooth and closed non-convex curve, decreases monotonically, in order the curve to become convex. Then, the isoperimetric ratio  $\mathcal{L}^2(t)/\mathcal{A}(t)$  of this convex shape decreases as the curve converges to a circular domain, before collapsing to a single point. The only closed curve that maintains its shape under the curve shortening flow, is a circle.*

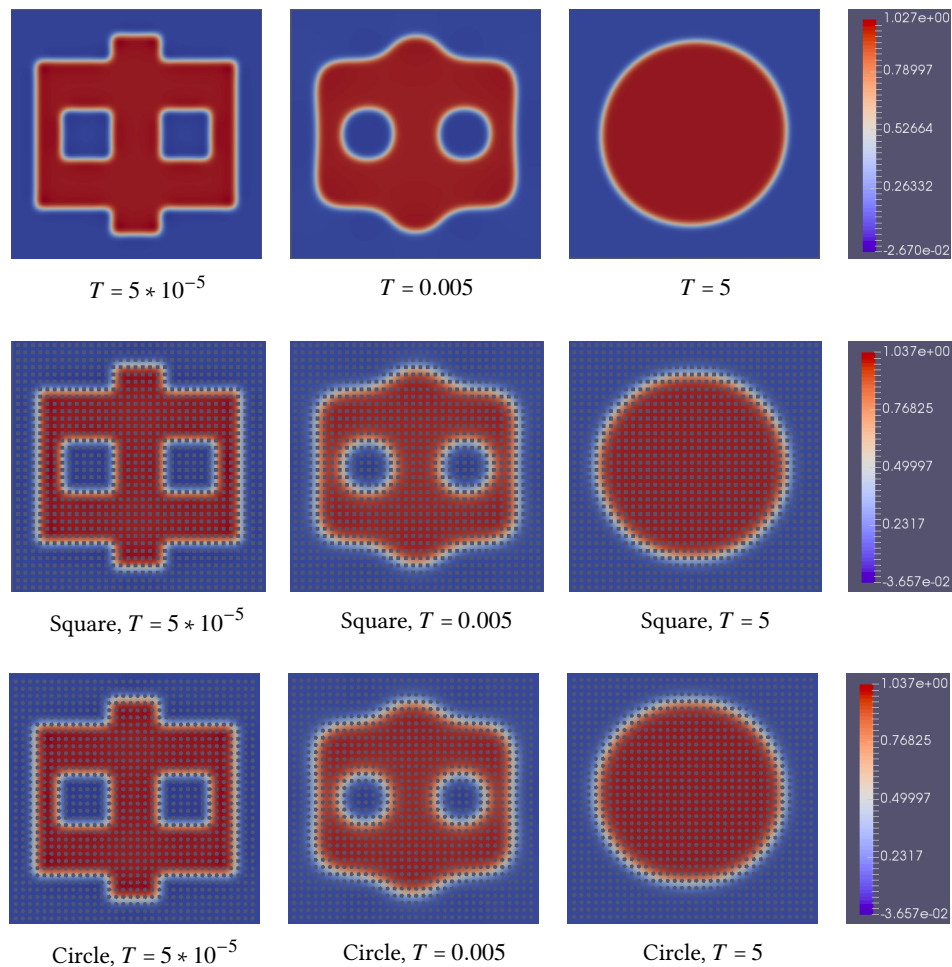


Figure 2.13: Time evolution of a more complex non-convex shape, as an initial condition under the classical Cahn-Hilliard equation (1.2.21) (for the same parameters as in Figure 2.12), in a homogeneous domain and in a porous medium with square-shaped (middle row) and circular periodic perforations (last row). Similarly as in the case of the cross, as the heterogeneity becomes sufficiently small ( $\varepsilon \approx 0.03$ ) the porous medium tends to become homogeneous and then the properties of the evolution in the homogeneous domain (the (almost) circular equilibrium shape for the minimum free energy) are recovered.

**Remark 2.25.** *We note that regarding the theory of curve shortening flows and the relation to the Cahn-Hilliard dynamics, it has been shown that, the following zero level set Cahn-Hilliard model (2.2.8) (slightly modified in order to approach the problem of the interfacial*

movement)

$$\begin{cases} \partial_t c^\lambda = \lambda \Delta \mu^\lambda & \text{in } D_T, \\ \mu^\lambda := \lambda^{-1} f'_L(c^\lambda) - \lambda \Delta c^\lambda & \text{in } D_T, \\ \nabla \mu^\lambda \cdot \mathbf{n} = 0 & \text{on } \partial D_T, \\ \nabla c^\lambda \cdot \mathbf{n} = 0 & \text{on } \partial D_T, \\ c^\lambda(\mathbf{r}, 0) = c_{init}^\lambda(\mathbf{r}) & \text{initial condition,} \end{cases} \quad (2.2.8)$$

evolves according to the Mullins-Sekerka area preserving flow (2.2.9), for infinitely small interaction length ( $\lambda \rightarrow 0$ ). In other words the interface  $\Gamma_t \subset D$  for all  $t \in [0, T]$  is embedded into a higher dimensional surface and its motion is achieved by advection of the level set function with local fluid velocity [238]

This result was formally derived using the method of matched asymptotic expansions, initially by R. L. Pego in 1989 [19], who concluded that in the fast timescale the solution of the Cahn-Hilliard equation satisfies a classic two-phase Stefan problem [239, 240] and on the slowest timescale a quasi-static solidification problem for the chemical potential.

Moreover, Pego's approach was followed by the work by N. Alikakos et al [212] in 1994, who showed the convergence of the Cahn-Hilliard to the Mullins-Sekerka problem [213](which can also be found in the literature as Hele-Shaw model, with surface tension). The convergence was rigorously shown (using basic spectral analysis and the method of asymptotic expansions), based on the assumption of existence of classical solutions of the Mullins-Sekerka flow. The evolution of a plane closed curve (the interface in this case), according to this model, is a curve-shortening motion which does not change the area of the domain enclosed by the curve. The flow can therefore be interpreted as a curve deformation with a normal velocity  $v_\Gamma$ , implicitly defined by the solution of the following problem:

**Definition 2.10 (Mullins-Sekerka flow).**

$$\begin{cases} \Delta \mu = 0 & \text{in } D \setminus \Gamma_t, \\ \nabla \mu \cdot \mathbf{n} = 0 & \text{on } \partial D_T, \\ \mu = C_{f'_L} K_\Gamma & \text{on } \Gamma_t, \\ v_\Gamma = [\partial_n \mu]_{\Gamma_t} / 2 & \text{on } \Gamma_t, \\ \Gamma_0 & \text{initial condition,} \end{cases} \quad (2.2.9)$$

where  $K_\Gamma$ , and  $v_\Gamma$ , stands for the mean curvature and the normal velocity of the interface  $\Gamma_t$ , respectively. In addition,  $[\partial_n \mu]_{\Gamma_t} := \partial_n \mu^- - \partial_n \mu^+$  in which  $\mu^+$  and  $\mu^-$ , are the restrictions of  $\mu$  on the exterior  $D_t^+$  and on the interior  $D_t^-$  of  $\Gamma_t$ .

Local and global existence of solutions of the problem (2.2.9) for an arbitrary and smooth initial curve, and an almost circular, respectively were established by X. Chen [241, 242].

**Remark 2.26 (Properties of the flow).** *The Mullins-Sekerka flow maintains the area  $A_{\Gamma_t}(t)$  over time, of the region enclosed by the interface, since it holds that*

$$\frac{dA_{\Gamma_t}(t)}{dt} = - \int_{\Gamma_t} v_\Gamma ds = - \frac{1}{2} \int_{\Gamma_t} [\partial_n \mu] ds = \frac{1}{2} \int_{\partial D} \partial_n \mu ds - \frac{1}{2} \int_{D \setminus \Gamma_t} \Delta \mu d\mathbf{r} = 0, \quad (2.2.10)$$

by the divergence theorem. In addition, the corresponding length of the interface is decreasing over time, namely:

$$\frac{d\mathcal{L}_{\Gamma_t}(t)}{dt} = - \int_{\Gamma_t} K_{\Gamma_t} V_{\Gamma_t} ds = - \frac{1}{2C_{f_L}'} \int_{\Gamma_t} \mu [\partial_{\mathbf{n}} \mu] ds = - \frac{1}{2C_{f_L}'} \int_D |\nabla \mu|^2 d\mathbf{r} \leq 0. \quad (2.2.11)$$

More details about the general problem of curve shortening flows can be found in [21, 22, 243–246].

The interesting and expected result that came up, is that the Gage-Hamilton-Grayson theorem hold in the porous media setting for a sufficiently small heterogeneity, i.e the initial non convex curve tends to converge to a circular domain, for very small heterogeneities  $\varepsilon$  of order  $10^{-2}$  and smaller. In the total free energy functional  $\mathcal{F}(c)$ , the homogeneous free energy density  $f_L(c)$  is responsible for the spinodal decomposition and the gradient term  $\lambda^2/2|\nabla c|^2$  is responsible for the interfacial reduction. Similar computational results related to this concept are presented in the following articles [247–249].

### 2.2.3 Deformation dynamics of a semi-circular interface located on the left boundary.

As an extension of the previous computational aspects, we examine the interfacial movement over time of a semi-circular shape with its barycentre to be located in the middle of the left boundary and we consider its radius to be equal to the half length of the domain. We investigate this evolution, in both homogeneous and porous media. Firstly, we study the influence of forces  $f > 0$  to the homogeneous interfacial evolution Figure 2.15 of both the classical Cahn-Hilliard formulation and the Allen-Cahn/Cahn-Hilliard dynamics. The forces are imposed as influx boundary conditions  $\nabla \mu \cdot \mathbf{n} = -f$  (see Figure 2.14). The above relation is a general influx condition, where  $f$  stands for the

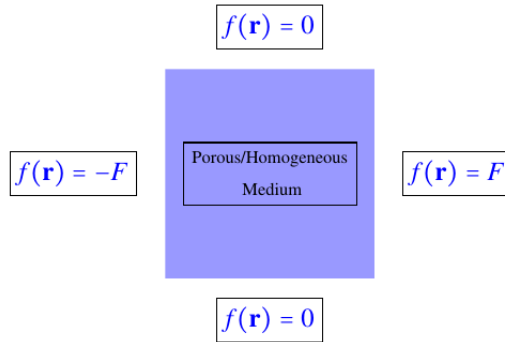


Figure 2.14: Schematic illustration of the imposed influx boundary conditions.

product of the surface density of intercalation sites and the net local rate of intercalant influx across the boundary (the rate at which material enters the system via boundary reactions). This rate depends on the local concentration and chemical potential. A system like this, is called the Cahn-Hilliard with reactions and is generally used to model the dynamics in Lithium-ion batteries [55, 250–252].

In the same context, the Cahn-Hilliard equation was recruited by Singh et al [253] in order to model the diffusion and the phase-separation of, rechargeable battery composite electrode materials. Their considerations based on thermodynamically-consistent

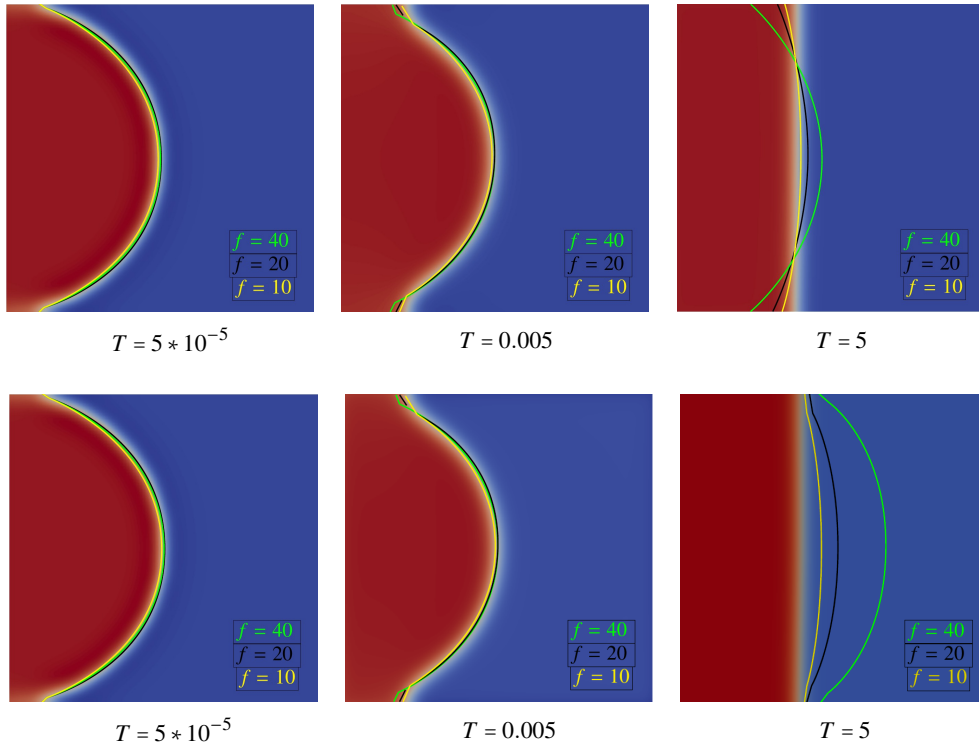


Figure 2.15: The red shape represents the interface for constant influx  $f = 0.2$  and the lines indicate the position of the interface for 3 other different values of  $f$  ( $f = 10, f = 20, f = 40$ ), as shown in the figure. The evolution over the classical Cahn-Hilliard formulation is represented with the figures in the first row, whereas the second row provides the evolution over the Allen-Cahn/Cahn-Hilliard formulation. Finally the red colour represents positive values of the composition  $c$  and the blue stands for negative. Finally, inside the white region, the values of  $c$  are very close to zero.

reaction rate laws for the intercalation dynamics of lithium insertion and extraction process between the electrolyte and the active crystals. This seems to be the first attempt to couple a bulk phase field model to boundary conditions (reactions). The following numerical results, are obtained for a double-well potential of the form  $f_L(c) = 100c^2(1-c)^2$  and time-step size  $dt = 10^{-6}$ . As one can observe in Figure 2.17, it seems that the way the interface evolves, is independent of the value of the heterogeneity  $\varepsilon$  and the type of perforation, for constant zero influx  $f$ .

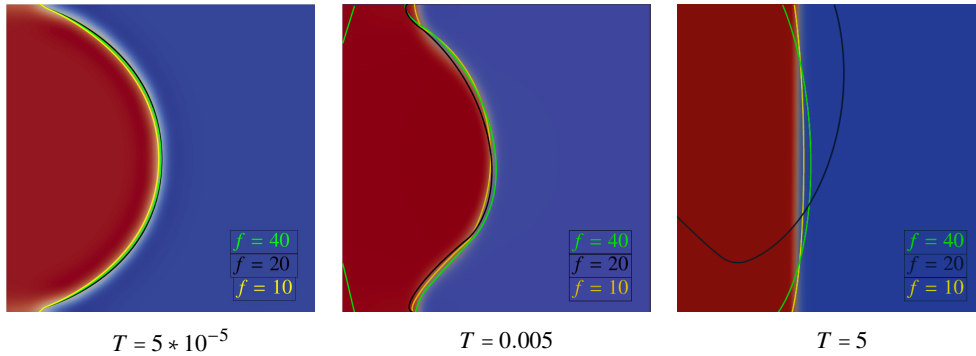


Figure 2.16: The red shape represents the interface evolving under the effective/homogenized Cahn-Hilliard formulation  $p\partial_t c_0 = \text{div}(m\mathbb{D}\nabla f'_L(c_0)) - p^{-1}\lambda^2 \text{div}(m\mathbb{D}\nabla(\text{div}(\mathbb{D}\nabla c_0)))$ , for  $m = 1$ , constant influx  $f = 0.2$  and porosity  $p = 0.5$ . The lines indicate the position of the interface for 3 other different values of  $f$  ( $f = 10, f = 20, f = 40$ ), as shown in the previous figures. As one can observe the evolution almost coincides with the homogeneous formulation (1st row Figure 2.15), except some unexpected behaviour of the interface which arises for  $f = 20$  at  $T = 5$  and  $f = 40$  at  $T = 0.005$ .

The results are different though, in the case of an advancing semi-circular interface that does not fully resolve the pore space  $D^\varepsilon$  (with radius much smaller than the half of

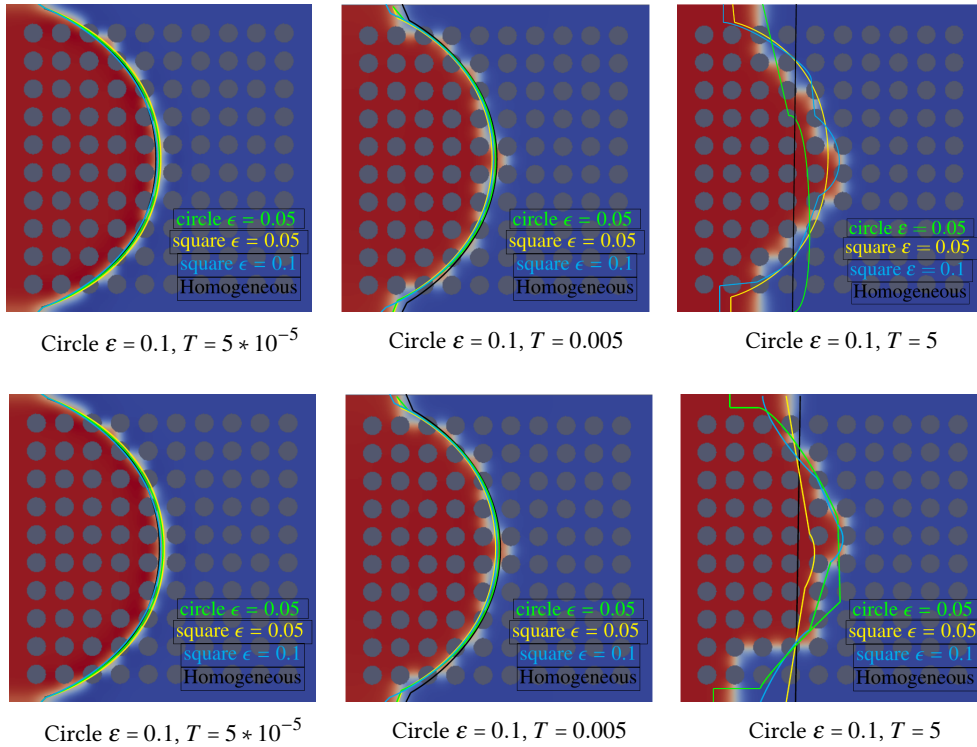


Figure 2.17: The lines indicate the position of the interface for periodic circular and square-shaped perforations, for two different values of heterogeneity and a comparison to the homogeneous formulation as well. We consider homogeneous Neumann and no-flux ( $f = 0$ ) in this case. The first row indicates the evolution under the classical Cahn-Hilliard formulation (2.1.1) and the second represents the interfacial movements under the Allen-Cahn/Cahn-Hilliard flow (2.1.21). The different coloured lines representing the different types of perforations and the two values of heterogeneity (as indicated in the inside figure's label) coincide in the first two time shots of study, for both the two formulations. Whereas the shape of the interface drastically varies among heterogeneities and types of perforation after long enough time, as illustrated in the last timeshot.

the domain, which is the energetically favourable location), as seen in Figure 2.18. As one can observe in the specific example, the higher the heterogeneity of the porous medium is, the more discrete is the behaviour of the interface. The interface also advances faster under lower porosities, as noted in a similar study that can be found in [20]. Hence, the interface is moving due to small perturbations in the composition  $c$  and is considered to be unstable. Finally, as one can observe the interface under the smallest heterogeneity of study  $\varepsilon \approx 0.05$  does not visibly move over time. We additionally notice a slight increase in the width of the thickness of the interface represented by the white region (and the corresponding small loss of interfacial mass (red colour)), as the heterogeneity becomes larger (Figure 2.18) and as time goes by (Figure 2.17). This means that, by definition of the thickness  $l_{\Theta-\Theta_c}$  of the interface, i.e.,

$$l_{\Theta-\Theta_c} = 2 \left( \frac{\lambda^2}{b(\Theta_c - \Theta)} \right)^{1/2}, \quad (2.2.12)$$

(see also section 1.1) and since the surface parameter  $\lambda$  is considered to be constant in all the computations), consequently temperature should be an increasing function of time or heterogeneity and approaches the critical temperature  $\Theta_c$ . The rise in temperature occurs possibly due to the interactions of the binary mixture with the pore walls.

In addition, the interface does not move monotonically with respect to the heterogeneity for both quadratic and circular periodic perforations. A possible explanation to this non-monotonic behaviour, could be an interface pinning and de-pinning mechanism

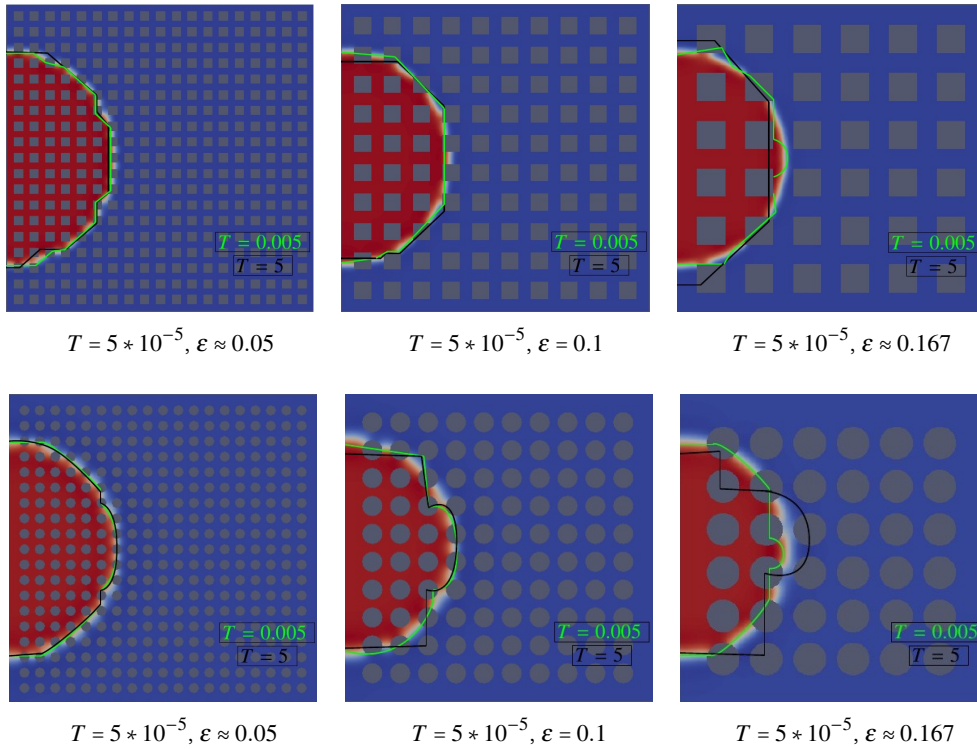


Figure 2.18: Influence of the heterogeneity  $\varepsilon$  to the evolution of a semi-circular advancing interface under the classical Cahn-Hilliard formulation, for zero influx  $f$ , in a porous medium with square-shaped and circular periodic perforations. The lines drawn upon the snapshots of the interface for time  $T = 5 \times 10^{-5}$ , indicate the position of it at time  $T = 0.005$  (green colour) and time  $T = 5$  (black colour). As one can observe the higher the heterogeneity, the more discrete is the behaviour of the interface over time. Very similar results hold for the evolution under the Allen-Cahn/Cahn-Hilliard equation.

on the pore walls [254, 255]. Finally, we obtain slightly smoother evolution in the case of quadratic perforations, than the circular ones. This may partially occur because the resolution of curved boundaries (circular perforations), requires more grid points than the flat surfaces/boundaries (quadratic perforations), in order to resolve the curvature [20]. In the same context, it would be a challenge to computationally investigate the Cahn-Hilliard dynamics (coarsening, curve shortening flow, etc.) in a porous medium with random pore geometry, involving the basic principles of stochastic homogenization [256–259].

As a brief conclusion, we may point out that there is no substantial change on the deformed shape of the interface for the different values of the force (see Figure 2.15). During the last time-shot of study though ( $t = 5$ ), we see that the higher the force we apply, the more curvy interfacial shape we get and especially with the Allen-Cahn/Cahn-Hilliard formulation  $\partial_t c = \Delta \mu(c) - \mu(c)$  with  $\mu(c) := f_L'(c) - \lambda^2 \Delta c$ , in which the additional chemical potential term  $\mu(c)$  for  $f = 40$ , seems to drastically influence the deformation. In addition, in the case of no-flux boundary conditions, it seems that the heterogeneity and the type of perforation do not influence the interfacial movement, which coincides with the evolution in a homogeneous domain with zero influx as shown in Figure 2.17. In comparison, it is also worth pointing out that the interfacial movements do not show monotonic behaviour with respect to the heterogeneity of a porous medium, in the case where the radius of the semi-circular interface, is much smaller than the half length of the domain. More precisely, we observed that the lower the heterogeneity, the more discrete

is the behaviour of the interface, and for a domain with square-shaped perforations we obtain smoother evolution than for perforated medium with circular ones, as one can see in Figure 2.18.

## Chapter 3

# Introduction to the GENERIC formalism and applications

This chapter is mainly focused on the thermodynamic background and principles, demonstrated in different levels of description and simultaneously with continuum mechanical aspects arising in Energetic Variational Approaches for modelling the dynamics in complex fluids. The major part is covered by the development of the corresponding motivation and applications of metriplectic systems which are state space formulations that have become well-known under the acronym GENERIC (General Equations of Reversible-Irreversible Coupling). The double bracket formulation induced by GENERIC via duality pairing is such that the dynamics of non-equilibrium systems under consideration is described by means of two generating functionals, supplemented by two complimentary non-interacting conditions.

### 3.1 Introductory concepts.

As an introduction to the mathematical theory associated with non-equilibrium systems and more precisely the GENERIC formalism [28], we are going to review some of the already established essential definitions and principles of the classical thermodynamics and statistical mechanics [260]. A thermodynamic interpretation of the dynamics and properties of a system often based in an overview of each particular model over different levels of description. Therefore a more detail description is generally provided from a microscopic point of view. In this context, we illustrate the concept of a system's "microstate", see Definition 3.1 below.

**Definition 3.1 (The microscopic level of description).** *The "microscopic" level of description of a system is being characterized by a set of variables  $\mathbf{x}$ , which specify the state ("microstate") of the microscopic particle quantities (atoms and molecules) that compose the system. The unit microscopic length scale is defined appropriately, such that the inter-atomic distance (of the neighbouring atoms) is of unit order.*

In order to understand better the representation over different levels of a thermodynamic system, we demonstrate the mathematical background and the different no-



tions, with a rather fundamental example in the context of two component multiphase flows. Therefore, we consider a mixture of different species  $\alpha, \beta = 1, \dots, M$ . The positions of say  $k_\alpha = 1, \dots, N_\alpha$  of mass  $m_{k_\alpha}$  interacting particles, denoted by  $\mathbf{r}_{k_\alpha} := \mathbf{r}_{k_\alpha}(t)$  and the corresponding momenta by  $\mathbf{p}_{k_\alpha} := \mathbf{p}_{k_\alpha}(t)$ . The set of microscopic variables, can be written as a vector of  $dN_\alpha$  position and  $dN_\alpha$  momentum components, namely:  $\mathbf{x} = [\mathbf{x}_{1_\alpha}, \dots, \mathbf{x}_{2dN_\alpha}]^T := [(\mathbf{r}_{1_\alpha}, \mathbf{p}_{1_\alpha}), \dots, (\mathbf{r}_{N_\alpha}, \mathbf{p}_{N_\alpha})]^T \in \Gamma_{N_\alpha} \subseteq \mathbb{R}^{2dN_\alpha}$  (where  $\Gamma_{N_\alpha}$  denotes the phase space) and evolves with time according to the laws of Hamiltonian mechanics. The dynamics is dictated by the Hamiltonian  $\mathcal{H}$  which can be expressed as a sum of kinetic energy of the particles with an interaction term defined by an inter-atomic potential which is usually of the general form:

**Definition 3.2 (Lennard-Jones potential).** *A potential function is said to be in the form of Lennard-Jones, if it can be expressed as follows:*

$$V_{\alpha,\beta}(\mathbf{r}_{k_\alpha}, \mathbf{r}_{l_\beta}) := 4e_p \sum_{k_\alpha}^{N_\alpha} \sum_{l_\beta}^{N_\beta} \left( \frac{\sigma^{12}}{|\mathbf{r}_{k_\alpha} - \mathbf{r}_{l_\beta}|^{12}} - \frac{\sigma^6}{|\mathbf{r}_{k_\alpha} - \mathbf{r}_{l_\beta}|^6} \right), \quad (3.1.1)$$

where  $e_p$  denotes generally the depth of the potential well and  $\sigma$ , is the finite distance at which the inter-particle potential is zero [261, 262].

The powers 12, 6 are generally empirical/experimental and model cases of many constitutes. The first  $|\mathbf{r}_{k_\alpha} - \mathbf{r}_{l_\beta}|^{12}$  term, is related to the short range Pauli repulsion at short ranges due to overlapping electron orbitals. These forces avoid the collapse of the substance onto itself. On the other hand the  $|\mathbf{r}_{k_\alpha} - \mathbf{r}_{l_\beta}|^6$  term, which is the attractive long-range interaction term, describes attraction at long ranges (van der Waals interactions etc.) and preventing the substance from disintegrating in the absence of a container.

Long-range interactions can be considered as the ones which are such that the distance over which particle position correlations occurred is bigger than the size of the volume element, describing the resolution of the continuum variables of the system.

**Definition 3.3 (Microscopic Lagrangian and Hamiltonians).** *The basic functions that summarize the dynamics of the system are the well known, microscopic Hamiltonian which can be defined by:*

$$\mathcal{H}(\mathbf{x}_{k_\alpha}) := \mathcal{H}(\mathbf{r}_{k_\alpha}, \mathbf{p}_{k_\alpha}) := \sum_{k_\alpha=1}^{N_\alpha} \left( \frac{\mathbf{p}_{k_\alpha}^2}{2m_{k_\alpha}} + \frac{1}{2} \sum_{k_\alpha \neq l_\beta=1}^{N_\beta} V_{\alpha,\beta}(\mathbf{r}_{k_\alpha}, \mathbf{r}_{l_\beta}) \right), \quad (3.1.2)$$

and the corresponding Lagrangian of the system, namely:

$$\mathcal{L}_G(\mathbf{x}_{k_\alpha}) := \mathcal{L}_G(\mathbf{r}_{k_\alpha}, \mathbf{p}_{k_\alpha}) := \sum_{k_\alpha=1}^{N_\alpha} \left( \frac{\mathbf{p}_{k_\alpha}^2}{2m_{k_\alpha}} - \frac{1}{2} \sum_{k_\alpha \neq l_\beta=1}^{N_\beta} V_{\alpha,\beta}(\mathbf{r}_{k_\alpha}, \mathbf{r}_{l_\beta}) \right). \quad (3.1.3)$$

**Remark 3.1 (Least Action Principle and Hamilton's equations).** *The basic law that governs the dynamics is the least action principle which states that the actual curve of motion, which has been followed by the system between two different times say  $t_1$  and  $t_2$ , is such as the action functional:*

$$\mathcal{A}(\mathbf{r}_{k_\alpha}, \mathbf{p}_{k_\alpha}) = \int_{t_1}^{t_2} \mathcal{L}_G(\mathbf{r}_{k_\alpha}, \mathbf{p}_{k_\alpha}) dt, \quad (3.1.4)$$

is not changed to first order, namely:

$$\delta \mathcal{A}(\mathbf{r}_{k_\alpha}, \mathbf{p}_{k_\alpha}) = 0. \quad (3.1.5)$$

A direct consequence of the least action principle, is the derivation of the Hamilton's equations of motion for a system with a single particle say  $k_\alpha$ , by plugging the relation between the Lagrangian and Hamiltonian:

$$\mathcal{L}_G(\mathbf{r}_{k_\alpha}, \mathbf{p}_{k_\alpha}) = \mathbf{p}_{k_\alpha} \dot{\mathbf{r}}_{k_\alpha} - \mathcal{H}(\mathbf{r}_{k_\alpha}, \mathbf{p}_{k_\alpha}), \quad (3.1.6)$$

into (3.1.5) which is also known as the Legendre transform. As a result, we obtain

$$\delta \int_{t_1}^{t_2} (\mathbf{p}_{k_\alpha} \dot{\mathbf{r}}_{k_\alpha} - \mathcal{H}) dt = \int_{t_1}^{t_2} ((\dot{\mathbf{r}}_{k_\alpha} - \partial_{\mathbf{p}_{k_\alpha}} \mathcal{H}) \delta \mathbf{p}_{k_\alpha} - (\dot{\mathbf{p}}_{k_\alpha} + \partial_{\mathbf{r}_{k_\alpha}} \mathcal{H}) \delta \mathbf{r}_{k_\alpha}) dt = 0. \quad (3.1.7)$$

The resulting dynamic relationships, are the Hamilton's equations of motion [260],[263]:

$$\dot{\mathbf{r}}_{k_\alpha} = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_{k_\alpha}} \quad \text{and} \quad \dot{\mathbf{p}}_{k_\alpha} = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_{k_\alpha}}. \quad (3.1.8)$$

The above equations can also be represented in a more useful block-diagonal form, that is:

$$\dot{\mathbf{x}} = \mathbb{L}_0 \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{x}} \iff \frac{d}{dt} [\mathbf{r}_{k_\alpha}, \mathbf{p}_{k_\alpha}]^T = \mathbb{L}_0 \left[ \frac{\partial \mathcal{H}}{\partial \mathbf{r}_{k_\alpha}}, \frac{\partial \mathcal{H}}{\partial \mathbf{p}_{k_\alpha}} \right]^T, k_\alpha = 1, \dots, N_\alpha, \quad (3.1.9)$$

endowed with an initial condition  $\mathbf{x}_0 = [\mathbf{r}_{k_\alpha}(0), \mathbf{p}_{k_\alpha}(0)]^T$  and let  $\mathbb{L}_0$  to be defined as the symplectic matrix which is given in the form

$$\mathbb{L}_0 = \begin{bmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{1} & \mathbf{0} \end{bmatrix}, \quad (3.1.10)$$

where  $\mathbf{0}$  and  $\mathbf{1}$  are the  $dN$ -dimensional zero matrix and the identity matrix, respectively. We consider for simplicity over the following definitions and principles, that we are dealing with a system of  $k = 1, \dots, N$  particles of the same species (we skip the subscript  $\alpha$  for simplicity). The phase space  $\Gamma_N$  as discussed earlier, can be considered as a collection of possible pairs  $(\mathbf{r}_k, \mathbf{p}_k), k = 1, \dots, N$ , under the conditions of the Heisenberg's Uncertainty Principle [264].

In summary, we can conclude that the microscopic description provides a full dynamic description of each particle in the particular system. In comparison, in the "mesoscopic level", the state of the system is described by a set of dynamical functions of the microstate  $\mathbf{x}$ . These functions are usually known as microscopic dynamical functions denoted by  $\Pi_{z_i}(\mathbf{x})$  and evolve over time in the phase space. One can identify those as coarse-grained or relevant variables, defining the corresponding level of description. The time evolution of dynamical quantities is usually expressed by means of the Poisson brackets defined below (see also [265, 266]).

**Definition 3.4 (Poisson bracket).** The Poisson bracket  $\{\cdot, \cdot\}$  of two phase-space functions of, say  $\Pi_{z_1}(\mathbf{x})$  and  $\Pi_{z_2}(\mathbf{x})$ , can be defined by

$$\{\Pi_{z_1}(\mathbf{x}), \Pi_{z_2}(\mathbf{x})\} = \sum_k^N \left( \frac{\partial \Pi_{z_1}(\mathbf{x})}{\partial \mathbf{r}_k} \frac{\partial \Pi_{z_2}(\mathbf{x})}{\partial \mathbf{p}_k} - \frac{\partial \Pi_{z_2}(\mathbf{x})}{\partial \mathbf{r}_k} \frac{\partial \Pi_{z_1}(\mathbf{x})}{\partial \mathbf{p}_k} \right). \quad (3.1.11)$$

Thus, the above Hamilton's equations of motion can be derived in the context of the

Poisson bracket from the evolution equation, which is well known as the Liouville equation [267]:

$$\dot{\Pi}_{z_i}(\mathbf{x}) = \sum_k^N \left( \frac{\partial \Pi_{z_i}(\mathbf{x})}{\partial \mathbf{r}_k} \dot{\mathbf{r}}_k + \frac{\partial \Pi_{z_i}(\mathbf{x})}{\partial \mathbf{p}_k} \dot{\mathbf{p}}_k \right) = \{ \Pi_{z_i}(\mathbf{x}), \mathcal{H}(\mathbf{x}) \}. \quad (3.1.12)$$

The above equation with solution  $\Pi_{z_i}(\mathbf{z}(t)) = e^{t\mathcal{L}}\Pi_{z_i}(\mathbf{x}(0))$ , can be rewritten as follows

$$\dot{\Pi}_{z_i}(\mathbf{x}) = \mathcal{L}\Pi_{z_i}(\mathbf{x}), \quad \text{where } \mathcal{L} = -\frac{\partial \mathcal{H}(\mathbf{x})}{\partial \mathbf{x}} \mathbb{L}_0 \frac{\partial}{\partial \mathbf{x}}, \quad (3.1.13)$$

which is known as the Liouville operator (also formulated alternatively as  $i\mathcal{L}$ ). It can be easily shown that the Poisson bracket is antisymmetric [28]:

$$\{ \Pi_{z_1}(\mathbf{x}), \Pi_{z_2}(\mathbf{x}) \} = -\{ \Pi_{z_2}(\mathbf{x}), \Pi_{z_1}(\mathbf{x}) \} \quad (3.1.14)$$

and satisfies the Jacobi Identity:

$$\{ \Pi_{z_1}(\mathbf{x}), \{ \Pi_{z_2}(\mathbf{x}), \Pi_{z_3}(\mathbf{x}) \} \} + \{ \Pi_{z_2}(\mathbf{x}), \{ \Pi_{z_3}(\mathbf{x}), \Pi_{z_1}(\mathbf{x}) \} \} + \{ \Pi_{z_3}(\mathbf{x}), \{ \Pi_{z_1}(\mathbf{x}), \Pi_{z_2}(\mathbf{x}) \} \} = 0. \quad (3.1.15)$$

**Definition 3.5 (Macroscopic level of description and state functions).** *The "macroscopic level" of description is considered to be the one in which the system is being considered as a whole. The macroscopic description is fully identified by a suitable set  $\mathbf{z}$  of both space and time dependent functions  $z_i, i = 1, \dots, m$  (also known as "macrostate"), which defined on some region  $D \subset \mathbb{R}^d$ :*

$$z_i := z_i(\mathbf{r}(t), t) \in \mathcal{Z}_i(D) \times [0, \infty), \quad (3.1.16)$$

where the  $\mathcal{Z}_i, i = 1, \dots, m$ , denote different functions spaces. The  $\mathbf{r}(t)$  denotes the position vector in a continuum setting. These functions are well known as state variables and are parameters such as momentum density, composition, etc.

The connection between the microscopic and macroscopic variables is based on the idea that the spatially smoothed and slowly evolving state variables  $z_i$  are in general averages of the functions  $\Pi_{z_i}(\mathbf{x})$ . So, it is of crucial importance to identify the proper mapping  $\Pi_{z_i}(\mathbf{x}) : \mathbf{x} \rightarrow \mathbf{z}$ , of the variables of one level to the other. Since Hamilton's equations provide a deterministic evolution of the system with a given initial condition but it is impossible to fix the position and momentum of every single particle though, one can introduce the concept of an ideal situation composed of many "virtual" copies of a system, that being considered simultaneously. Each particular "copy" indicates a possible state of the actual system. This concept is known as statistical ensemble, the state of which is given by a probability density function  $g_{\mathbf{z}}(\mathbf{x})$ , on the phase space that describes how much a microstate  $\mathbf{x}$  contributes to the properties of a given macrostate  $\mathbf{z}$ , or in other words where the probability of finding a system in a given macrostate.

One can say that an ensemble is a set of possible motions in the system. By assigning probabilities to the motions, the ensemble is given certain properties and as a result there may exist non measurable subsets of that. Thus, not all sets of motions can be considered

as ensembles. This probability distribution at a subsequent time, let us denote it by  $g_z(\mathbf{x}, t)$  in order to emphasize the time dependence, satisfies the Liouville's equation [267], i.e.,

$$\partial_t g_z(\mathbf{x}, t) = -\mathcal{L}g_z(\mathbf{x}, t). \quad (3.1.17)$$

A straightforward property of the above probability density is the normalized condition over the phase space  $\Gamma_{N\alpha}$ :

$$\int_{\Gamma_N} g_z(\mathbf{x}) d\mathbf{x} = 1. \quad (3.1.18)$$

Hence, one can obtain by averaging the dynamical functions the corresponding macroscopic variables by:

$$\int_{\Gamma_N} g_z(\mathbf{x}) \Pi_{z_i}(\mathbf{x}) d\mathbf{x} = z_i, \quad (3.1.19)$$

or by introducing a more convenient notation, the above expression can be rewritten as follows:

$$z_i = \langle \Pi_{z_i}(\mathbf{x}) \rangle_z. \quad (3.1.20)$$

One can think of the above average  $\langle \rangle_z$  to be taken with respect to the distribution  $g_z(\mathbf{x})$  of a certain macrostate  $\mathbf{z}$ , could also be defined by:

$$\langle \rangle_z := \frac{1}{V_{\Gamma_N}(\mathbf{z})} \int_{\Gamma_N} \delta(\Pi_z(\mathbf{x}) - \mathbf{z}) d\mathbf{x} := \frac{1}{V_{\Gamma_N}(\mathbf{z})} \int_{\Gamma_N} \prod_i (\Pi_{z_i}(\mathbf{x}) - z_i) d\mathbf{x}, \quad (3.1.21)$$

where the probability density is clearly defined by the form:  $g_z(\mathbf{x}) := \frac{1}{V_{\Gamma_N}(\mathbf{z})} \delta(\Pi_z(\mathbf{x}) - \mathbf{z})$ . In the above relations,  $V_{\Gamma_N}(\mathbf{z})$  stands for the volume of the phase space associated with a macrostate  $\mathbf{z}$  and can be defined by the relation:

$$V_{\Gamma_N}(\mathbf{z}) := \int_{\Gamma_N} \delta(\Pi_z(\mathbf{x}) - \mathbf{z}) d\mathbf{x}. \quad (3.1.22)$$

The evolution of the relevant variables can be described in terms of a stochastic process characterized by a sequence of joint probability distributions say  $\mathcal{P}(z_1, t_1, \dots, z_n, t_n)$ . For example the evolution of a microstate  $\mathbf{x} = \{\mathbf{r}_i, \mathbf{p}_i\}_{i=1, \dots, N}$  can be considered as a stochastic process itself with the corresponding joint probability distributions  $g_n = (x_1, t_1, \dots, x_n, t_n)$ . Since the mesoscopic probability and the ensemble are connected by the relationship

$$\mathcal{P}(\mathbf{z}, t) = \int_{\Gamma_N} \delta(\Pi_z(\mathbf{x}) - \mathbf{z}) g_z(\mathbf{x}, t) d\mathbf{x}. \quad (3.1.23)$$

**Remark 3.2 (Mori-Zwanzing projection and separation of time-scales).** *Zwanzing theory indicates that one can obtain a close dynamical equation that does not refer to the dynamics generated by the ensemble  $g_z(\mathbf{x}, t)$ , by applying a projection operator [28, 268, 269] with its action to be defined by*

$$\mathbb{P}\mathcal{A}(\mathbf{x}) = \langle \mathcal{A} \rangle_{\Pi_z(\mathbf{x})}, \quad (3.1.24)$$

where  $\mathcal{A}(\mathbf{x})$  is any arbitrary dynamical function over the phase space and the conditional average  $\langle \mathcal{A} \rangle_z$  is given by

$$\langle \mathcal{A} \rangle_z = \frac{1}{V_{\Gamma_N}(\mathbf{z})} \int_{\Gamma_N} g_N^0 \delta(\Pi_z(\mathbf{x}) - \mathbf{z}) \mathcal{A}(\mathbf{x}) d\mathbf{x}, \quad (3.1.25)$$

where  $g_N^0 = h^{-3N} (N!)^{-1}$ . Thus, the projection transforms any arbitrary function  $\mathcal{A}$  to a function

of the relevant variables  $\Pi_{\mathbf{z}}(\mathbf{x})$  and hence this projection operator separates "slow" (macroscopic) from "fast" (microscopic) variables, and the projector is then the key to the atomistic calculation of the several dynamic material properties [28].

The projection  $\mathbb{P}$  and its complementary  $\mathbb{P}' = 1 - \mathbb{P}$  satisfy the properties  $\mathbb{P}^2 = \mathbb{P}$  and the property  $\mathbb{P}\Pi_{z_j}(\mathbf{x}) = \Pi_{z_j}(\mathbf{x})$ . The second can be easily verified by differentiating the following fundamental average with respect to each state variable  $z_i, i = 1, \dots, d$  form the set  $\mathbf{z} = [z_1, \dots, z_m] \in \mathcal{Z}_1(D) \times \dots \times \mathcal{Z}_m(D) \times [0, \infty)$ , namely:

$$\int_{\Gamma_N} \Pi_{z_j}(\mathbf{x}) \partial_{z_i} g_{\mathbf{z}}(\mathbf{x}) d\mathbf{x} = \partial_{z_i} z_j = \delta_{ji}. \quad (3.1.26)$$

By plugging this result satisfies the definition for  $\mathcal{A}(\mathbf{x}) = \Pi_{z_j}(\mathbf{x})$ , the property is verified. In addition,  $\mathbb{P}\mathbb{P}' = 0$  and  $\mathbb{P}'^2 = \mathbb{P}'$ . The basic idea behind the introduction of this projection operator is to approximate the macroscopically relevant contribution of a phase space function, by simply ensemble averaging it and to indicate the variance from the average in linear terms of the deviations of the slowly evolving variables from their averages. The complementary projection  $\mathbb{P}'$  projects the "slow" rate of change of the  $\Pi_{z_i}(\mathbf{x})$  to its fast fluctuating part, lets denote it by  $\dot{\Pi}_{z_i}^f(\mathbf{x})$ . The "fast" time rate of change

$$\dot{\Pi}_{z_i}^f(\mathbf{x}) := \mathbb{P}' \dot{\Pi}_{z_i}(\mathbf{x}) := \mathbb{P}' \mathcal{L} \Pi_{z_i}(\mathbf{x}), \quad (3.1.27)$$

is orthogonal to the space of microscopic dynamic variables  $\Pi_{z_i}$  in the sense that  $\mathbb{P} \dot{\Pi}_{z_i}^f(\mathbf{x}) = 0$ . Using the same argument, the "fast" contribution to the time evolution is generated by a Liouville operator of the form:

$$\mathcal{L}' := \mathbb{P}' \mathcal{L} \mathbb{P}' \text{ and thus } \dot{\Pi}_{z_i}^f(\mathbf{x}) := \mathcal{L}' \Pi_{z_i}(\mathbf{x}). \quad (3.1.28)$$

We further introduce for simplicity, the more convenient notation  $X_{\mathbf{z}}(\mathbf{x}) = \delta(\Pi_{\mathbf{z}}(\mathbf{x}) - \mathbf{z})$ . The evolution of the phase function  $X_{\mathbf{z}}(\mathbf{x})$  is dictated by the Liouville's equation namely,

$$X_{\mathbf{z}}(T_t \mathbf{x}) = e^{\mathcal{L}t} X_{\mathbf{z}}(\mathbf{x}). \quad (3.1.29)$$

Thus, it is straightforward that

$$\partial_t X e^{\mathcal{L}t} = e^{\mathcal{L}t} \mathbb{P} + \int_0^t e^{\mathcal{L}t'} \mathbb{P} \mathcal{L} \mathbb{P}' e^{\mathcal{L}(t-t')} + \mathbb{P}' e^{\mathbb{P}' \mathcal{L} t'} \mathcal{L}' X_{\mathbf{z}}(T_t \mathbf{x}) dt' = \mathcal{L} e^{\mathcal{L}t} X_{\mathbf{z}}(\mathbf{x}). \quad (3.1.30)$$

The following identity between the operators  $\mathbb{P}$  and  $\mathbb{P}'$  holds which can be proved by taking the time derivative in both sides. Using the forms for the operators [39] [28] and  $\mathcal{L}X_{\mathbf{z}}(\mathbf{x}) = \mathcal{L}\Pi_{z_i}(\mathbf{x}) \partial_{z_i} X_{\mathbf{z}}(\mathbf{x})$ , which is a consequence of the chain rule and by plugging this into the equation (3.1.29), one obtains from (3.1.30) that

$$\begin{aligned} \partial_t X_{\mathbf{z}}(T_t \mathbf{x}) &= -\partial_{z_i} \cdot m_i(\mathbf{z}) X_{\mathbf{z}}(T_t \mathbf{x}) + \mathbb{P}' e^{\mathbb{P}' \mathcal{L} t} \mathbb{P}' \mathcal{L} X_{\mathbf{z}}(T_t \mathbf{x}) \\ &\quad + \int_0^t \int V_{\Gamma_N}(\mathbf{z}') \partial_{z_i} \cdot \mathbb{M}^{ij}(\mathbf{z}, \mathbf{z}', t-t') \cdot \partial_{z_j}' V_{\Gamma_N}(\mathbf{z}')^{-1} X_{\mathbf{z}'}(T_t' \mathbf{x}) dt' d\mathbf{z}', \end{aligned} \quad (3.1.31)$$

in which we have defined  $m_i(\mathbf{z}) = \langle \mathcal{L}\Pi_{z_i}(\mathbf{x}) \rangle_{\mathbf{z}}$  and the matrix

$$\mathbb{M}^{ij}(\mathbf{z}, \mathbf{z}', t-t') = \langle (\mathcal{L}\Pi_{z_i}(\mathbf{x}) - \langle \Pi_{z_i}(\mathbf{x}) \rangle_{\mathbf{z}'}) e^{\mathbb{P}' \mathcal{L} t'} X_{\mathbf{z}'}(\mathcal{L}\Pi_{z_i}(\mathbf{x}) - \langle \mathcal{L}\Pi_{z_i}(\mathbf{x}) \rangle_{\mathbf{z}'}) \rangle_{\mathbf{z}'}. \quad (3.1.32)$$

Finally, by multiplying equation (3.1.31) by the ensemble  $g_{\mathbf{z}}(\mathbf{x}, 0)$  and integrate over  $\mathbf{x}$  we

obtain the following form for  $\mathcal{P}$ :

$$\partial_t \mathcal{P}(\mathbf{z}, t) = -\partial_{z_i} \cdot m_i(\mathbf{z}) \mathcal{P}(\mathbf{z}, t) + \int_0^t \int V_{\Gamma_N}(\mathbf{z}') \partial_{z_i} \cdot \mathbb{M}^{ij}(\mathbf{z}, \mathbf{z}', t-t') \cdot \partial_{z_j}' \mathcal{P}(\mathbf{z}', t') V_{\Gamma_N}(\mathbf{z}')^{-1} d\mathbf{z}' dt', \quad (3.1.33)$$

since we introduced the initial ensemble as  $g_{\mathbf{z}}(\mathbf{x}, 0) := \mathcal{P}(\Pi_{z_i}(\mathbf{x}), 0) V_{\Gamma_N}(\Pi_{z_i}(\mathbf{x}))^{-1}$  and from the properties of the projection one finally deduces that

$$\int g_{\mathbf{z}}(\mathbf{x}, 0) \mathbb{P}' e^{\mathbb{P}' \mathcal{L} t} \mathbb{P}' \mathcal{L} X_{\mathbf{z}}(T_t \mathbf{x}) d\mathbf{x} = 0. \quad (3.1.34)$$

**Definition 3.6 (The Markovian approximation).** *The Markovian approximation [270] indicates the separation of the timescales between the scale of evolution of the microscopic dynamical functions  $\Pi_{\mathbf{z}}(\mathbf{x})$  and the other variables. Mathematically can be summarized in the expression:*

$$\int_0^t \mathbb{M}(\mathbf{z}, \mathbf{z}', t-t') \mathcal{P}(\mathbf{z}, t') dt' \approx \mathcal{P}(\mathbf{z}, t) \int_0^\tau \mathbb{M}(\mathbf{z}, \mathbf{z}', t') dt', \quad (3.1.35)$$

where  $\tau$  is a large enough timescale for  $\mathbb{M}$  to be eliminated.

Since the timescale of the set of the microscopic dynamical functions  $\Pi_{\mathbf{z}}(\mathbf{x})$  is the same as that of the evolution of the probability density  $\mathcal{P}$ , the result of performing the above approximation is to eliminate third order derivatives over time of  $\Pi_{\mathbf{z}}(\mathbf{x})$  prior to the terms of second order. The idea to get a rough approximation is to apply an expansion of  $\mathbb{M}^{ij}(\mathbf{z}, \mathbf{z}', t-t')$  in terms of  $\mathcal{L}\Pi_{\mathbf{z}}(\mathbf{x})$  and keep only second order terms, which leads to,

$$e^{\mathcal{L}\mathbb{P}' t} X_{\mathbf{z}} \mathbb{P}' \mathcal{L} X_{\mathbf{z}} e^{\mathcal{L}\mathbb{P}' t} \mathcal{L} \mathbb{P}' \Pi_{\mathbf{z}}(\mathbf{x}) + \mathcal{O}(\mathcal{L}\Pi_{\mathbf{z}}(\mathbf{x}))^2. \quad (3.1.36)$$

As a result, up to terms of order  $\mathcal{O}(\mathcal{L}\Pi_{\mathbf{z}}(\mathbf{x}))^3$  we have

$$\mathbb{M}^{ij}(\mathbf{z}, \mathbf{z}', t) = \delta(\mathbf{z} - \mathbf{z}') \langle (\mathcal{L}\Pi_{z_i}(\mathbf{x})) - \langle \mathcal{L}\Pi_{z_i}(\mathbf{x}) \rangle_{\mathbf{z}} \rangle e^{\mathcal{L}\mathbb{P}' t} \langle (\mathcal{L}\Pi_{z_j}(\mathbf{x})) - \langle \mathcal{L}\Pi_{z_j}(\mathbf{x}) \rangle_{\mathbf{z}} \rangle_{\mathbf{z}}. \quad (3.1.37)$$

By plugging (3.1.37) into (3.1.33) and with the help of the approximation (3.1.35), we deduce:

$$\partial_t \mathcal{P}(\mathbf{z}, t) = -\frac{\partial}{\partial z_i} m_i(\mathbf{z}) \mathcal{P}(\mathbf{z}, t) + \frac{\partial}{\partial z_i} V_{\Gamma_N}(\mathbf{z}) M_{ij}(\mathbf{z}) \frac{\partial}{\partial z_j} \frac{\mathcal{P}(\mathbf{z}, t)}{V_{\Gamma_N}(\mathbf{z})}, \quad (3.1.38)$$

with the diffusion tensor to be defined by

$$\mathbb{M}^{ij}(\mathbf{z}) = \int_0^\tau \langle (\mathcal{L}\Pi_{z_j}(\mathbf{x})) - \langle \mathcal{L}\Pi_{z_j}(\mathbf{x}) \rangle_{\mathbf{z}} \rangle e^{\mathcal{L}\mathbb{P}' t'} \langle (\mathcal{L}\Pi_{z_i}(\mathbf{x})) - \langle \mathcal{L}\Pi_{z_i}(\mathbf{x}) \rangle_{\mathbf{z}} \rangle_{\mathbf{z}} dt'. \quad (3.1.39)$$

**Definition 3.7 (Partition function).** *If one considers a system of  $N$  identical particles, the state of the system can be defined as the vector of microstates  $\mathbf{x} = (\mathbf{x}_1, \dots, \mathbf{x}_N)$ , where  $\mathbf{x}_i := (\mathbf{r}_i, \mathbf{p}_i)$  denotes the microstate of the  $i$ -th particle. We define the canonical partition function for the corresponding Hamiltonian  $\mathcal{H}_{\mathcal{Z}}^N(\mathbf{x})$  in the state  $\mathbf{x}$  as follows:*

$$\mathbf{f}_{\mathcal{Z}}(\beta, N) := \frac{1}{N! h^{3N}} \int_{\mathcal{Z}} e^{-\beta \mathcal{H}_{\mathcal{Z}}^N(\mathbf{x})} d\mathbf{x}, \quad (3.1.40)$$

where  $\beta = (k_B \Theta)^{-1} > 0$  is a term corresponding to the inverse of the system's temperature  $\Theta$ , with  $k_B$  to denote the Boltzmann constant.

**Remark 3.3 (Entropy, Internal and Free energy of the system).** *The second postulate of statistical mechanics indicates that the entropy (Gibbs-Boltzmann entropy) is a measure of the number of microstates occupied by the system, quantified by:*

$$S(P_{\mathbf{x}}) := -k_{\beta} \int_{\mathcal{Z}} P_{\mathbf{x}} \ln(P_{\mathbf{x}}) d\mathbf{x}, \quad (3.1.41)$$

where  $P_{\mathbf{x}}$  denotes the probability that system is found in the microstate  $\mathbf{x}$ . One can identify the relation between entropy and the partition function (3.1.40) as

$$S(P_{\mathbf{x}}) := -k_{\beta} \int_{\mathcal{Z}} P_{\mathbf{x}} \ln(P_{\mathbf{x}}) d\mathbf{x} = \frac{\partial}{\partial \Theta} (k_{\beta} \Theta \ln(\mathbf{f}_{\mathcal{Z}})) = -\frac{\partial \mathcal{F}}{\partial \Theta}. \quad (3.1.42)$$

Therefore, in terms of the partition function the free energy of the system can be defined by:  $\mathcal{F} := -\Theta \ln \mathbf{f}_{\mathcal{Z}}$ . The Helmholtz free energy is a scalar valued function defined on probability distributions and composed by a combination of an internal energy  $\mathcal{U}$  term and an entropy functional  $\mathcal{S}$  and can be expressed in the following variational form

$$\mathcal{F}(P_{\mathbf{x}}) = \mathcal{U}(P_{\mathbf{x}}) - \Theta \mathcal{S}(P_{\mathbf{x}}), \quad (3.1.43)$$

where  $P_{\mathbf{x}}$  is a probability density function which represents the probability of finding the system in the state  $\mathbf{x}$  and it is defined on a "continuous" state space  $\mathcal{Z}$ . For a system in a continuous state space one can define the internal energy functional, given a Hamiltonian  $\mathcal{H}_{\mathcal{Z}}^N(\mathbf{x})$ , in an integral form, i.e.,

$$\mathcal{U}(P_{\mathbf{x}}) := \int_{\mathcal{Z}} \mathcal{H}_{\mathcal{Z}}^N(\mathbf{x}) P_{\mathbf{x}} d\mathbf{x}. \quad (3.1.44)$$

More details on these introductory concepts can be found in many textbooks about statistical mechanics and thermodynamics such as [260, 263, 271–273].

The total entropy functional  $\mathcal{S}(\mathbf{z})$  of the system, is commonly associated with the amount of order, disorder, or chaos in a thermodynamic system, the higher the entropy the greater the disorder. On the other hand, the energy  $\mathcal{E}(\mathbf{z})$  can be defined as the capacity for doing work. It may exist in a variety of forms and may be transformed from one type of energy to another. Roughly speaking, the internal interactions between particles and all motions are expressed in the total energy  $\mathcal{E}$  and all the internal organization in entropy  $\mathcal{S}$ . It is natural to assume that the energy  $\mathcal{E}$  of the macrostate  $\mathbf{z}$  should be identified by the ensemble average of the Hamiltonian over the corresponding microstates  $\mathbf{x}$ :

$$\mathcal{E}(\mathbf{z}) = \langle \mathcal{H}_{\mathcal{Z}}^N(\mathbf{x}) \rangle_{\mathbf{z}} := -\frac{1}{\mathbf{f}_{\mathcal{Z}}(\beta, N)} \frac{\partial \mathbf{f}_{\mathcal{Z}}(\beta, N)}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln(\mathbf{f}_{\mathcal{Z}}(\beta, N)), \quad (3.1.45)$$

which also follows by the definition (3.1.40) of the partition function. Similarly, the probability density  $g_{\mathbf{z}}(\mathbf{x})$ , is such that, to maximize the following form of the entropy  $\mathcal{S}(\mathbf{z})$  first introduced by Gibbs' .

**Definition 3.8 (Gibbs' entropy).** *The entropy of the system can be defined according to Gibbs as the following functional, in terms of the probability distribution  $g_{\mathbf{z}}(\mathbf{x})$ :*

$$\mathcal{S}_G(g_{\mathbf{z}}(\mathbf{x})) := -k_{\beta} \int_{\Gamma_N} g_{\mathbf{z}}(\mathbf{x}) \ln(g_{\mathbf{z}}(\mathbf{x})) d\mathbf{x} = -k_{\beta} \ln(V_{\Gamma_N}(\mathbf{z})), \quad (3.1.46)$$

where  $k_{\beta}$  is the well know Boltzmann's constant.

In addition, The Boltzmann entropy is obtained if one assumes one can treat all the component particles of a thermodynamic system as statistically independent. The probability distribution of the system as a whole then factorises into the product of  $N$  separate identical terms, one term for each particle; and the Gibbs entropy simplifies to the Boltzmann entropy, which is a function on the macrostates, and consequently also a function on the phase points in  $\Gamma_N$ :

**Definition 3.9 (Boltzmann entropy).** *In comparison to the form (3.1.46) the entropy functional can be also expressed according to Boltzmann for the marginal distribution of a small part of an equilibrium ensemble, as follows:*

$$S_B(\mathbf{z}) := -Nk_B \int_{\Gamma_N} g_1(\mathbf{x}_1) \ln(g_1(\mathbf{x}_1)) d\mathbf{x}_1, \quad (3.1.47)$$

where  $g_1(\mathbf{x}_1) := \int_{\Gamma_N} g_z(\mathbf{x}) d\mathbf{x}_{-1}$  is the marginal one-particle (probability) distribution and  $d\mathbf{x}$ ,  $d\mathbf{x}_1$ ,  $d\mathbf{x}_{-1}$  stand for phase-volume elements in the whole phase space, the space of one particle and the space of all particles except one, respectively, see also [274] for more details on Boltzmann entropy.

According to Boltzmann the entropy is proportional to the logarithm of the number of states and finally leads to a description of the equilibrium states as probability measures (on the phase space of the system), given by the Gibbs formula. Further details regarding the relation between the Boltzmann and Gibbs entropies are beyond the scope of this report and can be found in [275]. The definition (3.1.46) is motivated by a strong physical background. The entropy is actually a measure of disorder, and the more disordered a macrostate is the higher is the entropy. This definition resolves the Gibbs' Paradox [276] which states that the entropy of closed systems is decreasing and the related Gibb's-mixing Paradox which states that the entropy of mixing tends to be eliminated, discontinuously as the mixing features become the same. In the Boltzmann's approach we are dealing with probabilities and hence it indicates our knowledge or ignorance of the microstate.

It is straightforward that one can consider the notion of disorder as loss of information and uncertainty and therefore in an ideal and perfectly ordered state, we can deduce all the required information about each microscopic quantity. Hence, the higher the entropy (disorder) is, the more loss of information about the microscopic constituents we experience. This consequently leads to the assignment of a probability for the identification of each possible particle position and momentum. Each particular ensemble  $g_z(\mathbf{x})$  describes a different configuration of the system's exchanges with the surroundings, varying from a completely isolated system to an open system (exchanges energy and matter with the surroundings).

In this context, the second law of thermodynamics as we will see later, indicates that the equilibrium state of the system is characterised by the maximization of entropy of the system and its reservoir as a whole, in any ensemble. A summary of the aspects related to the second law, is provided in the following statement.

**Remark 3.4 (The Second Law of Thermodynamics).** *The Second Law of Thermodynamics simply indicates that entropy never decreases and can be summarised in the statement*



by Clausius, who came to the conclusion that that there are no thermodynamic processes, in which the only net change is a transfer of heat between two reservoirs with temperature difference (lower temperature body transfers to the higher temperature body). In comparison, the Kelvin-Planck statement indicates that it does not exist any thermodynamic process, in which the only effect is to extract a specific amount of heat from a reservoir and fully convert it into work [277, 278].

Isolated thermodynamic systems are considered to be systems, without any thermal or mechanical interaction with the surroundings. Hence, the role of any interaction with the environment and any boundary effects are negligible. In addition, any internal interaction in an isolated system involves no change in the internal energy  $\mathcal{U}$ , in the volume  $V$ , or in the number of particles. If one considers the case of closed isolated systems (systems with fixed internal energy  $\mathcal{U}$ ), will point out the Planck's statement of the Second Law of Thermodynamics. According to that, the sum of the entropies of all partial systems that are interacting inside a natural process, is increasing. Mathematically can be summarized in the simple expression:  $dS/dt \geq 0$ . In comparison, the conservation of energy principle implies that the total energy  $\mathcal{E}$  of an isolated system remains constant.

The several energy transformations are constrained by this conservation of energy principle. In addition, for closed systems with fixed entropy (non isolated) the restatement for the second law states that, the internal energy will decrease and approach a minimum value at equilibrium. As a consequence, the total energy  $\mathcal{E}$  approaches a minimum in equilibrium in this case.

**Remark 3.5 (Fundamental equations of state).** *The following fundamental equation of state that combine all these state variables, hold for a  $k$  component system [28, 51, 279].*

$$d\mathcal{U} = \Theta dS - p dV + \sum_i^k \mu_i dN_i = \partial_S \mathcal{U} dS + \partial_V \mathcal{U} dV + \partial_N \mathcal{U} dN, \quad (3.1.48)$$

where  $\mu_i$  are the chemical potentials corresponding to particles of type  $i$  and  $N_i$  are the related amounts of the chemical components of type  $i$ , in the system (i.e. the composition which is non-uniform in this case). The last term is eliminated in a reversible process. Additionally, following [28] and any other standard text book for non-equilibrium thermodynamics, it is easy to derive a useful identity for the pressure, by considering the following expression for the internal energy and its density  $u$ :

$$\mathcal{U}(S, V, N) = Vu(mN/V, S/V) \quad (3.1.49)$$

and the entropy fundamental relation

$$dS = \frac{1}{\Theta} d\mathcal{U} + \frac{p}{\Theta} dV - \frac{\mu m}{\Theta} dN = \partial_U S d\mathcal{U} + \partial_V S dV + \partial_N S dN, \quad (3.1.50)$$

where the last equality is a consequence of the chain rule.

Hence one can identify:

$$\begin{cases} \partial_S \mathcal{U} = \Theta, \quad \partial_V \mathcal{U} = -p, \quad \partial_N \mathcal{U} = \mu, \\ \partial_U S = \Theta^{-1}, \quad \partial_V S = p\Theta^{-1}, \quad \partial_N S = -\mu m\Theta^{-1}. \end{cases} \quad (3.1.51)$$

Thus, it is straightforward to rewrite the identifications (3.1.51) as follows:

$$\begin{cases} \Theta = \partial_S \mathcal{U} = V \partial_s u \frac{1}{V}, & \mu m = \partial_N \mathcal{U} = V \partial_\rho u \frac{m}{V}, \\ -p = \partial_V \mathcal{U} = u - V \partial_\rho u \frac{mN}{V^2} - V \partial_s u \frac{S}{V^2} = u - \mu \rho - \Theta s. \end{cases} \quad (3.1.52)$$

In the above relations  $\mu m$  stands for the chemical potential per particle and  $N$  is the total number of interacting particles in the system. This could be the right point to recall the notion of equilibrium.

**Remark 3.6 (Thermodynamic equilibrium).** *The "Equilibrium State" of a thermodynamic system can be identified by a relatively small number of variables that characterised it, such as pressure, volume, temperature, internal energy and entropy. According to the definitions that can be found in a variety of textbooks, such as [51, 280], in the "Equilibrium State", the temperature, pressure and the chemical potential are uniformly allocated throughout the system.*

*The general principle that governs an isolated system that reaches the "Equilibrium State", is that it occurs when the entropy functional approaches a maximum value. If the system can be divided into small partial systems with still enough many particles in each one, each of those can be individually described by thermodynamic state quantities and the notion of the "Equilibrium State". Note that, the several state variables though may be different from partial to partial system and these changes affect heat flow, volume changes and particle fluxes which are driven by the corresponding potential differences.*

**Remark 3.7 (Reversibility-irreversibility).** *Reversible thermodynamic processes are processes without any increase in entropy and can be "reversed" with infinitesimal changes to some of the system's properties, via its surroundings. If one considers the system that undergoes a reversible process as a whole, it is in thermodynamic equilibrium with the environment. The concept of microscopic reversibility is based on the fact that the microscopic detailed dynamics of particles and fields is time-reversible because the microscopic equations of motion are symmetric with respect to inversion in time. Moreover, it relates to the statistical description of the kinetics of macroscopic or mesoscopic systems as an ensemble of elementary processes such as collisions, elementary transitions or reactions. On the other hand, macroscopically irreversible processes are considered as the processes that involve energy dissipation at the presence of some friction force, with respect to inconsiderable changes in the external conditions [281, 282].*

The general mathematical background beyond the thermodynamic theory of irreversible processes, was initially demonstrated by L. Onsager in two papers of 1931 [33, 34] and included the study of thermoelectric phenomena, the transference phenomena in electrolytes and heat conduction in anisotropic media. To this end, the investigations were focused on the identification of the connection between measurable quantities such as transport coefficients and thermodynamic derivatives and the related experimental measurements.

**Remark 3.8 (Onsager relations and entropy production).** According to L. Onsager the average thermodynamic flux is proportional to the partial derivative of the entropy (entropy production), over a random variable and can be mathematically summarised in the following relationship between the non-conjugate forces  $g_i$  and fluxes  $\mathbf{J}_i$  [283–285]:

$$\mathbf{J}_i = \sum_j \mathbb{M}^{ij} g_j, \quad (3.1.53)$$

where the coefficients  $\mathbb{M}^{ij}$  are constants, that are often called the phenomenological or kinetic coefficients and are considered to be symmetric, i.e.,  $\mathbb{M}^{ji} = \mathbb{M}^{ij}$ . In terms of the fluxes according to the second law of thermodynamics, the entropy production [287] can be expressed as follows:

$$\pi_S = \sum_{ij} \mathbb{M}^{ij} \mathbf{J}_i \mathbf{J}_j \geq 0. \quad (3.1.54)$$

### 3.2 Metriplectic flows/Generic formalism.

Time evolution equations for non-equilibrium systems have a well-defined mathematical structure in which reversible and irreversible contributions are identified separately forming two-generator framework in which the energy generates the reversible contribution to time evolution by means of a Poisson bracket and the entropy generates the irreversible contribution by a dissipative bracket. This formalism provides a unification of reversible dynamics obtained like Hamiltonian effects via a Poisson structure  $\mathbb{L}$  and an energy functional  $\mathcal{E}$  and in addition, dissipative dynamics like gradient flows obtained from a dissipative geometric structure  $\mathbb{M}$  and an entropy functional  $S$ . The general form of the evolution equations and properties is summarised in the the following Definition [28, 29, 288–291]:

**Definition 3.10 (General Equation for Non-Equilibrium Reversible-Irreversible Coupling (GENERIC)).** We assume that  $\mathcal{Z}^{mz}(D) := \mathcal{Z}_1(D) \times \dots \times \mathcal{Z}_m(D) \subset \mathcal{D}_z := W^{1,p}(D, \mathbb{R}^m) |_{1 \leq p \leq +\infty}$  is (re-) arranged such that  $\mathbf{z} = [z_1, \dots, z_m]^T \in \mathcal{Z}^{mz}(D)$  for each  $z_i \in \mathcal{Z}_i(D)$ ,  $i = 1, \dots, m$ , i.e.,  $\mathbf{z}: I \rightarrow \mathcal{Z}^{mz}(D)$  for a bounded time interval  $I := [0, T]$ . Then, the evolution equations of the whole  $\mathbf{z}$  in terms of the total energy and entropy functions  $\mathcal{E}, S \in C^\infty(\mathcal{Z}^{mz})$  read in the following form

$$\partial_t \mathbf{z} = \mathbb{L}(\mathbf{z}) \cdot \nabla_z^2 \mathcal{E}(\mathbf{z}) + \mathbb{M}(\mathbf{z}) \cdot \nabla_z^2 S(\mathbf{z}) \text{ in } \mathcal{D}_z^*, \quad (3.2.1)$$

where  $\mathcal{D}_z^*$  stands for the dual space of  $\mathcal{D}_z$ . The equation can be written in the equivalent component form for a set of  $m$  state variables in terms of the energy and entropy densities, as below:

$$\partial_t z_i = \sum_{j=1}^m \mathbb{L}^{z_i z_j}(\mathbf{z}) \partial_{z_j} e(\mathbf{z}) + \mathbb{M}^{z_i z_j}(\mathbf{z}) \partial_{z_j} s(\mathbf{z}), \quad i = 1, \dots, m. \quad (3.2.2)$$

An orthogonality requirement for the Poisson tensor  $\mathbb{L}$  is imposed and expressed as follows:

$$\mathbb{L}(\mathbf{z}) \cdot \partial_z s(\mathbf{z}) = \mathbf{0}. \quad (3.2.3)$$

The requirement expresses the reversible nature of the the Poisson tensor's contribution to the dynamics: the functional form of the entropy is such that it cannot be affected by the

operator generating the reversible dynamics. Furthermore,  $\mathbb{M}$  is also supplemented with a degeneracy requirement similar to that for  $\mathbb{L}$ , namely:

$$\mathbb{M}(\mathbf{z}) \cdot \partial_{\mathbf{z}} e(\mathbf{z}) = \mathbf{0}. \quad (3.2.4)$$

This relation indicates the conservation of the total energy by the  $\mathbb{M}$  contribution to the evolution equations.

The initial motivation for developing this formalism, comes from the modelling of the several rheological properties of complex fluids, such as time evolution of the whole set of state variables should be formulated such that the form of each equation, guarantee the approach of thermodynamic equilibrium.

**Remark 3.9 (Metriplectic systems).** *The GENERIC evolution pattern can be also identified by the term "metriplectic flows" [30], in close connection with the Onsager reciprocal relations [33], where the evolution equations are formulated using the generalised free energy  $\mathcal{F}$  in a similar way, as follows:*

$$\partial_t z_i = \sum_{j=1}^m \mathbb{L}^{z_i z_j}(\mathbf{z}) \partial_{z_j} f(\mathbf{z}) + \mathbb{M}_M^{z_i z_j}(\mathbf{z}) \partial_{z_j} f(\mathbf{z}), \quad i = 1, \dots, m, \quad (3.2.5)$$

where  $f$  stands for density of the free energy  $\mathcal{F}$  and  $\mathbb{M}_M$  (analogously to the previous dissipative term), denotes a symmetric and positive semi-definite tensor. Hence, it is clear that the GENERIC evolution equations can be obtained via this metriplectic form by identifying  $f(\mathbf{z}) := e(\mathbf{z}) - \Theta s(\mathbf{z})$  and  $\mathbb{M}_M(\mathbf{z}) = -\Theta^{-1} \mathbb{M}(\mathbf{z})$  [45].

Moreover, it is worth pointing out that GENERIC provides a systematic method to derive thermodynamically consistent evolution equations. Further to the application in the context of complex fluids (hydrodynamic equations and phase-field Navier stokes [28, 42, 43]) more recently has been applied in the context of large-deviation principles and Wasserstein gradient flows [292, 293] and more precisely to the Vlasov-Fokker-Planck equation [294]. Applications also involve a framework for anisotropic inelastic solids, viscoplastic solids and thermoelastic dissipative materials [288, 295–297]. The set  $\mathbf{z}$  must be such that, the several variables are independent and sufficient to capture the physics of the particular problem. The particular choice of variables depends on the specific model each time and the separation of reversible and irreversible contributions, indicates a separation of slow and fast degrees of freedom [28, 35].

### 3.2.1 Properties of GENERIC.

The Poisson tensor  $\mathbb{L}$  [28],[29] (reversible contribution) transforms the vector  $\partial_{\mathbf{z}} e$  into a vector  $\mathbb{L} \cdot \partial_{\mathbf{z}} e$  and has its origins to the Poisson brackets of classical mechanics. It describes kinematics, symplecticity and time-reversal invariance, which means that the property of antisymmetry is a natural requirement [29, 298]. One can compare the energy included into the reversible part of the evolution, to the Hamiltonian in the simple case where we have particles of the same species  $\mathcal{H}(\mathbf{r}_k, \mathbf{p}_k)$  of a discrete system of  $N$  interacting particles with positions  $\mathbf{r}_k = \mathbf{r}_k(t)$  and the corresponding momenta  $\mathbf{p}_k = \mathbf{p}_k(t)$ , for  $k = 1, \dots, N$ . Thus, it is

straightforward to extend the idea of the time evolution of a state variable presented in the first section and the Poisson bracket of classical mechanics, to define the elements of the Poisson tensor  $\mathbb{L}$ . Under the above considerations we are able know to define the elements of the Poisson tensor. As a first guess, one might use the transformation formula

$$\frac{\partial \Pi_{z_i}(\mathbf{x})}{\partial \mathbf{x}} \cdot \mathbb{L}_0 \cdot \frac{\partial \Pi_{z_j}(\mathbf{x})}{\partial \mathbf{x}}, \quad (3.2.6)$$

for transforming from the Poisson tensor of classical mechanics to the variables  $\mathbf{z}$ . However, the expression is still a function of microstates  $\mathbf{x}$  rather than  $\mathbf{z}$ . This transformation is certainly not one-to-one thus, it cannot be inverted so that there are many possible microstates in which the above expression for given macrostate could be evaluated. The most natural way to proceed, is by averaging over the ensemble  $g_{\mathbf{z}}$  these contributions and assume that

$$\mathbb{L}^{z_i z_j}(\mathbf{z}) = \left\langle \frac{\partial \Pi_{z_i}(\mathbf{x})}{\partial \mathbf{x}} \cdot \mathbb{L}_0 \cdot \frac{\partial \Pi_{z_j}(\mathbf{x})}{\partial \mathbf{x}} \right\rangle_{\mathbf{z}}. \quad (3.2.7)$$

Using the Poisson brackets the above expression can be written in a more convenient and compact form as follows:

$$\mathbb{L}^{z_i z_j}(\mathbf{z}) = \langle \{ \Pi_{z_i}, \Pi_{z_j} \} \rangle_{\mathbf{z}}. \quad (3.2.8)$$

**Remark 3.10 (Jacobi identity and Leibniz's rule).** *Let the state space  $\mathcal{Z}^{m\mathbb{Z}}(D) := \mathcal{Z}_1(D) \times \dots \times \mathcal{Z}_m(D)$  consists of sufficiently smooth enough functions which not necessarily vanish at the boundary. The first property, which is a direct result from its definition, using the Poisson brackets, is that the Poisson tensor is antisymmetric  $-\mathbb{L} = \mathbb{L}^T$ . Furthermore, it also satisfies the Jacobi identity, i.e., for three arbitrary and sufficiently regular real valued functionals  $\mathcal{A}_i: \mathcal{Z}^{m\mathbb{Z}} \rightarrow \mathbb{R}$ ,  $i = 1, 2, 3$ , on a space of the set  $\mathbf{z} \in \mathcal{Z}^{m\mathbb{Z}}(D)$  of independent state variables  $z_i, i = 1, \dots, m$  defined for all times, the following relationship holds:*

$$\{ \mathcal{A}_1, \{ \mathcal{A}_2, \mathcal{A}_3 \} \} + \{ \mathcal{A}_2, \{ \mathcal{A}_3, \mathcal{A}_1 \} \} + \{ \mathcal{A}_3, \{ \mathcal{A}_1, \mathcal{A}_2 \} \} = 0, \quad (3.2.9)$$

where  $\{ \cdot, \cdot \}: C^\infty(\mathcal{Z}^{m\mathbb{Z}}) \times C^\infty(\mathcal{Z}^{m\mathbb{Z}}) \rightarrow C^\infty(\mathcal{Z}^{m\mathbb{Z}})$  stands for the Poisson bracket, which can be defined in terms of the positions vectors  $\mathbf{r}$  and  $\mathbf{r}'$  by

$$\{ \mathcal{A}_1(\mathbf{z}), \mathcal{A}_2(\mathbf{z}) \} := \int_{D \times D} \sum_{ij} \frac{\delta \mathcal{A}_1(\mathbf{z})}{\delta z_i(\mathbf{r})} \mathbb{L}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2(\mathbf{z})}{\delta z_j(\mathbf{r}')} dr dr', \quad (3.2.10)$$

where the functional derivative  $\frac{\delta \mathcal{A}_k}{\delta \mathbf{z}}$  is defined by

$$\int_D \frac{\delta \mathcal{A}_k}{\delta \mathbf{z}} \mathbf{u} d\mathbf{r} = \frac{d}{d\epsilon} \mathcal{A}_k(\mathbf{z} + \epsilon \mathbf{u})|_{\epsilon=0}, \quad \forall \mathbf{u} \in \mathcal{X}(D) \subseteq \mathcal{Z}^{m\mathbb{Z}}(D) \quad (3.2.11)$$

and is interpreted as partial derivatives of the related density function of each particular functional  $\mathcal{A}_k$ . In addition, it is required that it should also satisfy the Leibniz rule, namely:

$$\{ \mathcal{A}_1 \mathcal{A}_2, \mathcal{A}_3 \} = \mathcal{A}_1 \{ \mathcal{A}_2, \mathcal{A}_3 \} + \mathcal{A}_2 \{ \mathcal{A}_1, \mathcal{A}_3 \}, \quad (3.2.12)$$

In order to proceed further we will make use of the following property for functional derivatives. For any arbitrary observables  $\mathcal{A}_1, \mathcal{A}_2 \in C^\infty(\mathcal{Z}^{m\mathbb{Z}})$  the following product rule is valid,

(see [313, p. 225], [314, Section 1.3] and also [291]),

$$\frac{\delta(\mathcal{A}_1\mathcal{A}_2)}{\delta z_i(\mathbf{r})} = \mathcal{A}_1(\mathbf{z}) \frac{\delta\mathcal{A}_2}{\delta z_i(\mathbf{r})} + \mathcal{A}_2(\mathbf{z}) \frac{\delta\mathcal{A}_1}{\delta z_i(\mathbf{r})}, \quad i = 1, \dots, m, \quad (3.2.13)$$

with  $\mathbf{z} := [z_1, \dots, z_m]^T \in \mathcal{Z}^{mz}(D)$  representing the set of state variables. In other words the functional derivative satisfies the Leibniz rule. Hence, we can equivalently rewrite the Leibniz rule in terms of the definition (3.2.10) of the Poisson brackets and with the help of the property (3.2.13), as follows:

$$\begin{aligned} & \int_{D \times D} \sum_{ij} \frac{\delta(\mathcal{A}_1\mathcal{A}_2)(\mathbf{z})}{\delta z_i(\mathbf{r})} \mathbb{L}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \frac{\delta\mathcal{A}_3(\mathbf{z})}{\delta z_j(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ &= \int_{D \times D} \sum_{ij} \left( \mathcal{A}_1(\mathbf{z}) \frac{\delta\mathcal{A}_2(\mathbf{z})}{\delta z_i(\mathbf{r})} + \mathcal{A}_2(\mathbf{z}) \frac{\delta\mathcal{A}_1(\mathbf{z})}{\delta z_i(\mathbf{r})} \right) \mathbb{L}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \frac{\delta\mathcal{A}_3(\mathbf{z})}{\delta z_j(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ &= \mathcal{A}_1(\mathbf{z}) \int_{D \times D} \sum_{ij} \frac{\delta\mathcal{A}_2(\mathbf{z})}{\delta z_i(\mathbf{r})} \mathbb{L}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \frac{\delta\mathcal{A}_3(\mathbf{z})}{\delta z_j(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ & \quad + \mathcal{A}_2(\mathbf{z}) \int_{D \times D} \sum_{ij} \frac{\delta\mathcal{A}_1(\mathbf{z})}{\delta z_i(\mathbf{r})} \mathbb{L}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \frac{\delta\mathcal{A}_3(\mathbf{z})}{\delta z_j(\mathbf{r}')} d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (3.2.14)$$

On the other hand the tensor  $\mathbb{M}$  (friction tensor) is related to irreversible processes and hence contains material parameters such as diffusion coefficients, viscosities etc. [28] The definition and properties of  $\mathbb{M}$  are based on the fundamental idea that the state variables  $z_i$  evolve on a large time scale compared to some intermediate scale  $\tau$ , and the microscopic variables are assumed to evolve much more rapidly compared to  $\tau$ , which has already been discussed earlier. Hence, the previously derived expression (3.1.39) for the friction tensor  $\mathbb{M}$ , can be simplified to the following Green-Kubo type formula [299]:

$$\mathbb{M}^{z_i z_j}(\mathbf{z}) = (k_B)^{-1} \int_0^\tau \langle \dot{\Pi}_{z_i}^f(\mathbf{x}(t)) \dot{\Pi}_{z_j}^f(\mathbf{x}(0)) \rangle_{\mathbf{z}} dt, \quad (3.2.15)$$

where  $\dot{\Pi}_{z_i}^f$  denotes the fast, fluctuating part of the time derivative of  $\Pi_{z_i}$  defined in (3.1.27) (see also [28, 42, 300]) and is connected to the dissipative bracket  $[\cdot, \cdot]$  defined for two observables  $\mathcal{A}_1, \mathcal{A}_2$  in an analogous way as the Poisson bracket (3.2.10), namely:

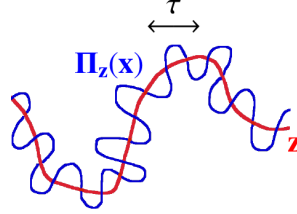
$$[\mathcal{A}_1(\mathbf{z}), \mathcal{A}_2(\mathbf{z})] := \int_{D \times D} \sum_{ij} \frac{\delta\mathcal{A}_1(\mathbf{z})}{\delta z_i(\mathbf{r})} \mathbb{M}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') \frac{\delta\mathcal{A}_2(\mathbf{z})}{\delta z_j(\mathbf{r}')} d\mathbf{r} d\mathbf{r}'. \quad (3.2.16)$$

This bracket similarly should satisfy the symmetry property  $[\mathcal{A}_1(\mathbf{z}), \mathcal{A}_2(\mathbf{z})] = [\mathcal{A}_2(\mathbf{z}), \mathcal{A}_1(\mathbf{z})]$ , the Leibniz rule (3.2.77), (3.2.14) and the following non-negativity condition:  $[\mathcal{A}_1(\mathbf{z}), \mathcal{A}_1(\mathbf{z})] \geq 0$ . The physical motivation is given by Onsager's regression hypothesis [33], stating that microscopic fluctuations are present in every system in equilibrium. The projected dynamics is governed by the use of the dynamic operator  $e^{\mathbb{P}'\mathcal{L}t}$  and the quantity  $\mathbb{P}'\mathcal{L}\Pi_{z_i}(\mathbf{x}(0))$  is also known as the projected current.

Thus, the friction tensor  $\mathbb{M}$  arises due to fast fluctuations that are not resolved on the macroscopic level. The time correlation between the "fast" variables, has been declined for  $t = \tau$  and at the same time "slow" variables  $z_i$  practically do not change over the interval  $(0, \tau)$ . The "fast" variables eliminated through the projection operator approach change on a time scale shorter than  $\tau$ . The average  $\langle \cdot \rangle_{\mathbf{z}}$  in the expression (3.2.15) indicates that the microscopic "fast" trajectories must be in consistency with the slow evolution of the variables  $\mathbf{z}$  at time  $t = 0$ .

The general idea is illustrated roughly in Figure 3.1 below, where the integrand can be considered as the time correlation between fluctuations of the thin curve, which represents the microscopic dynamical functions  $\Pi_z(\mathbf{x})$ , around the thick curve, representing  $\mathbf{z}$ . More precisely,  $\Pi_z(\mathbf{x})$ , is the time derivative of the thin curve, and the projection operator  $\mathbb{P}'$  indicates that only the rapid fluctuations on top of the slower changes of the thick curve should be taken into account.

Figure 3.1: Rough illustration of trajectories on the two levels of description (the idea for the figure taken from [90]).



The friction tensor in analogous way with the Poisson tensor is positive semi-definite and symmetric in the sense that  $\tilde{\mathbb{M}} = \mathbb{M}^T$ , where the tilde ( $\sim$ ) means the time-reversal operation, usually called "Onsager-Casimir time-reversal operation" [301]. Time reversal changes the sign of time, velocities, and magnetic field. Thus, in more detail the matrix  $\mathbb{M}$  should satisfy the reciprocal symmetry relationships:  $\mathbb{M}^{ij}(\mathbf{z}) = \varepsilon_i \varepsilon_j \mathbb{M}^{ji}(\mathbf{z})$ ,  $\varepsilon_i = \pm 1$ . We used the same notation for the related Onsager kinetic coefficients (3.1.53) as for the GENERIC friction tensor elements, in order to show the motivation and some how the connection between the two theories, since the dissipative contribution term  $\mathbb{M}(\mathbf{z}) \cdot \partial_{\mathbf{z}} s(\mathbf{z})$ , can be considered as a nonlinear Onsager relation in the sense of [302, Eqn (2.14)].

**Remark 3.11.** *The bracket-formalism of GENERIC for isolated systems can be expressed analogously as in Definition 3.10 and indicates that the time evolution of an arbitrary smooth observable  $A \in C^\infty(\mathcal{Z}^{mz})$  in terms of the total energy  $\mathcal{E} \in C^\infty(\mathcal{Z}^{mz})$  and entropy  $S \in C^\infty(\mathcal{Z}^{mz})$ , is given by*

$$\frac{dA}{dt} = \{A, \mathcal{E}\} + [A, S], \quad (3.2.17)$$

supplemented with the degeneracy conditions  $\{A, S\} = 0$  and  $[A, \mathcal{E}] = 0$ .

**Remark 3.12 (Conservation of energy and increase in entropy).** *If we take into account the above requirement, the corresponding requirement for  $\mathbb{L}$  and the properties of these two tensors one can verify two important thermodynamic laws:*

$$\begin{cases} \frac{de(\mathbf{z})}{dt} = \partial_{\mathbf{z}} e(\mathbf{z}) \cdot \partial_t \mathbf{z} = \partial_{\mathbf{z}} e \cdot (\mathbb{L} \cdot \partial_{\mathbf{z}} e(\mathbf{z}) + \mathbb{M} \cdot \partial_{\mathbf{z}} s(\mathbf{z})) = (\mathbb{M} \cdot \partial_{\mathbf{z}} e(\mathbf{z})) \cdot \partial_{\mathbf{z}} s(\mathbf{z}) = 0, \\ \frac{ds(\mathbf{z})}{dt} = \partial_{\mathbf{z}} s(\mathbf{z}) \cdot \partial_t \mathbf{z} = \partial_{\mathbf{z}} s(\mathbf{z}) \cdot (\mathbb{L} \cdot \partial_{\mathbf{z}} e(\mathbf{z}) + \mathbb{M} \cdot \partial_{\mathbf{z}} s(\mathbf{z})) = \partial_{\mathbf{z}} s(\mathbf{z}) \cdot (\mathbb{M} \cdot \partial_{\mathbf{z}} s(\mathbf{z})) \geq 0, \end{cases} \quad (3.2.18)$$

which is equivalent to say that we obtained conservation of the total energy  $\mathcal{E}(\mathbf{z})$  and an increase in entropy  $S(\mathbf{z})$ , as expected.

Since in the specific study we discuss a general problem, with the state variables  $z_i$ , that are directly depend on the spatial position  $\mathbf{r}$ , as a consequence  $\mathbf{z}$  has both discrete indices for the  $m$  different state functions  $z_i$ , as well as continuous indices to evaluate

the fields at a specific position in space, one can introduce an integral form for the time evolution of the  $k = 1, \dots, N$  particles with positions  $\mathbf{r}_k$ , as follows:

$$\partial_t z_i(\mathbf{r}) = \int_D \sum_{j=1}^m \mathbb{L}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j} e(\mathbf{z}(\mathbf{r}')) + \mathbb{M}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j} s(\mathbf{z}(\mathbf{r}')) d\mathbf{r}', \text{ for } i = 1, \dots, m. \quad (3.2.19)$$

Note that we obtain  $m$  evolution equations, i.e., one for each particular function  $z_i$ , for  $i = 1, \dots, m$  and in the same context, the degeneracy requirements take the form

$$\left\{ \begin{array}{l} \int_D \sum_{j=1}^m \mathbb{M}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j} e(\mathbf{z}(\mathbf{r}')) d\mathbf{r}' = 0, \\ \int_D \sum_{j=1}^m \mathbb{L}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j} s(\mathbf{z}(\mathbf{r}')) d\mathbf{r}' = 0. \end{array} \right. \quad (3.2.20)$$

More details about the specific form of these expressions, can be found in [42], [28].

**Remark 3.13 (GENERIC for open systems).** *A later extension by H. C. Öttinger for open systems [303], suggests to add two extra boundary integrals to the evolution of  $\mathbf{z} = [z_1, \dots, z_m]^T \in \mathcal{Z}^{mz}(D)$  and obtain the extended form*

$$\begin{aligned} \partial_t z_i(\mathbf{r}) &= \int_D \sum_{j=1}^m \mathbb{L}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j} e(\mathbf{z}(\mathbf{r}')) + \mathbb{M}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j} s(\mathbf{z}(\mathbf{r}')) d\mathbf{r}' \\ &+ \int_{\partial D} \sum_{j=1}^m \mathbb{L}_{\partial D}^{z_i z_j}(\mathbf{r}) \partial_{z_j} e(\mathbf{z}(\mathbf{r})) + \mathbb{M}_{\partial D}^{z_i z_j}(\mathbf{r}) \partial_{z_j} s(\mathbf{z}(\mathbf{r})) d^2 r, \text{ for } i = 1, \dots, m. \end{aligned} \quad (3.2.21)$$

The tensors  $\mathbb{L}_{\partial D}, \mathbb{M}_{\partial D}$  are related to the boundary conditions and are expressed as summation and difference between two symmetric and antisymmetric parts respectively, as follows:

$$\mathbb{L}_{\partial D} := \mathbb{L}_{\partial} + \mathbb{L}_{\partial r} \text{ and } \mathbb{M}_{\partial D} := \mathbb{M}_{\partial} - \mathbb{M}_{\partial r}, \quad (3.2.22)$$

where the tensors  $\mathbb{L}_{\partial}, \mathbb{M}_{\partial}$  accounting for exchange and interaction with the environment and  $\mathbb{L}_{\partial r}, \mathbb{M}_{\partial r}$  denote their transposed tensors. These boundary tensors satisfy the following degeneracy requirements,

$$\left\{ \begin{array}{l} \int_{\partial D} \sum_{j=1}^m \mathbb{M}_{\partial}^{z_i z_j}(\mathbf{r}) \partial_{z_j} e(\mathbf{z}(\mathbf{r})) d^2 r = 0, \\ \int_{\partial D} \sum_{j=1}^m \mathbb{L}_{\partial}^{z_i z_j}(\mathbf{r}) \partial_{z_j} s(\mathbf{z}(\mathbf{r})) d^2 r = 0. \end{array} \right. \quad (3.2.23)$$

Analogously we can define the bulk Poisson and dissipative brackets for observables  $\mathcal{A}_1, \mathcal{A}_2$  as follows:

$$\left\{ \begin{array}{l} \{\mathcal{A}_1(\mathbf{z}), \mathcal{A}_2(\mathbf{z})\}_{\text{boundary}} := \int_{\partial D} \sum_{i,j=1}^m \frac{\delta \mathcal{A}_1}{\delta z_i(\mathbf{r})} \mathbb{L}_{\partial}^{z_i z_j}(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta z_j(\mathbf{r})} d^2 r, \\ [\mathcal{A}_1(\mathbf{z}), \mathcal{A}_2(\mathbf{z})]_{\text{boundary}} := \int_{\partial D} \sum_{i,j=1}^m \frac{\delta \mathcal{A}_1}{\delta z_i(\mathbf{r})} \mathbb{M}_{\partial}^{z_i z_j}(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta z_j(\mathbf{r})} d^2 r. \end{array} \right. \quad (3.2.24)$$

The above and the following relations can be found in both H. C. Öttinger's book [28] and M. Hütter and J. M. Brader's article [42] and is convenient for the calculations in the examples that will follow. To summarise in terms of two position vectors  $\mathbf{r}, \mathbf{r}'$  the elements of the Poisson and friction tensors, can be obtained by the following expressions:

$$\mathbb{L}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') = \langle \{\Pi_{z_i}(\mathbf{x}, \mathbf{r}), \Pi_{z_j}(\mathbf{x}, \mathbf{r}')\} \rangle_{\mathbf{z}}, \quad (3.2.25)$$



$$\mathbb{M}^{z_i z_j}(\mathbf{z})(\mathbf{r}, \mathbf{r}') = (k_B)^{-1} \int_0^\tau \langle \dot{\Pi}_{z_i}^f(\mathbf{x}(t), \mathbf{r}) \dot{\Pi}_{z_j}^f(\mathbf{x}(0), \mathbf{r}') \rangle_{\mathbf{z}} dt, \quad (3.2.26)$$

where the Poisson bracket  $\{\cdot, \cdot\}$  between the  $\Pi_{z_i}$ , is given by the more analytic and useful formula in terms of both the momenta  $\mathbf{p}_i$  and the positions  $\mathbf{r}_i$ :

$$\{\Pi_{z_i}(\mathbf{x}, \mathbf{r}), \Pi_{z_j}(\mathbf{x}, \mathbf{r}')\} = \sum_{n=1}^N \left( \frac{\partial \Pi_{z_i}(\mathbf{x}, \mathbf{r})}{\partial \mathbf{r}_n} \cdot \frac{\partial \Pi_{z_j}(\mathbf{x}, \mathbf{r}')}{\partial \mathbf{p}_n} - \frac{\partial \Pi_{z_i}(\mathbf{x}, \mathbf{r})}{\partial \mathbf{p}_n} \cdot \frac{\partial \Pi_{z_j}(\mathbf{x}, \mathbf{r}')}{\partial \mathbf{r}_n} \right). \quad (3.2.27)$$

As one can observe, according to the GENERIC formalism, the structure of time evolution equations is such that the reversible and irreversible contributions are distinctly identified. An interesting future challenging work, would be to identify how the structure of thermodynamically admissible evolution equations can be preserved under time-discretization, which is the key point for numerical calculations. In order to understand better how GENERIC can be applied, we demonstrate it in three examples, e.g., the classical equations of hydrodynamics from a macroscopic point of view and also the connection to the microscopic description, the Cahn-Hilliard/Navier-Stokes system with influence of an external forcing (section 3.2.2-3.2.5) and a variant of this formulated for particle adsorption isotherms (section 4.1.1).

### 3.2.2 The equations of hydrodynamics via GENERIC in the macroscale.

The specific example is based on an overview of the application of GENERIC to the classical hydrodynamic equations following Öttinger's approach [28] and can be used as a basis for a better understanding of the main objectives and principles of this formalism and provides the motivation for further applications to more complex thermodynamic systems. We start our considerations by illustrating the classical approach of the derivation of Navier-Stokes equations [304, p 11-28] and [305] and an alternative approach involving the Lagrangian representation and flow maps, which is demonstrated in details in section 3.2.4. We examine the flow taking place in sufficiently small moving control volume  $V(t) \in D_T \subseteq \mathbb{R}^3 \times [0, T]$ . In this context, the following theorem will be useful for the rest of this part.

**Remark 3.14.** For a smooth function  $z := z(\mathbf{r}, t)$  in the Eulerian setting the following identity holds:

$$\frac{d}{dt} \int_{V(t)} z d\mathbf{r} = \int_{V(t)} \frac{Dz}{Dt} + z \operatorname{div}(\mathbf{v}) d\mathbf{r} = \int_{V(t)} \partial_t z + \operatorname{div}(z\mathbf{v}) d\mathbf{r}, \quad (3.2.28)$$

where  $\frac{D}{Dt} := \partial_t + \mathbf{v} \cdot \nabla$  stands for the material derivative and  $\mathbf{v} := \mathbf{v}(\mathbf{r}, t) \in C^\infty(D_T; \mathbb{R}^3)$  is the velocity of the moving control volume  $V(t)$ .

- **Equation of continuity:** According to the law of conservation of mass, the total mass of fluid within its volume  $D \subseteq \mathbb{R}^3$ , will increase only because of a net influx of fluid across the boundary  $\partial D$ . This axiom simply expresses the fact that the mass of a material body does not change with time. This principle is referred to as

the conservation of mass. For a material body, occupying the material volume  $D$ , mathematically the above principle can be expressed as below:

$$-\int_{\partial D} \rho \mathbf{v} \cdot \mathbf{n} \, ds = -\int_D \operatorname{div}(\mathbf{v}\rho) \, d\mathbf{r} = \partial_t \int_D \rho \, d\mathbf{r} \text{ by Gauss theorem.} \quad (3.2.29)$$

where the non-negative scalar field  $\rho := \rho(\mathbf{r}, t) \in L^1_{loc}(D_T)$  represents the mass density of the fluid,  $\mathbf{n}$  denotes the outward unit normal to  $\partial D$  as usual. Thus, since the volume is arbitrary the integrand must be zero and as a result the final form for the mass balance is

$$\partial_t \rho = -\operatorname{div}(\mathbf{v}\rho). \quad (3.2.30)$$

- **Momentum balance:** According to Newton's second law, the change over time of the total momentum vector field  $\mathbf{P}(\mathbf{r}, t) := (\rho\mathbf{v})(\mathbf{r}, t) \in L^1_{loc}(D_T; \mathbb{R}^3)$  inside a control volume  $D$  equals the sum of the forces  $F_i := F_i(\mathbf{r}, t)$ ,  $i = 1, 2, 3$  per unit volume, acting on the body, i.e.,

$$\frac{D}{Dt} \int_D \mathbf{P} \, d\mathbf{r} = \int_D \mathbf{F} \, d\mathbf{r}. \quad (3.2.31)$$

The forces are generally assumed to admit the form

$$F_i := f_i^g - \frac{\partial \Pi_{ij}}{\partial r_j}, \quad i, j = 1, 2, 3, \quad (3.2.32)$$

where  $\mathbf{f}^g$  stands for a body force (exerted from the “outside”) and will be taken to be a uniform gravitational field  $\mathbf{f}^g = \rho\mathbf{g}$ , where  $\mathbf{g}$  is the constant gravitational acceleration. In addition,  $\mathbf{\Pi} \in L^1_{loc}(D_T; \mathbb{R}^{3 \times 3}_{sym})$  is a positive definite second-order tensor, called the stress tensor. Hence, by definition of the material derivative (see Remark 3.14) we equivalently obtain

$$\int_D \partial_t \mathbf{P} \, d\mathbf{r} + \int_D \mathbf{v} \cdot \partial_{\mathbf{r}} \mathbf{P} \, d\mathbf{r} = \int_D \mathbf{F} \, d\mathbf{r}, \quad (3.2.33)$$

Hence, in the absence of external forcing (isolated system) at any position on the surface the force acting by the gas outside the volume onto the gas inside the volume is  $-\mathbf{\Pi} \cdot \mathbf{n}$ . (Note that the arguments  $\mathbf{r}$  and  $t$  of the functions are being skipped sometimes for convenience, where it is clear from the context). As result, one can deduce that

$$\partial_t \int_D \mathbf{P} \, d\mathbf{r} = -\int_{\partial D} (\mathbf{v} \otimes \mathbf{P}) \cdot \mathbf{n} \, ds - \int_{\partial D} \mathbf{\Pi} \cdot \mathbf{n} \, ds. \quad (3.2.34)$$

This law after applying Gauss theorem and since the volume is arbitrary, takes the final form

$$\partial_t \mathbf{P} = -\operatorname{div}(\mathbf{v} \otimes \mathbf{P}) - \operatorname{div}(\mathbf{\Pi}), \quad (3.2.35)$$

where the momentum density  $\mathbf{P}$  can be interpreted as a tensor quantity. The meaning of the term  $\operatorname{div}(\mathbf{v})$  that appears frequently in the equations of fluid dynamics, can be physically motivated as follows: If one considers a control volume which is moving with the fluid and made up of the same fluid particles as it advances with the flow,

which implies that its mass is fixed and is invariant with time. The volume  $v$  and the control surface  $s$  are changing with time as it moves to different regions of the flow, with various values of the density  $\rho$ . Herewith, this moving control volume of fixed mass is constantly increasing or decreasing its volume and is transforming its shape, depending on the flow features.

- **Internal energy balance:** Starting from the flow of the internal energy  $\mathbf{n} \cdot \mathbf{v} u dA$  and the flow of the kinetic energy  $\mathbf{n} \cdot \mathbf{v} (\rho \mathbf{v}^2 / 2) dA$ , one can first obtain a form for the change in kinetic energy using the two previous balance equations, i.e.,

$$\partial_t (\rho \mathbf{v}^2 / 2) + \text{div}(\mathbf{v} \rho \mathbf{v}^2 / 2) = \mathbf{v}^2 / 2 (\partial_t \rho + \text{div}(\mathbf{v} \rho)) + \rho \mathbf{v} \cdot \frac{D}{Dt} \mathbf{v} = -\mathbf{v} \cdot \text{div}(\mathbf{\Pi}). \quad (3.2.36)$$

The above equation can be rewritten as follows:

$$\partial_t (\rho \mathbf{v}^2 / 2) = -\text{div}(\mathbf{v} \rho \mathbf{v}^2 / 2 + \mathbf{\Pi} \cdot \mathbf{v}) - \mathbf{\Pi} : (\partial_{\mathbf{r}} \mathbf{v})^T. \quad (3.2.37)$$

Conservation of the total energy in the absence of external forces implies that there should exist an accompanied equation for the change in the internal energy density, namely

$$\partial_t u = -\text{div}(\mathbf{v} u + \mathbf{J}^q) - \mathbf{\Pi} : (\partial_{\mathbf{r}} \mathbf{v})^T, \quad (3.2.38)$$

where  $\mathbf{J}^q$  represents the conductivity flow of the internal energy, according to the Fourier's law of (see remark 3.15).

- **Entropy balance:** Using the identities (3.1.51) and the balance equations, one obtains for the time evolution of the entropy density that,

$$\begin{aligned} \partial_t s &= -\mu \Theta^{-1} \partial_t \rho + \Theta^{-1} \partial_t u \\ &= \mu \Theta^{-1} \text{div}(\mathbf{v} \rho) - \Theta^{-1} \text{div}(\mathbf{v} u + \mathbf{J}^q) - \Theta^{-1} \mathbf{\Pi} : (\partial_{\mathbf{r}} \mathbf{v})^T, \end{aligned} \quad (3.2.39)$$

which with the help of the relation (3.1.52) for the pressure  $p$ , leads to the following equation

$$\partial_t s = -\text{div}(\mathbf{v} s + \mathbf{J}^q \Theta^{-1}) - \pi_S, \quad (3.2.40)$$

where  $\pi_S$  denotes the entropy production [287] which arises from the dissipative effects in irreversible processes and is given by the relationship,

$$\pi_S := -(\tau \Theta^{-1}) : (\partial_{\mathbf{r}} \mathbf{v})^T + \mathbf{J}^q \cdot \partial_{\mathbf{r}} \Theta^{-1} \geq 0, \quad (3.2.41)$$

which follows from the second law of thermodynamics [285, 306].

In addition, the hydrostatic pressure connected to the total pressure by the relation for the viscous stress tensor:  $\tau := \mathbf{\Pi} - p \mathbf{1}$  which can be represented by the Newton's expression in terms of the viscosity  $\eta$  and the bulk viscosity  $m$ , as follows:

$$\tau := -\eta \left( \partial_{\mathbf{r}} \mathbf{v} + (\partial_{\mathbf{r}} \mathbf{v})^T - \frac{2}{3} \text{div}(\mathbf{v} \mathbf{1}) \right) - m \text{div}(\mathbf{v} \mathbf{1}). \quad (3.2.42)$$

Note that we assume that the velocity gradient  $\partial_{\mathbf{r}}\mathbf{v} \in L^1_{loc}(D_T; \mathbb{R}^{3 \times 3})$  is decomposed into a symmetric and an antisymmetric part, i.e.,  $\partial_{\mathbf{r}}\mathbf{v} = \dot{\gamma} + \dot{\omega}$ , where we defined  $\dot{\gamma} := \frac{1}{2}(\partial_{\mathbf{r}}\mathbf{v} + (\partial_{\mathbf{r}}\mathbf{v})^T)$  and  $\dot{\omega} := \frac{1}{2}(\partial_{\mathbf{r}}\mathbf{v} - (\partial_{\mathbf{r}}\mathbf{v})^T)$ .

**Remark 3.15 (Fourier's Law).** *The conductivity flow appearing in the equation for the internal energy can be expressed according to Fick's law of diffusion [307, 308], for thermal conductivity  $k^q := k^q(\mathbf{r})$  in which the temperature gradient drives the heat flux, namely*

$$\mathbf{J}^q := -k^q \partial_{\mathbf{r}} \Theta, \quad (3.2.43)$$

*which is also known as the Fourier's law of heat conduction and was first formulated by Fourier in 1822 [309].*

We aim to represent the above system by using the GENERIC formulation. The starting point is to identify the total energy of the system, a part of which consists of a kinetic energy density term, namely:  $m|\mathbf{v}|^2/2$  where instead of mass  $m$  and velocity  $\mathbf{v}$  one can use the density  $\rho$  and the momentum density,  $\mathbf{P}$  respectively. Thus, the total energy of the system, can be considered as the sum of the kinetic energy and the internal energy density  $u$  that corresponds to the third independent field. Under this consideration and based on the assumption of local equilibrium, the total energy of the system, over the domain  $D \subset \mathbb{R}^3$  reads:

$$\mathcal{E}(\mathbf{r}) := \int_D e(\mathbf{r}) d\mathbf{r} = \int_D (\mathbf{P}^2(\mathbf{r})/2\rho(\mathbf{r}) + u(\mathbf{r})) d\mathbf{r}. \quad (3.2.44)$$

In addition, one should identify the total entropy of the system as

$$\mathcal{S}(\mathbf{r}) := \int_D s(\mathbf{r}) d\mathbf{r} = \int_D s(\rho(\mathbf{r}), u(\mathbf{r})) d\mathbf{r}. \quad (3.2.45)$$

The above relations hold once the set of state variables is considered to be the  $\mathbf{z} = [\rho, \mathbf{P}, u]^T \in \mathcal{Z}^{3z}(D)$ ,  $D \subset \mathbb{R}^3$ , where  $\mathcal{Z}^{3z}(D) := \mathcal{Z}_1(D) \times \mathcal{Z}_2(D) \times \mathcal{Z}_3(D)$  with  $\mathcal{Z}_i(D)$ ,  $i = 1, 2, 3$  representing different function spaces. On the other hand one can simplify the derivations, by considering alternatively the entropy density  $s$  as the third variable instead of the internal energy density  $u$ , the total energy and entropy functionals, can be expressed using similar relations, i.e.,

$$\mathcal{E}'(\mathbf{r}) := \int_D e'(\mathbf{r}) d\mathbf{r} = \int_D (\mathbf{P}^2(\mathbf{r})/2\rho(\mathbf{r}) + u(\rho(\mathbf{r}), s(\mathbf{r}))) d\mathbf{r} \text{ and } \mathcal{S}'(\mathbf{r}) = \int_D s'(\mathbf{r}) d\mathbf{r}, \quad (3.2.46)$$

where the total entropy in terms of the entropy density, which in this case is considered as independent the other fields  $u, \rho$  so it is a function just of  $\mathbf{r}$ . Thus for the time evolution as discussed in the previous subsection one obtains in terms of  $e'$  and  $s'$  for the evolution of each state function  $z_i$ , the following form:

$$\partial_t z_i(\mathbf{r}) = \int_D \sum_{j=1}^3 \mathbb{L}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j(\mathbf{r}')} e'(\mathbf{z}) d\mathbf{r}' + \int_D \sum_{j=1}^3 \mathbb{M}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j(\mathbf{r}')} s'(\mathbf{z}) d\mathbf{r}', \text{ for } i = 1, 2, 3 \quad (3.2.47)$$

and in this particular case,  $z_1 := \rho$ ,  $z_2 := \mathbf{P}$ ,  $z_3 := s$ . In addition, for the derivation below, we

will also combine the related degeneracy requirements

$$\left\{ \begin{array}{l} \int_D \sum_{j=1}^3 \mathbb{L}'^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j(\mathbf{r}')} s'(\mathbf{z}) d\mathbf{r}' = 0, \\ \int_D \sum_{j=1}^3 \mathbb{M}'^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j(\mathbf{r}')} e'(\mathbf{z}) d\mathbf{r}' = 0 \end{array} \right. \quad (3.2.48)$$

and the results for the functional derivatives

$$\begin{aligned} \partial_{\mathbf{z}} s' &:= (\partial_{\rho} s', \partial_{\mathbf{P}} s', \partial_{s'} s')^T = (0, 0, 1)^T, \\ \partial_{\mathbf{z}} e' &:= (\partial_{\rho} e', \partial_{\mathbf{P}} e', \partial_{s'} e')^T = \left( \partial_{\rho} u - \frac{1}{2\rho^2} \mathbf{P}^2, \mathbf{P}/\rho, \Theta \right)^T = (\mu - \mathbf{v}^2/2, \mathbf{v}, \Theta)^T, \end{aligned} \quad (3.2.49)$$

where the definition of the momentum  $\mathbf{P} := \rho \mathbf{v}$  has been used in the second step of the differentiation and the fundamental relation  $\partial_{s'} u = \Theta$ . The variable  $\mu$  denotes the chemical potential as usual and  $\Theta$  is the temperature. The first form can be obtained using the fundamental thermodynamic relations (3.1.52) (see also [28]). The following theorem 3.2.1 summarises one of the primary applications of GENERIC introduced by H. C. Öttinger in [28].

**Theorem 3.2.1 (Tensor representation with GENERIC).** *Let the set of representative state variables to be chosen as  $\mathbf{z} = [\rho, \mathbf{P}, s]^T \in \mathcal{Z}^{3z}(D)$ ,  $D \subset \mathbb{R}^3$ . Then the classical equations of hydrodynamics (3.2.30), (3.2.35) supplemented with the entropy balance (3.2.39), are shown to satisfy GENERIC and can be expressed with the help of the following Poisson and friction tensors:*

$$\mathbb{L}'(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} 0 & \rho(\mathbf{r}') \partial_{\mathbf{r}'} \delta & 0 \\ -\partial_{\mathbf{r}} \delta \rho(\mathbf{r}) & \mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta - \partial_{\mathbf{r}} \delta \mathbf{P}(\mathbf{r}) & -\partial_{\mathbf{r}} \delta s(\mathbf{r}) \\ 0 & s(\mathbf{r}') \partial_{\mathbf{r}'} \delta & 0 \end{pmatrix}, \quad (3.2.50)$$

where we set  $\delta := \delta(\mathbf{r} - \mathbf{r}')$  for simplicity of notation and

$$\mathbb{M}'(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mathbb{M}'^{\mathbf{PP}}(\mathbf{r}, \mathbf{r}') & \mathbb{M}'^{\mathbf{Ps}}(\mathbf{r}, \mathbf{r}') \\ 0 & \mathbb{M}'^{s\mathbf{P}}(\mathbf{r}, \mathbf{r}') & \mathbb{M}'^{ss}(\mathbf{r}, \mathbf{r}') \end{pmatrix}, \quad (3.2.51)$$

in which the elements can be defined as follows:

$$\mathbb{M}'^{ss}(\mathbf{r}, \mathbf{r}') = \left( \frac{\eta}{2\Theta} \dot{\gamma} : \dot{\gamma} + \frac{\tilde{k}}{4\Theta} (tr \dot{\gamma})^2 + \frac{k^q}{\Theta^2} \left( \frac{\partial \Theta}{\partial \mathbf{r}} \right)^2 \right) \delta(\mathbf{r} - \mathbf{r}'), \quad (3.2.52)$$

where  $\tilde{k} = m - 2\eta/3$  and  $\dot{\gamma}$  to be defined as the rate-of-strain tensor  $\dot{\gamma}(\mathbf{r}) := \partial_{\mathbf{r}} \mathbf{v}(\mathbf{r}) + (\partial_{\mathbf{r}} \mathbf{v}(\mathbf{r}))^T$ , for which more details and physical interpretation can be found in [310, p 151]. Furthermore and for symmetry reasons, we subsequently obtain

$$\mathbb{M}'^{s\mathbf{P}}(\mathbf{r}, \mathbf{r}') = \partial_{\mathbf{r}'} \cdot \eta \dot{\gamma} \delta + \tilde{k} \partial_{\mathbf{r}'} (tr \dot{\gamma}) \delta / 2 \text{ and } \mathbb{M}'^{\mathbf{Ps}}(\mathbf{r}, \mathbf{r}') = \partial_{\mathbf{r}} \cdot \eta \dot{\gamma} \delta + \tilde{k} \partial_{\mathbf{r}} (tr \dot{\gamma}) \delta / 2. \quad (3.2.53)$$

Finally,  $\mathbb{M}'^{\mathbf{PP}}(\mathbf{r}, \mathbf{r}') = (\partial_{\mathbf{r}'} \partial_{\mathbf{r}} + \mathbf{1} \partial_{\mathbf{r}'} \cdot \partial_{\mathbf{r}}) \eta \Theta \delta + \partial_{\mathbf{r}} \partial_{\mathbf{r}'} k \Theta \delta$ . and as one can easily check the tensor  $\mathbb{L}'$  satisfy the property of antisymmetry, since:  $-\rho(\mathbf{r}') \partial_{\mathbf{r}'} \delta = -\partial_{\mathbf{r}} \delta \rho(\mathbf{r})$  and  $s(\mathbf{r}') \partial_{\mathbf{r}'} \delta = \partial_{\mathbf{r}} \delta s(\mathbf{r})$ . In the same way the symmetry property can be easily verified for the tensor  $\mathbb{M}'$ .

*Proof.* The proof consists of two parts. In the first part we deduce a certain form for each element of the Poisson and frictions tensors, according to the proper satisfaction of the GENERIC evolution equations (3.2.47), the corresponding symmetry arguments and the related degeneracy requirements (3.2.48) and in the second part we verify that this particular choice of the Poisson and dissipative brackets satisfy the Jacoby Identity and the Leibniz rule for arbitrary observables.

**Part 1.** The elements of the Poisson and friction tensors  $\mathbb{L}', \mathbb{M}'$  can be evaluated according to the general ideas of GENERIC as follows, (note that we are skipping the arguments of some functions for convenience, where it is clear from the context). From equation (3.2.47) and the functional derivatives, one can deduce

$$\begin{cases} \partial_t \rho = -\text{div}(\mathbf{v}\rho) = \int_D \mathbb{L}'^{\rho\rho}(\mathbf{r}, \mathbf{r}')(\mu - \mathbf{v}^2/2)(\mathbf{r}') + \mathbb{L}'^{\rho\mathbf{P}}(\mathbf{r}, \mathbf{r}')\mathbf{v}(\mathbf{r}') + \mathbb{L}'^{\rho s}(\mathbf{r}, \mathbf{r}')\Theta(\mathbf{r}') + \mathbb{M}'^{\rho s}(\mathbf{r}, \mathbf{r}') d\mathbf{r}', \\ \partial_t \mathbf{P} = -\text{div}(\mathbf{v} \otimes \mathbf{P}) = \int_D \mathbb{L}'^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}')(\mu - \mathbf{v}^2/2)(\mathbf{r}') + \mathbb{L}'^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}')\mathbf{v}(\mathbf{r}') + \mathbb{L}'^{\mathbf{P}s}(\mathbf{r}, \mathbf{r}')\Theta(\mathbf{r}') + \mathbb{M}'^{\mathbf{P}s}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \end{cases} \quad (3.2.54)$$

and from the entropy balance

$$\begin{aligned} \partial_t s &= -\text{div}(\mathbf{v}s + \mathbf{J}^q \Theta^{-1}) - \tau \Theta^{-1} : (\text{div}(\mathbf{v}))^T + \mathbf{J}^q \cdot \partial_t \Theta^{-1} \\ &= \int_D \mathbb{L}'^{s\rho}(\mathbf{r}, \mathbf{r}')(\mu - \mathbf{v}^2/2)(\mathbf{r}') + \mathbb{L}'^{s\mathbf{P}}(\mathbf{r}, \mathbf{r}')\mathbf{v}(\mathbf{r}') + \mathbb{L}'^{ss}(\mathbf{r}, \mathbf{r}')\Theta(\mathbf{r}') + \mathbb{M}'^{ss}(\mathbf{r}, \mathbf{r}') d\mathbf{r}'. \end{aligned} \quad (3.2.55)$$

On the other hand the degeneracy requirements for  $z_i \in \{\rho, \mathbf{P}, s\}$  yields

$$\int_D \mathbb{L}'^{z_i s}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 0 \text{ and } \int_D \mathbb{M}'^{z_i \rho}(\mathbf{r}, \mathbf{r}')(\mu - \mathbf{v}^2/2)(\mathbf{r}') + \mathbb{M}'^{z_i \mathbf{P}}(\mathbf{r}, \mathbf{r}')\mathbf{v}(\mathbf{r}') + \mathbb{M}'^{z_i s}(\mathbf{r}, \mathbf{r}')\Theta(\mathbf{r}') d\mathbf{r}' = 0. \quad (3.2.56)$$

Comparing the left with the right hand side of equation (3.2.54), in combination with the degeneracy requirements (3.2.56), integration by parts and the properties of the Dirac delta function, we obtain

$$\int_D \rho(\mathbf{r}') \partial_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') \mathbf{v}(\mathbf{r}') d\mathbf{r}' = -\text{div}[\mathbf{v}(\mathbf{r})\rho(\mathbf{r})] \text{ and } \mathbb{L}'^{\rho\rho}(\mathbf{r}, \mathbf{r}') = \mathbb{L}'^{\rho s}(\mathbf{r}, \mathbf{r}') = 0. \quad (3.2.57)$$

Hence, in view of (3.2.47) we deduce

$$\int_D \rho(\mathbf{r}') \partial_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') \mathbf{v}(\mathbf{r}') d\mathbf{r}' = \int_D \mathbb{L}'^{\rho\mathbf{P}}(\mathbf{r}, \mathbf{r}')\mathbf{v}(\mathbf{r}') d\mathbf{r}', \quad (3.2.58)$$

which implies that the remaining element  $\mathbb{L}'^{\rho\mathbf{P}}$ , has to be of the form

$$\mathbb{L}'^{\rho\mathbf{P}}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') \partial_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}'). \quad (3.2.59)$$

In the above result, we used also the argument that the equation of continuity is not affected by irreversible effects and thus,

$$\mathbb{M}'^{\rho\rho}(\mathbf{r}, \mathbf{r}') = \mathbb{M}'^{\rho\mathbf{P}}(\mathbf{r}, \mathbf{r}') = \mathbb{M}'^{\rho s}(\mathbf{r}, \mathbf{r}') = \mathbb{M}'^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') = \mathbb{M}'^{s\rho}(\mathbf{r}, \mathbf{r}') = 0. \quad (3.2.60)$$

Furthermore, from the momentum balance (3.2.54), the relation for pressure (3.1.52) and the related degeneracy requirements we obtain for the momentum components:

$$\begin{aligned}
 & \int_D \mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta \mathbf{v}(\mathbf{r}') d\mathbf{r}' - \partial_{\mathbf{r}} \cdot \boldsymbol{\tau} + \mu \partial_{\mathbf{r}} \rho + s \partial_{\mathbf{r}} \Theta \\
 &= \int_D \mathbb{L}^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') \mu(\mathbf{r}') - \mathbb{L}'^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}')/2 + \mathbb{L}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') d\mathbf{r}' \\
 &+ \int_D \mathbb{L}'^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') \Theta(\mathbf{r}') + \mathbb{M}'^{\mathbf{P}s}(\mathbf{r}, \mathbf{r}') d\mathbf{r}'. \tag{3.2.61}
 \end{aligned}$$

In order to proceed further we consider some arguments for the friction matrix. The functional derivative of  $s'$  implies that the element  $\mathbb{M}'^{ss}$  of the friction matrix can be deduced by the entropy production  $\Theta_S$  (3.2.41). This can be extended using the analytic forms for  $\boldsymbol{\tau}$  (3.2.42) and  $\mathbf{J}^q$  (3.2.43) and provides a form for the  $\mathbb{M}'^{ss}$  element, namely:

$$\begin{aligned}
 \mathbb{M}'^{ss}(\mathbf{r}, \mathbf{r}') &= \left[ \frac{\eta}{\Theta} \left( \partial_{\mathbf{r}} \mathbf{v} + (\partial_{\mathbf{r}} \mathbf{v})^T - \frac{2}{3} \partial_{\mathbf{r}} \cdot \mathbf{v} \mathbf{1} \right) : (\partial_{\mathbf{r}} \mathbf{v})^T + \left( \frac{m}{\Theta} \text{div}(\mathbf{v} \mathbf{1}) \right) : (\partial_{\mathbf{r}} \mathbf{v})^T - k^q \partial_{\mathbf{r}} \Theta \cdot \partial_{\mathbf{r}} \Theta^{-1} \right] \delta(\mathbf{r} - \mathbf{r}') \\
 &= \left( \frac{\eta}{2\Theta} \dot{\gamma} : \dot{\gamma} + \frac{\tilde{k}}{4\Theta} (\text{tr} \dot{\gamma})^2 + \frac{k^q}{\Theta^2} \left( \frac{\partial \Theta}{\partial \mathbf{r}} \right)^2 \right) \delta(\mathbf{r} - \mathbf{r}'), \tag{3.2.62}
 \end{aligned}$$

where  $\tilde{k} = m - 2\eta/3$ . One can understand better the tensorial nature of this quantity, by writing down carefully the elements, namely for example:  $\dot{\gamma}_{11} = \partial_{r_1} v_1$ ,  $\dot{\gamma}_{12} = \partial_{r_2} v_1 + \partial_{r_1} v_2$ , etc. Hence, by plugging the form for the  $\mathbb{M}'^{ss}$  into the degeneracy requirement (3.2.56) we obtain:

$$\int_D \mathbb{M}'^{s\mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') d\mathbf{r}' = - \int_D \left( \frac{\eta}{2\Theta} \dot{\gamma} : \dot{\gamma} + \frac{\tilde{k}}{4\Theta} (\text{tr} \dot{\gamma})^2 + \frac{k^q}{\Theta^2} \left( \frac{\partial \Theta}{\partial \mathbf{r}} \right)^2 \right) \delta(\mathbf{r} - \mathbf{r}') \Theta(\mathbf{r}') d\mathbf{r}'. \tag{3.2.63}$$

As a result, for symmetry reasons we additionally deduce that

$$\mathbb{M}'^{s\mathbf{P}}(\mathbf{r}, \mathbf{r}') = \partial_{\mathbf{r}'} \cdot \eta \dot{\gamma} \delta + \tilde{k} \partial_{\mathbf{r}'} (\text{tr} \dot{\gamma}) \delta / 2 \text{ and } \mathbb{M}'^{\mathbf{P}s}(\mathbf{r}, \mathbf{r}') = \partial_{\mathbf{r}} \cdot \eta \dot{\gamma} \delta + \tilde{k} \partial_{\mathbf{r}} (\text{tr} \dot{\gamma}) \delta / 2. \tag{3.2.64}$$

Finally, for the element  $\mathbb{M}'^{\mathbf{P}\mathbf{P}}$  we use the following degeneracy requirement for  $\mathbb{M}'$ , namely:

$$\int_D \mathbb{M}'^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') d\mathbf{r}' = - \int_D (\partial_{\mathbf{r}} \cdot \eta \dot{\gamma} \delta + \tilde{k} \partial_{\mathbf{r}} (\text{tr} \dot{\gamma}) \delta / 2) \Theta(\mathbf{r}') d\mathbf{r}', \tag{3.2.65}$$

we deduce that

$$\mathbb{M}'^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') = (\partial_{\mathbf{r}'} \partial_{\mathbf{r}} + \mathbf{1} \partial_{\mathbf{r}'} \cdot \partial_{\mathbf{r}}) \eta \Theta \frac{\delta}{2} + \partial_{\mathbf{r}} \partial_{\mathbf{r}'} k \Theta \frac{\delta}{2}. \tag{3.2.66}$$

Hence by plugging the form for the  $\mathbb{M}'^{\mathbf{P}s}$  into the equation (3.2.61) we obtain

$$\begin{aligned}
 & \int_D \mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta \mathbf{v}(\mathbf{r}') d\mathbf{r}' - \partial_{\mathbf{r}} \cdot \boldsymbol{\tau} + \mu \partial_{\mathbf{r}} \rho + s \partial_{\mathbf{r}} \Theta \\
 &= \int_D \mathbb{L}^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') \mu(\mathbf{r}') - \mathbb{L}'^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}')/2 d\mathbf{r}' \\
 &+ \int_D \mathbb{L}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') + \mathbb{L}'^{\mathbf{P}s}(\mathbf{r}, \mathbf{r}') \Theta(\mathbf{r}') d\mathbf{r}' + \int_D \partial_{\mathbf{r}} \cdot \eta \dot{\gamma} \delta + \tilde{k} \partial_{\mathbf{r}} (\text{tr} \dot{\gamma}) \delta / 2 d\mathbf{r}'. \tag{3.2.67}
 \end{aligned}$$

Thus we can deduce that:  $\mathbb{L}'^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') = -\partial_{\mathbf{r}} \delta \rho(\mathbf{r})$ ,  $\mathbb{L}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') = \mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta - \partial_{\mathbf{r}} \delta \mathbf{P}(\mathbf{r})$ ,  $\mathbb{L}'^{\mathbf{P}s}(\mathbf{r}, \mathbf{r}') = -\partial_{\mathbf{r}} \delta s(\mathbf{r})$ .

**Remark 3.16.** *The result above is a consequence of the standard properties of the Dirac*

delta and more precisely of the following identities:

$$\left\{ \begin{array}{l} \delta(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}'-\mathbf{r}), \quad \frac{\partial}{\partial \mathbf{r}} \delta(\mathbf{r}-\mathbf{r}') = -\frac{\partial}{\partial \mathbf{r}'} \delta(\mathbf{r}-\mathbf{r}') \text{ and } f(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') = f(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'), \\ \int_D f(\mathbf{r})\partial_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}')g(\mathbf{r}') d\mathbf{r}' = f(\mathbf{r})\partial_{\mathbf{r}}g(\mathbf{r}), \text{ and } \int_D f(\mathbf{r}')\partial_{\mathbf{r}'}\delta(\mathbf{r}-\mathbf{r}')g(\mathbf{r}') d\mathbf{r}' = \partial_{\mathbf{r}}(f(\mathbf{r})g(\mathbf{r})), \end{array} \right. \quad (3.2.68)$$

see also [311, p. 694-696] for more details on the properties of the delta function.

**Part 2.** According to the forms for the elements we obtain in the previous part, we can write the Poisson and dissipative brackets for two arbitrary observables  $\mathcal{A}_1, \mathcal{A}_2 \in C^\infty(\mathcal{Z}^{3z})$  for the whole system (3.2.30), (3.2.35), (3.2.39) as below:

$$\begin{aligned} \{\mathcal{A}_1, \mathcal{A}_2\}_{\mathbb{G}} := & \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} \mathbb{G}'^{\rho\rho}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} \mathbb{G}'^{\rho\mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ & + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} \mathbb{G}'^{\rho s}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathbb{G}'^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ & + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathbb{G}'^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathbb{G}'^{\mathbf{P}s}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ & + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \mathbb{G}'^{s\rho}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \mathbb{G}'^{s\mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ & + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \mathbb{G}'^{ss}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r}')} d\mathbf{r} d\mathbf{r}', \end{aligned} \quad (3.2.69)$$

where  $\mathbb{G} \in \{\mathbb{M}, \mathbb{L}\}$ . Hence, we can deduce for the Poisson bracket  $\{\mathcal{A}_1, \mathcal{A}_2\}$  in terms of only one space argument  $\mathbf{r}$  that

$$\begin{aligned} \{\mathcal{A}_1, \mathcal{A}_2\}_{\mathbb{L}'} := \{\mathcal{A}_1, \mathcal{A}_2\} := & \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} d\mathbf{r} - \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r})} d\mathbf{r} \\ & + \int_D \mathbf{P}(\mathbf{r}) \cdot \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} - \int_D \mathbf{P}(\mathbf{r}) \cdot \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} \\ & + \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} d\mathbf{r} - \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} d\mathbf{r}. \end{aligned} \quad (3.2.70)$$

In the same way the dissipative bracket reads

$$\begin{aligned} \{\mathcal{A}_1, \mathcal{A}_2\}_{\mathbb{M}'} := & [\mathcal{A}_1, \mathcal{A}_2] \\ = & \int_D \frac{\eta}{2} \Theta(\mathbf{r}) \left( \nabla \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) : \left( \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\ & + \int_D \tilde{k} \Theta(\mathbf{r}) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\ & + \int_D k^q \Theta^2(\mathbf{r}) \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) \cdot \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) d\mathbf{r}. \end{aligned} \quad (3.2.71)$$

**Proof of symmetry arguments.** As discussed earlier, conservation of energy and time-reversal symmetry imposes the antisymmetry requirement on the Poisson brackets for two arbitrary and sufficiently regular real valued functionals  $\mathcal{A}_1, \mathcal{A}_2 \in C^\infty(\mathcal{Z}^{3z})$ , i.e.,



$$\begin{aligned}
 \{\mathcal{A}_1, \mathcal{A}_2\} &:= \int_{D \times D} \sum_{ij} \frac{\delta \mathcal{A}_1}{\delta z_i(\mathbf{r})} \mathbb{L}^{jz_i, z_j}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta z_j(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &= - \int_{D \times D} \sum_{ij} \frac{\delta \mathcal{A}_2}{\delta z_j(\mathbf{r})} \mathbb{L}^{jz_j, z_i}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta z_i(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &=: -\{\mathcal{A}_2, \mathcal{A}_1\}, i, j \in \{1, 2, 3\}.
 \end{aligned} \tag{3.2.72}$$

Hence, if we consider the elements  $\mathbb{L}^{jP}(\mathbf{r}, \mathbf{r}') = f(\mathbf{r}') \partial_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}')$ , for  $f(\mathbf{r}) = s(\mathbf{r})$  or  $f(\mathbf{r}) = \rho(\mathbf{r})$  the requirement implies

$$\int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta f(\mathbf{r})} f(\mathbf{r}') \partial_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' = - \int_{D \times D} \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbb{L}^{jP}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta f(\mathbf{r}')} d\mathbf{r} d\mathbf{r}', \tag{3.2.73}$$

from which with the help of the properties of the Dirac delta (3.2.68), we obtain

$$\begin{aligned}
 \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta f(\mathbf{r})} \mathbb{L}^{jP}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' &:= \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta f(\mathbf{r})} f(\mathbf{r}') \partial_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &= - \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta f(\mathbf{r}')} f(\mathbf{r}) \partial_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} d\mathbf{r}' \\
 &= - \int_D \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} f(\mathbf{r}) \partial_{\mathbf{r}} \left( \frac{\delta \mathcal{A}_1}{\delta f(\mathbf{r})} \right) d\mathbf{r} \\
 &= - \int_D \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} f(\mathbf{r}) \partial_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta f(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &=: - \int_{D \times D} \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbb{L}^{jP}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta f(\mathbf{r}')} d\mathbf{r} d\mathbf{r}'.
 \end{aligned} \tag{3.2.74}$$

Analogously we deduce using that,

$$\begin{aligned}
 \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathbb{L}^{jPP}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' &:= \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} (\mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta - \partial_{\mathbf{r}} \delta \mathbf{P}(\mathbf{r})) \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &= \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &\quad - \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \partial_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \mathbf{P}(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &= - \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r}')} \mathbf{P}(\mathbf{r}) \partial_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} d\mathbf{r}' \\
 &\quad - \int_D \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathbf{P}(\mathbf{r}) \partial_{\mathbf{r}} \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right) d\mathbf{r} \\
 &= - \int_D \partial_{\mathbf{r}} \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right) \mathbf{P}(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} \\
 &\quad - \int_D \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathbf{P}(\mathbf{r}) \partial_{\mathbf{r}} \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right) d\mathbf{r} \\
 &= - \int_{D \times D} \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} \mathbf{P}(\mathbf{r}) \partial_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} d\mathbf{r}' \\
 &\quad - \int_{D \times D} \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbf{P}(\mathbf{r}) \partial_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &= \int_{D \times D} \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &\quad - \int_{D \times D} \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbf{P}(\mathbf{r}) \partial_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 &=: - \int_{D \times D} \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbb{L}^{jPP}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r}')} d\mathbf{r} d\mathbf{r}'
 \end{aligned} \tag{3.2.75}$$

As a result we deduce from (3.2.75) and (3.2.74) in view of the definition (3.2.72), that

$$\begin{aligned}
 \{\mathcal{A}_1, \mathcal{A}_2\} &:= \int_{D \times D} \left( \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} \mathbb{L}'^{\rho \mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} + \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \mathbb{L}'^{s \mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} + \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathbb{L}'^{\rho \mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r}')} \right) d\mathbf{r} d\mathbf{r}' \\
 &= \int_{D \times D} \left( -\frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbb{L}'^{\rho \mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r}')} - \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbb{L}'^{s \mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r}')} - \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathbb{L}'^{\rho \mathbf{P}}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r}')} \right) d\mathbf{r} d\mathbf{r}' \\
 &=: -\{\mathcal{A}_2, \mathcal{A}_1\}.
 \end{aligned} \tag{3.2.76}$$

Similarly we can verify the symmetry of the friction tensor, i.e., the symmetry of the dissipative brackets  $[\mathcal{A}_1, \mathcal{A}_2] = [\mathcal{A}_2, \mathcal{A}_1]$ , which follows from (3.2.176) directly by construction.

### 3.2.3 Appendix

**Proof of the Leibniz rule.** The proof is based on a recent and comprehensive article about GENERIC formalism and detail proof of the Jacoby identity for multicomponent fluid mixtures by A. Moses Badlyan and C. Zimmer [291] and earlier works by H. C. Öttinger, such as for example [28, 312]. As discussed earlier, conservation of energy and time-reversal symmetry imposes the antisymmetry requirement (3.2.72) on the Poisson brackets for two arbitrary and sufficiently regular real valued functionals  $\mathcal{A}_1, \mathcal{A}_2 \in C^\infty(\mathcal{Z}^{3z})$ . We also have to show that the following identity (Leibniz rule) holds:

$$\{\mathcal{A}_1 \mathcal{A}_2, \mathcal{A}_3\} = \mathcal{A}_1 \{\mathcal{A}_2, \mathcal{A}_3\} + \mathcal{A}_2 \{\mathcal{A}_1, \mathcal{A}_3\}, \tag{3.2.77}$$

for three arbitrary smooth observables  $\mathcal{A}_1, \mathcal{A}_2, \mathcal{A}_3 \in C^\infty(\mathcal{Z}^{3z})$ . Therefore, in light of the bracket form for two arbitrary functionals  $\mathcal{A}_1, \mathcal{A}_2$  given in (3.2.70), we can easily deduce the extension to three observables as follows:

$$\begin{aligned}
 \{\mathcal{A}_1 \mathcal{A}_2, \mathcal{A}_3\} &:= \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \left( \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} \mathcal{A}_2 + \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r})} \mathcal{A}_1 \right) d\mathbf{r} \\
 &\quad - \int_D \rho(\mathbf{r}) \left( \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathcal{A}_2 + \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathcal{A}_1 \right) \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \rho(\mathbf{r})} d\mathbf{r} \\
 &\quad + \int_D \mathbf{P}(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathcal{A}_2 + \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathcal{A}_1 \right) d\mathbf{r} \\
 &\quad - \int_D \mathbf{P}(\mathbf{r}) \left( \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathcal{A}_2 + \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathcal{A}_1 \right) \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} \\
 &\quad + \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \left( \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \mathcal{A}_2 + \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \mathcal{A}_1 \right) d\mathbf{r} \\
 &\quad - \int_D s(\mathbf{r}) \left( \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \mathcal{A}_2 + \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \mathcal{A}_1 \right) \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} d\mathbf{r}.
 \end{aligned} \tag{3.2.78}$$

In order to proceed further, we recall the product rule for functional derivatives discussed earlier in (3.2.13), i.e.,

$$\frac{\delta(\mathcal{A}_1 \mathcal{A}_2)}{\delta z_i(\mathbf{r})} = \mathcal{A}_1(\mathbf{z}) \frac{\delta \mathcal{A}_2}{\delta z_i(\mathbf{r})} + \mathcal{A}_2(\mathbf{z}) \frac{\delta \mathcal{A}_1}{\delta z_i(\mathbf{r})}, \quad i = 1, \dots, m, \tag{3.2.79}$$

with  $\mathbf{z} := [z_1, \dots, z_m]^T \in \mathcal{Z}^{mz}(D)$  representing the set of state variables. Hence, by analysing the terms, and in view of (3.2.79) we can ignore the indirect dependence of the observables

$\mathcal{A}_1, \mathcal{A}_2$  to the space variable  $\mathbf{r}$ . Therefore, each time we can pull out of the space integrals one of the  $\mathcal{A}_1, \mathcal{A}_2$ , as follows:

$$\begin{aligned}
 \{\mathcal{A}_1, \mathcal{A}_2, \mathcal{A}_3\} := & \mathcal{A}_2 \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} d\mathbf{r} + \mathcal{A}_1 \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r})} d\mathbf{r} \\
 & - \mathcal{A}_2 \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \rho(\mathbf{r})} d\mathbf{r} - \mathcal{A}_1 \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \rho(\mathbf{r})} d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D \mathbf{P}(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} + \mathcal{A}_1 \int_D \mathbf{P}(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} \\
 & - \mathcal{A}_2 \int_D \mathbf{P}(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} - \mathcal{A}_1 \int_D \mathbf{P}(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} d\mathbf{r} + \mathcal{A}_1 \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} d\mathbf{r} \\
 & - \mathcal{A}_2 \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} d\mathbf{r} - \mathcal{A}_1 \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} d\mathbf{r}. \tag{3.2.80}
 \end{aligned}$$

Similarly we evaluate also the brackets

$$\begin{aligned}
 \mathcal{A}_1 \{\mathcal{A}_2, \mathcal{A}_3\} := & \mathcal{A}_1 \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r})} d\mathbf{r} - \mathcal{A}_1 \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \rho(\mathbf{r})} d\mathbf{r} \\
 & + \mathcal{A}_1 \int_D \mathbf{P}(\mathbf{r}) \cdot \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} - \mathcal{A}_1 \int_D \mathbf{P}(\mathbf{r}) \cdot \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} \\
 & + \mathcal{A}_1 \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} d\mathbf{r} - \mathcal{A}_1 \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} d\mathbf{r} \tag{3.2.81}
 \end{aligned}$$

and

$$\begin{aligned}
 \mathcal{A}_2 \{\mathcal{A}_1, \mathcal{A}_3\} := & \mathcal{A}_2 \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} d\mathbf{r} - \mathcal{A}_2 \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \rho(\mathbf{r})} d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D \mathbf{P}(\mathbf{r}) \cdot \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} - \mathcal{A}_2 \int_D \mathbf{P}(\mathbf{r}) \cdot \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} d\mathbf{r} - \mathcal{A}_1 \int_D s(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} d\mathbf{r}. \tag{3.2.82}
 \end{aligned}$$

It is easy to check that the sum of (3.2.82) with (3.2.81), is equivalent to (3.2.80) and therefore we end up with (3.2.77) and hence the Leibniz rule is satisfied for the specific bracket defined in (3.2.70). We can now proceed by proving that the Leibniz rule holds for the dissipative bracket (3.2.176). Hence, we obtain

$$\begin{aligned}
 & [\mathcal{A}_1, \mathcal{A}_2, \mathcal{A}_3] \\
 := & \int_D \frac{\eta}{2} \Theta(\mathbf{r}) \left( \nabla \frac{\delta(\mathcal{A}_1 \mathcal{A}_2)}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta(\mathcal{A}_1 \mathcal{A}_2)}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta(\mathcal{A}_1 \mathcal{A}_2)}{\delta s(\mathbf{r})} \right) : \left( \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \int_D \tilde{k} \Theta(\mathbf{r}) \left( \operatorname{div} \left( \frac{\delta(\mathcal{A}_1 \mathcal{A}_2)}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta(\mathcal{A}_1 \mathcal{A}_2)}{\delta s(\mathbf{r})} \right) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \int_D k^q \Theta^2(\mathbf{r}) \nabla \left( \Theta(\mathbf{r}) \frac{\delta(\mathcal{A}_1 \mathcal{A}_2)}{\delta s(\mathbf{r})} \right) \cdot \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r}. \tag{3.2.83}
 \end{aligned}$$

We subsequently obtain by performing the calculations inside (3.2.83) and in view of the product rule (3.2.79), that

$$\begin{aligned}
 & [\mathcal{A}_1 \mathcal{A}_2, \mathcal{A}_3] \\
 & := \mathcal{A}_1 \int_D \frac{\eta}{2} \Theta(\mathbf{r}) \left( \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) : \left( \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D \frac{\eta}{2} \Theta(\mathbf{r}) \left( \nabla \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) : \left( \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_1 \int_D \tilde{k} \Theta(\mathbf{r}) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D \tilde{k} \Theta(\mathbf{r}) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_1 \int_D k^q \Theta^2(\mathbf{r}) \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) \cdot \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D k^q \Theta^2(\mathbf{r}) \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) \cdot \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \tag{3.2.84}
 \end{aligned}$$

In addition, we also have

$$\begin{aligned}
 & \mathcal{A}_1 [\mathcal{A}_2, \mathcal{A}_3] \\
 & := \mathcal{A}_1 \int_D \frac{\eta}{2} \Theta(\mathbf{r}) \left( \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) : \left( \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_1 \int_D \tilde{k} \Theta(\mathbf{r}) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_1 \int_D k^q \Theta^2(\mathbf{r}) \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta s(\mathbf{r})} \right) \cdot \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r}. \tag{3.2.85}
 \end{aligned}$$

Finally, the bracket  $\mathcal{A}_2[\mathcal{A}_1, \mathcal{A}_3]$  can be explicitly defined by

$$\begin{aligned}
 & \mathcal{A}_2[\mathcal{A}_1, \mathcal{A}_3] \\
 & := \mathcal{A}_2 \int_D \frac{\eta}{2} \Theta(\mathbf{r}) \left( \nabla \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) : \left( \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma} \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D \tilde{k} \Theta(\mathbf{r}) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) \left( \operatorname{div} \left( \frac{\delta \mathcal{A}_3}{\delta \mathbf{P}(\mathbf{r})} \right) - \frac{1}{2} \operatorname{tr}(D) \frac{1}{\Theta(\mathbf{r})} \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r} \\
 & + \mathcal{A}_2 \int_D k^q \Theta^2(\mathbf{r}) \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_1}{\delta s(\mathbf{r})} \right) \cdot \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_3}{\delta s(\mathbf{r})} \right) d\mathbf{r}. \tag{3.2.86}
 \end{aligned}$$

Combining (3.2.84), (3.2.85) and (3.2.86) it follows that the Leibniz rule in this case, is again satisfied.

**Proof of the Jacoby identity.** Following similar arguments as above we recall that we have to prove the Jacoby identity

$$\{\mathcal{A}_1, \{\mathcal{A}_2, \mathcal{A}_3\}\} + \{\mathcal{A}_2, \{\mathcal{A}_3, \mathcal{A}_1\}\} + \{\mathcal{A}_3, \{\mathcal{A}_1, \mathcal{A}_2\}\} = 0, \tag{3.2.87}$$

for all arbitrary smooth observables  $\mathcal{A}_1, \mathcal{A}_2, \mathcal{A}_3 \in C^\infty(\mathcal{Z}^{3z})$ . For the proof we will make use of the following Lemma.

**Lemma 3.1.** *We consider the functionals  $\mathcal{A}_1, \mathcal{A}_2 \in C^\infty(\mathcal{Z}^{mz})$  such that*

$$\begin{aligned} \mathcal{A}_1(\mathbf{z}) &= \int_D a_k(\mathbf{r}, \mathbf{z}(\mathbf{r})) g^{kl}(\mathbf{r}) \nabla_l f(\mathbf{r}, \mathbf{z}(\mathbf{r})) \, d\mathbf{r}, \\ \mathcal{A}_2(\mathbf{z}) &= \int_D G_{ik}(\mathbf{r}, \mathbf{z}(\mathbf{r})) g^{kl}(\mathbf{r}) \nabla_l g^{ij}(\mathbf{r}) a_j(\mathbf{r}, \mathbf{z}(\mathbf{r})) \, d\mathbf{r}, \end{aligned} \quad (3.2.88)$$

where  $f(\mathbf{r}, \mathbf{z}(\mathbf{r}))$ ,  $a_k(\mathbf{r}, \mathbf{z}(\mathbf{r}))$  and  $G_{ik}(\mathbf{r}, \mathbf{z}(\mathbf{r}))$  are coordinate representations of a scalar, a co-vector and a two-covariant tensor field, respectively, which map the domain  $D$  into the real numbers and depend smoothly enough on  $\mathbf{r}$ . Moreover, the quantity  $g^{kl}$  stands here and elsewhere for the contravariant metric tensor. Then, for all  $\varphi \in W^{1,p}(D) \setminus \{0\}$  and  $\mathbf{h} \in (W^{1,p}(D))^d \setminus \{0\}$  the following differentiation formulas hold

$$\begin{aligned} \int_D \varphi \frac{\delta \mathcal{A}_1}{\delta z} \, d\mathbf{r} &= \int_D \varphi \frac{\partial a_k}{\partial z} g^{kl} \nabla_l f + a_k g^{kl} \nabla_l \left( \varphi \frac{\partial f}{\partial z} \right) \, d\mathbf{r}, \\ \int_D \varphi \frac{\delta \mathcal{A}_2}{\delta z} \, d\mathbf{r} &= \int_D \varphi \frac{\partial G_{ik}}{\partial z} g^{kl} \nabla_l (g^{ij} a_j) + G_{ik} g^{kl} \nabla_l \left( \varphi g^{ij} \frac{\partial a_j}{\partial z} \right) \, d\mathbf{r}, \end{aligned} \quad (3.2.89)$$

where  $z = \{\rho, s\}$  and also

$$\begin{aligned} \int_D h_p g^{pq} \frac{\delta \mathcal{A}_1}{\delta M_p} \, d\mathbf{r} &= \int_D h_p g^{pq} \frac{\partial a_k}{\partial M_q} g^{kl} \nabla_l f + a_k g^{kl} \nabla_l \left( h_q g^{pq} \frac{\partial f}{\partial M_q} \right) \, d\mathbf{r}, \\ \int_D h_p g^{pq} \frac{\delta \mathcal{A}_2}{\delta M_p} \, d\mathbf{r} &= \int_D h_p g^{pq} \frac{\partial G_{ik}}{\partial M_q} g^{kl} \nabla_l (g^{ij} a_j) + G_{ik} g^{kl} \nabla_l \left( h_p g^{pq} g^{ij} \frac{\partial a_j}{\partial M_q} \right) \, d\mathbf{r}. \end{aligned} \quad (3.2.90)$$

Moreover, for the covariant derivative of the functional derivatives of  $\mathcal{A}_1$  and  $\mathcal{A}_2$ , we similarly obtain

$$\begin{aligned} \int_D \varphi P_p g^{pq} \nabla_q \frac{\delta \mathcal{A}_1}{\delta z} \, d\mathbf{r} &= \int_D \varphi P_p g^{pq} \nabla_q \left( \frac{\partial a_k}{\partial z} g^{kl} \nabla_l f + a_k g^{kl} \nabla_l \frac{\partial f}{\partial z} \right) \, d\mathbf{r} \\ &\quad + \int_D \nabla_l (\varphi P_p g^{pq}) \nabla_q \left( a_k g^{kl} \frac{\partial f}{\partial z} \right) \, d\mathbf{r}, \\ \int_D \varphi P_p g^{pq} \nabla_q \frac{\delta \mathcal{A}_2}{\delta z} \, d\mathbf{r} &= \int_D \varphi P_p g^{pq} \nabla_q \left( \frac{\partial G_{ik}}{\partial z} g^{kl} \nabla_l (g^{ij} a_j) + G_{ik} g^{kl} \nabla_l \left( g^{ij} \frac{\partial a_j}{\partial z} \right) \right) \, d\mathbf{r} \\ &\quad + \int_D \nabla_l (\varphi P_p g^{pq}) \nabla_q \left( G_{ik} g^{kl} g^{ij} \frac{\partial a_j}{\partial z} \right) \, d\mathbf{r} \end{aligned} \quad (3.2.91)$$

and analogously

$$\begin{aligned} \int_D h_s P_p g^{pq} \nabla_q \left( g^{st} \frac{\delta \mathcal{A}_1}{\delta P_t} \right) \, d\mathbf{r} &= \int_D h_s P_p g^{pq} \nabla_q \left( g^{st} \frac{\partial a_k}{\partial P_t} g^{kl} \nabla_l f + g^{st} a_k g^{kl} \nabla_l \frac{\partial f}{\partial P_t} \right) \, d\mathbf{r} \\ &\quad + \int_D \nabla_l (h_s P_p g^{pq}) \nabla_q \left( g^{st} a_k g^{kl} \frac{\partial f}{\partial P_t} \right) \, d\mathbf{r}, \\ \int_D h_s P_p g^{pq} \nabla_q \left( g^{st} \frac{\delta \mathcal{A}_2}{\delta P_t} \right) \, d\mathbf{r} &= \int_D h_s P_p g^{pq} \nabla_q \left( g^{st} \frac{\partial G_{ik}}{\partial P_t} g^{kl} \nabla_l (g_{ij} a_j) + g^{st} G_{ik} g^{kl} \nabla_l \left( \frac{\partial a_j}{\partial P_t} \right) \right) \, d\mathbf{r} \\ &\quad + \int_D \nabla_l (h_s P_p g^{pq}) \nabla_q \left( g^{st} G_{ik} g^{kl} g^{ij} \frac{\partial a_j}{\partial P_t} \right) \, d\mathbf{r}. \end{aligned} \quad (3.2.92)$$

*Proof.* The proof of this Lemma is carried out in [291, Lemma A.1.], is quite elementary and is based on the formal definition of the functional derivatives, so we can skip it.  $\square$

Hence, for the verification of the Jacoby identity we consider all possible combinations of the brackets and number the terms which arise from the application of Lemma 3.1 in the Poisson bracket integral combinations. Then, these terms will be split into sub-terms and

we will show which combination of sub-terms sum up to zero under cyclic summation. Evaluation of the bracket  $\{A, \{B, C\}\}$ : Since the bracket  $\{B, C\}$  is a sum of three terms, i.e.,

$$\begin{aligned} \{B, C\} &:= - \int_D \rho(\mathbf{r}) \left[ \left( \frac{\delta B}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta C}{\delta \rho(\mathbf{r})} - \left( \frac{\delta C}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta B}{\delta \rho(\mathbf{r})} \right] d\mathbf{r} \\ &\quad - \int_D \mathbf{P}(\mathbf{r}) \left[ \left( \frac{\delta B}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta C}{\delta \mathbf{P}(\mathbf{r})} - \left( \frac{\delta C}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta B}{\delta \mathbf{P}(\mathbf{r})} \right] d\mathbf{r} \\ &\quad - \int_D s(\mathbf{r}) \left[ \left( \frac{\delta B}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta C}{\delta s(\mathbf{r})} - \left( \frac{\delta C}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta B}{\delta s(\mathbf{r})} \right] d\mathbf{r}, \end{aligned} \quad (3.2.93)$$

we are splitting it into three parts, i.e.,  $\{B, C\} := \{B, C\}_\rho + \{B, C\}_s + \{B, C\}_\mathbf{P}$ , which are defined and interpreted with the help of index notation, as follows:

$$\begin{aligned} \{B, C\}_\rho &:= - \int_D \rho(\mathbf{r}) \left[ \left( \frac{\delta B}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta C}{\delta \rho(\mathbf{r})} - \left( \frac{\delta C}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta B}{\delta \rho(\mathbf{r})} \right] d\mathbf{r} \\ &= - \int_D \rho(\mathbf{r}) \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta \rho(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta \rho(\mathbf{r})} \right] d\mathbf{r}. \end{aligned} \quad (3.2.94)$$

Similarly we deduce,

$$\begin{aligned} \{B, C\}_\mathbf{P} &:= - \int_D \mathbf{P}(\mathbf{r}) \left[ \left( \frac{\delta B}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta C}{\delta \mathbf{P}(\mathbf{r})} - \left( \frac{\delta C}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta B}{\delta \mathbf{P}(\mathbf{r})} \right] d\mathbf{r} \\ &= - \int_D P_i(\mathbf{r}) \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \left( g^{ij} \frac{\delta C}{\delta P_j(\mathbf{r})} \right) - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \left( g^{ij} \frac{\delta B}{\delta P_j(\mathbf{r})} \right) \right] d\mathbf{r} \end{aligned} \quad (3.2.95)$$

and finally

$$\begin{aligned} \{B, C\}_s &:= - \int_D s(\mathbf{r}) \left[ \left( \frac{\delta B}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta C}{\delta s(\mathbf{r})} - \left( \frac{\delta C}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta B}{\delta s(\mathbf{r})} \right] d\mathbf{r} \\ &= - \int_D s(\mathbf{r}) \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta s(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta s(\mathbf{r})} \right] d\mathbf{r}. \end{aligned} \quad (3.2.96)$$

The full bracket  $\{A, \{B, C\}\}$  then can be evaluated by applying the property  $\{A, \{B, C\}\} = \{A, \{B, C\}_\rho\} + \{A, \{B, C\}_\mathbf{P}\} + \{A, \{B, C\}_s\}$ , where each of the partial brackets admits the following representation

$$\begin{aligned} \{A, \{B, C\}_z\} &:= - \int_D \rho(\mathbf{r}) \left[ \left( \frac{\delta A}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \{B, C\}_z}{\delta \rho(\mathbf{r})} - \left( \frac{\delta \{B, C\}_z}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta A}{\delta \rho(\mathbf{r})} \right] d\mathbf{r} \\ &\quad - \int_D \mathbf{P}(\mathbf{r}) \left[ \left( \frac{\delta A}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \{B, C\}_z}{\delta \mathbf{P}(\mathbf{r})} - \left( \frac{\delta \{B, C\}_z}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta A}{\delta \mathbf{P}(\mathbf{r})} \right] d\mathbf{r} \\ &\quad - \int_D s(\mathbf{r}) \left[ \left( \frac{\delta A}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \{B, C\}_z}{\delta s(\mathbf{r})} - \left( \frac{\delta \{B, C\}_z}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta A}{\delta s(\mathbf{r})} \right] d\mathbf{r}, \end{aligned} \quad (3.2.97)$$

where  $\mathbf{z} = [\rho, \mathbf{P}, s]^T \in \mathcal{Z}^{3z}(D)$ . At first stage, we can evaluate the bracket  $\{A, \{B, C\}_\mathbf{P}\}_\mathbf{P}$  using (3.2.95) and (3.2.97) with the help of index notation and the contra-variant metric tensor  $g^{ij}$ , as follows:

$$\begin{aligned}
 \{A, \{B, C\}_{\mathbf{P}}\}_{\mathbf{P}} & := - \int_D \mathbf{P}(\mathbf{r}) \left[ \left( \frac{\delta A}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \{B, C\}_{\mathbf{P}}}{\delta \mathbf{P}(\mathbf{r})} - \left( \frac{\delta \{B, C\}_{\mathbf{P}}}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta A}{\delta \mathbf{P}(\mathbf{r})} \right] d\mathbf{r} \\
 & = - \int_D P_i(\mathbf{r}) \left[ \frac{\delta A}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \left( g^{ij} \frac{\delta \{B, C\}_{\mathbf{P}}}{\delta P_j(\mathbf{r})} \right) - \frac{\delta \{B, C\}_{\mathbf{P}}}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \left( g^{ij} \frac{\delta A}{\delta P_j(\mathbf{r})} \right) \right] d\mathbf{r} \\
 & = \int_D P_s(\mathbf{r}) \left[ \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \frac{\delta}{\delta P_t(\mathbf{r})} \left( \int_D P_i(\mathbf{r}') \left[ \frac{\delta B}{\delta P_k(\mathbf{r}')} g^{kl} \nabla_l \left( g^{ij} \frac{\delta C}{\delta P_j(\mathbf{r}')} \right) \right] d\mathbf{r}' \right) \right] d\mathbf{r} \\
 & \quad - \int_D P_s(\mathbf{r}) \left[ \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \frac{\delta}{\delta P_t(\mathbf{r})} \left( \int_D P_i(\mathbf{r}') \left( \frac{\delta C}{\delta P_k(\mathbf{r}')} g^{kl} \nabla_l \left( g^{ij} \frac{\delta B}{\delta P_j(\mathbf{r}')} \right) \right) d\mathbf{r}' \right) \right] d\mathbf{r} \\
 & \quad - \int_D P_s(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{pq} \frac{\delta}{\delta P_p(\mathbf{r})} \left( \int_D P_i(\mathbf{r}') \left[ \frac{\delta B}{\delta P_k(\mathbf{r}')} g^{kl} \nabla_l \left( g^{ij} \frac{\delta C}{\delta P_j(\mathbf{r}')} \right) \right] d\mathbf{r}' \right) d\mathbf{r} \\
 & \quad + \int_D P_s(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{pq} \frac{\delta}{\delta P_p(\mathbf{r})} \left( \int_D P_i(\mathbf{r}') \left[ \frac{\delta C}{\delta P_k(\mathbf{r}')} g^{kl} \nabla_l \left( g^{ij} \frac{\delta B}{\delta P_j(\mathbf{r}')} \right) \right] d\mathbf{r}' \right) d\mathbf{r}. \quad (3.2.98)
 \end{aligned}$$

Thus, we subsequently obtain  $\{A, \{B, C\}_{\mathbf{P}}\}_{\mathbf{P}} := (\{A, \{B, C\}_{\mathbf{P}}\}_{\mathbf{P}})_1 + (\{A, \{B, C\}_{\mathbf{P}}\}_{\mathbf{P}})_2$ , where we defined

$$(\{A, \{B, C\}_{\mathbf{P}}\}_{\mathbf{P}})_1 = \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_t(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta P_t(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.99a)$$

$$+ \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta^2 B}{\delta P_k(\mathbf{r}) \delta P_t(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_j(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.99b)$$

$$+ \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta^2 C}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.99c)$$

$$- \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta^2 C}{\delta P_k(\mathbf{r}) \delta P_t(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta P_j(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.99d)$$

$$- \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta^2 B}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.99e)$$

$$- \int_D P_s(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{qp} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_p(\mathbf{r})} \right] d\mathbf{r} \quad (3.2.99f)$$

$$+ \int_D P_s(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{qp} \left[ \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta P_p(\mathbf{r})} \right] d\mathbf{r} \quad (3.2.99g)$$

and also

$$(\{A, \{B, C\} \mathbf{P}\} \mathbf{P})_2 - \int_D P_s(\mathbf{r}) P_i(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{qp} g^{ij} \left[ \frac{\delta^2 B}{\delta P_p(\mathbf{r}) \delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_j(\mathbf{r})} \right] d\mathbf{r} \quad (3.2.100a)$$

$$+ \int_D P_s(\mathbf{r}) P_i(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{qp} g^{ij} \left[ \frac{\delta^2 C}{\delta P_p(\mathbf{r}) \delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta P_j(\mathbf{r})} \right] d\mathbf{r} \quad (3.2.100b)$$

$$- \int_D P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \left( \frac{\delta^2 C}{\delta P_j(\mathbf{r}) \delta P_p(\mathbf{r})} P_s(\mathbf{r}) g^{pq} \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) \right) \right] d\mathbf{r} \quad (3.2.100c)$$

$$+ \int_D P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \left( \frac{\delta^2 B}{\delta P_j(\mathbf{r}) \delta P_p(\mathbf{r})} P_s(\mathbf{r}) g^{pq} \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) \right) \right] d\mathbf{r} \quad (3.2.100d)$$

$$+ \int_D \nabla_l \left( P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{lk} g^{pq} \nabla_q \left[ g^{st} P_i(\mathbf{r}) \left( \frac{\delta B}{\delta P_k(\mathbf{r})} \frac{\delta^2 C}{\delta P_t(\mathbf{r}) \delta P_j(\mathbf{r})} \right) \right] d\mathbf{r} \quad (3.2.100e)$$

$$- \int_D \nabla_l \left( P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{lk} g^{pq} \nabla_q \left[ g^{st} P_i(\mathbf{r}) \left( \frac{\delta C}{\delta P_k(\mathbf{r})} \frac{\delta^2 B}{\delta P_t(\mathbf{r}) \delta P_j(\mathbf{r})} \right) \right] d\mathbf{r}. \quad (3.2.100f)$$

We have to examine each term of the above sum in (3.2.99) and (3.2.100) separately, as follows: A simple calculation in the first term (3.2.99a) gives

$$\begin{aligned} & \int_D P_s(\mathbf{r}) \left[ \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_t(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta P_t(\mathbf{r})} \right] \right) \right] d\mathbf{r} \\ &= \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta C}{\delta P_t(\mathbf{r})} \right) - \frac{\delta C}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta B}{\delta P_t(\mathbf{r})} \right) \right] d\mathbf{r} \end{aligned} \quad (3.2.101a)$$

$$+ \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \left[ \nabla_q \left( \frac{\delta B}{\delta P_k(\mathbf{r})} \right) g^{kl} \nabla_l \frac{\delta C}{\delta P_t(\mathbf{r})} - \nabla_q \left( \frac{\delta C}{\delta P_k(\mathbf{r})} \right) g^{kl} \nabla_l \frac{\delta B}{\delta P_t(\mathbf{r})} \right] d\mathbf{r}. \quad (3.2.101b)$$

Moreover, the sum of the subterms (3.2.99b) and (3.2.99c) with (3.2.99d), (3.2.99e) implies

$$\int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta^2 B}{\delta P_k(\mathbf{r}) \delta P_t(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_j(\mathbf{r})} + \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta^2 C}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} \right] \right) d\mathbf{r}$$

$$- \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta^2 C}{\delta P_k(\mathbf{r}) \delta P_t(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta P_j(\mathbf{r})} + \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta^2 B}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} \right] \right) d\mathbf{r}$$

$$= \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} P_i(\mathbf{r}) g^{ij} \left[ \frac{\delta^2 B}{\delta P_k(\mathbf{r}) \delta P_t(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_j(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta^2 B}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} \right] \right) d\mathbf{r}$$

$$+ \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \nabla_q \left( P_i(\mathbf{r}) \frac{\delta B}{\delta P_k(\mathbf{r})} \right) g^{ij} g^{kl} \nabla_l \frac{\delta^2 C}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} d\mathbf{r} \quad (3.2.102a)$$

$$- \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \nabla_q \left( P_i(\mathbf{r}) \frac{\delta C}{\delta P_k(\mathbf{r})} \right) g^{ij} g^{kl} \nabla_l \frac{\delta^2 B}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} d\mathbf{r} \quad (3.2.102b)$$

$$+ \int_D P_s(\mathbf{r}) P_i(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} g^{st} g^{ij} \frac{\delta B}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta^2 C}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} \right) d\mathbf{r} \quad (3.2.102c)$$

$$- \int_D P_s(\mathbf{r}) P_i(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} g^{st} g^{ij} \frac{\delta C}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta^2 B}{\delta P_j(\mathbf{r}) \delta P_t(\mathbf{r})} \right) d\mathbf{r}. \quad (3.2.102d)$$



Finally, we also obtain

$$\begin{aligned} & \int_D \nabla_l \left( P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{lk} g^{pq} \nabla_q \left[ g^{st} P_t(\mathbf{r}) \left( \frac{\delta B}{\delta P_k(\mathbf{r})} \frac{\delta^2 C}{\delta P_t(\mathbf{r}) \delta P_j(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} \frac{\delta^2 B}{\delta P_t(\mathbf{r}) \delta P_j(\mathbf{r})} \right) \right] d\mathbf{r} \\ &= \int_D P_i(\mathbf{r}) \nabla_l \left( P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{ij} g^{lk} g^{pq} g^{st} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} \nabla_q \frac{\delta^2 C}{\delta P_t(\mathbf{r}) \delta P_j(\mathbf{r})} \right] d\mathbf{r} \end{aligned} \quad (3.2.103a)$$

$$- \int_D P_i(\mathbf{r}) \nabla_l \left( P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{ij} g^{lk} g^{pq} g^{st} \left[ \frac{\delta C}{\delta P_k(\mathbf{r})} \nabla_q \frac{\delta^2 B}{\delta P_t(\mathbf{r}) \delta P_j(\mathbf{r})} \right] d\mathbf{r} \quad (3.2.103b)$$

$$\begin{aligned} &+ \int_D \nabla_l \left( P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{lk} g^{pq} g^{st} \left[ \nabla_q \left( P_t(\mathbf{r}) \frac{\delta B}{\delta P_k(\mathbf{r})} \right) g^{ij} \frac{\delta^2 C}{\delta P_t(\mathbf{r}) \delta P_j(\mathbf{r})} \right] d\mathbf{r} \\ &- \int_D \nabla_l \left( P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{lk} g^{pq} g^{st} \left[ \nabla_q \left( P_t(\mathbf{r}) \frac{\delta C}{\delta P_k(\mathbf{r})} \right) g^{ij} \nabla_q \frac{\delta^2 B}{\delta P_t(\mathbf{r}) \delta P_j(\mathbf{r})} \right] d\mathbf{r}. \end{aligned} \quad (3.2.103c)$$

Thus, we can easily observe that the cyclic sum of (3.2.101a) vanish, i.e.,

$$\begin{aligned} 0 &= \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta C}{\delta P_t(\mathbf{r})} \right) - \frac{\delta C}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta B}{\delta P_t(\mathbf{r})} \right) \right] d\mathbf{r} \\ &+ \int_D P_s(\mathbf{r}) \frac{\delta B}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \left[ \frac{\delta C}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta A}{\delta P_t(\mathbf{r})} \right) - \frac{\delta A}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta C}{\delta P_t(\mathbf{r})} \right) \right] d\mathbf{r} \\ &+ \int_D P_s(\mathbf{r}) \frac{\delta C}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \left[ \frac{\delta A}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta B}{\delta P_t(\mathbf{r})} \right) - \frac{\delta B}{\delta P_k(\mathbf{r})} \nabla_q \left( g^{kl} \nabla_l \frac{\delta A}{\delta P_t(\mathbf{r})} \right) \right] d\mathbf{r}. \end{aligned} \quad (3.2.104)$$

Analogously the cyclic sum of (3.2.99f) and (3.2.99g) together with (3.2.101b) vanish, i.e.,

$$\begin{aligned} 0 &= \int_D P_s(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \left[ \nabla_q \left( \frac{\delta B}{\delta P_k(\mathbf{r})} \right) g^{kl} \nabla_l \frac{\delta C}{\delta P_t(\mathbf{r})} - \nabla_q \left( \frac{\delta C}{\delta P_k(\mathbf{r})} \right) g^{kl} \nabla_l \frac{\delta B}{\delta P_t(\mathbf{r})} \right] d\mathbf{r} \\ &+ \int_D P_s(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{qp} \left[ \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta P_p(\mathbf{r})} - \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_p(\mathbf{r})} \right] d\mathbf{r} \\ &+ \int_D P_s(\mathbf{r}) \frac{\delta B}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \left[ \nabla_q \left( \frac{\delta C}{\delta P_k(\mathbf{r})} \right) g^{kl} \nabla_l \frac{\delta A}{\delta P_t(\mathbf{r})} - \nabla_q \left( \frac{\delta A}{\delta P_k(\mathbf{r})} \right) g^{kl} \nabla_l \frac{\delta C}{\delta P_t(\mathbf{r})} \right] d\mathbf{r} \\ &+ \int_D P_s(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta B}{\delta P_t(\mathbf{r})} \right) g^{qp} \left[ \frac{\delta A}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta P_p(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta A}{\delta P_p(\mathbf{r})} \right] d\mathbf{r} \\ &+ \int_D P_s(\mathbf{r}) \frac{\delta C}{\delta P_p(\mathbf{r})} g^{pq} g^{st} \left[ \nabla_q \left( \frac{\delta A}{\delta P_k(\mathbf{r})} \right) g^{kl} \nabla_l \frac{\delta B}{\delta P_t(\mathbf{r})} - \nabla_q \left( \frac{\delta B}{\delta P_k(\mathbf{r})} \right) g^{kl} \nabla_l \frac{\delta A}{\delta P_t(\mathbf{r})} \right] d\mathbf{r} \\ &+ \int_D P_s(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta C}{\delta P_t(\mathbf{r})} \right) g^{qp} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta A}{\delta P_p(\mathbf{r})} - \frac{\delta A}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta P_p(\mathbf{r})} \right] d\mathbf{r}. \end{aligned} \quad (3.2.105)$$

In the same way, the cyclic sum of (3.2.99c) and (3.2.99d) with (3.2.100c) and (3.2.100d) vanish. Moreover, the cyclic sum of (3.2.102c), (3.2.102) and also the cyclic sums of (3.2.102b) and (3.2.102a) together with (3.2.103b) and (3.2.103a) and the remaining terms in (3.2.100) vanish as well. As a result, we have so far verified that

$$\{A, \{B, C\}_{\mathbf{P}}\}_{\mathbf{P}} + \{B, \{C, A\}_{\mathbf{P}}\}_{\mathbf{P}} + \{C, \{A, B\}_{\mathbf{P}}\}_{\mathbf{P}} = 0. \quad (3.2.106)$$

We next proceed by evaluating the brackets  $\{A, \{B, C\}_{\rho}\}_{\rho}$  and  $\{A, \{B, C\}_s\}_s$ . Hence, we obtain

$$\begin{aligned}
 \{A, \{B, C\}_\rho\}_\rho &:= - \int_D \rho(\mathbf{r}) \left[ \left( \frac{\delta A}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \{B, C\}_\rho}{\delta \rho(\mathbf{r})} - \left( \frac{\delta \{B, C\}_\rho}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta A}{\delta \rho(\mathbf{r})} \right] d\mathbf{r} \\
 &= - \int_D \rho(\mathbf{r}) \left[ \frac{\delta A}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta \{B, C\}_\rho}{\delta \rho(\mathbf{r})} - \frac{\delta \{B, C\}_\rho}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta A}{\delta \rho(\mathbf{r})} \right] d\mathbf{r} \\
 &= \int_D \rho(\mathbf{r}) \left[ \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \frac{\delta}{\delta \rho(\mathbf{r})} \left( \int_D \rho(\mathbf{r}') \left[ \frac{\delta B}{\delta P_k(\mathbf{r}')} g^{kl} \nabla_l \left( g^{ij} \frac{\delta C}{\delta \rho(\mathbf{r}')} \right) \right] d\mathbf{r}' \right) \right) \right] d\mathbf{r} \\
 &\quad - \int_D \rho(\mathbf{r}) \left[ \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \frac{\delta}{\delta P_t(\mathbf{r})} \left( \int_D \rho(\mathbf{r}') \left( \frac{\delta C}{\delta P_k(\mathbf{r}')} g^{kl} \nabla_l \left( g^{ij} \frac{\delta B}{\delta \rho(\mathbf{r}')} \right) \right) d\mathbf{r}' \right) \right) \right] d\mathbf{r} \\
 &\quad - \int_D \rho(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta \rho(\mathbf{r})} \right) g^{pq} \frac{\delta}{\delta P_p(\mathbf{r})} \left( \int_D \rho(\mathbf{r}') \left[ \frac{\delta B}{\delta P_k(\mathbf{r}')} g^{kl} \nabla_l \left( g^{ij} \frac{\delta C}{\delta \rho(\mathbf{r}')} \right) \right] d\mathbf{r}' \right) d\mathbf{r} \\
 &\quad + \int_D \rho(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta \rho(\mathbf{r})} \right) g^{pq} \frac{\delta}{\delta P_p(\mathbf{r})} \left( \int_D \rho(\mathbf{r}') \left[ \frac{\delta C}{\delta P_k(\mathbf{r}')} g^{kl} \nabla_l \left( g^{ij} \frac{\delta B}{\delta \rho(\mathbf{r}')} \right) \right] d\mathbf{r}' \right) d\mathbf{r}. \quad (3.2.107)
 \end{aligned}$$

Therefore by analysing the four terms in (3.2.107), we obtain  $\{A, \{B, C\}_\rho\}_\rho := (\{A, \{B, C\}_\rho\}_\rho)_1 + (\{A, \{B, C\}_\rho\}_\rho)_2$ , where we defined

$$(\{A, \{B, C\}_\rho\}_\rho)_1 := \int_D \rho(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta \rho(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta \rho(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.108a)$$

$$+ \int_D \rho(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \rho(\mathbf{r}) g^{ij} \left[ \frac{\delta^2 B}{\delta \rho(\mathbf{r}) \delta P_t(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta \rho(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.108b)$$

$$+ \int_D \rho(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \rho(\mathbf{r}) g^{ij} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta^2 C}{\delta^2 \rho(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.108c)$$

$$- \int_D \rho(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \rho(\mathbf{r}) g^{ij} \left[ \frac{\delta^2 C}{\delta \rho(\mathbf{r}) \delta P_t(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta \rho(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.108d)$$

$$- \int_D \rho(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \rho(\mathbf{r}) g^{ij} \left[ \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta^2 B}{\delta^2 \rho(\mathbf{r})} \right] \right) d\mathbf{r} \quad (3.2.108e)$$

$$- \int_D \rho^2(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{qp} g^{ij} \left[ \frac{\delta^2 B}{\delta \rho(\mathbf{r}) P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta \rho(\mathbf{r})} \right] d\mathbf{r} \quad (3.2.108f)$$

and also

$$(\{A, \{B, C\}_\rho\}_\rho)_2 := \int_D \rho^2(\mathbf{r}) \nabla_q \left( g^{st} \frac{\delta A}{\delta P_t(\mathbf{r})} \right) g^{qp} g^{ij} \left[ \frac{\delta^2 C}{\delta \rho(\mathbf{r}) \delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta \rho(\mathbf{r})} \right] d\mathbf{r} \quad (3.2.109a)$$

$$- \int_D \rho(\mathbf{r}) g^{ij} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \left( \frac{\delta^2 C}{\delta \rho(\mathbf{r}) \delta P_p(\mathbf{r})} \rho(\mathbf{r}) g^{pq} \nabla_q \left( g^{st} \frac{\delta A}{\delta \rho(\mathbf{r})} \right) \right) \right] d\mathbf{r} \quad (3.2.109b)$$

$$+ \int_D \rho(\mathbf{r}) g^{ij} \left[ \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \left( \frac{\delta^2 B}{\delta \rho(\mathbf{r}) \delta P_p(\mathbf{r})} \rho(\mathbf{r}) g^{pq} \nabla_q \left( g^{st} \frac{\delta A}{\delta \rho(\mathbf{r})} \right) \right) \right] d\mathbf{r} \quad (3.2.109c)$$

$$+ \int_D \nabla_l \left( \rho(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{lk} g^{pq} \nabla_q \left[ g^{st} \rho(\mathbf{r}) \left( \frac{\delta B}{\delta P_k(\mathbf{r})} \frac{\delta^2 C}{\delta P_t(\mathbf{r}) \delta \rho(\mathbf{r})} \right) \right] d\mathbf{r} \quad (3.2.109d)$$

$$- \int_D \nabla_l \left( \rho(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} \right) g^{lk} g^{pq} \nabla_q \left[ g^{st} \rho(\mathbf{r}) \left( \frac{\delta C}{\delta P_k(\mathbf{r})} \frac{\delta^2 B}{\delta P_t(\mathbf{r}) \delta \rho(\mathbf{r})} \right) \right] d\mathbf{r}. \quad (3.2.109e)$$

Following the procedure discussed above for the bracket  $\{A, \{B, C\}_\mathbf{P}\}_\mathbf{P}$ , it is easy to check that most of the terms vanish under the proper cyclic summation combination as for the

bracket  $\{A, \{B, C\}_{\mathbf{P}}\}_{\mathbf{P}}$ , with the exception of the term

$$\int_D \rho(\mathbf{r}) \frac{\delta A}{\delta P_p(\mathbf{r})} g^{pq} \nabla_q \left( g^{st} \left[ \frac{\delta B}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta C}{\delta \rho(\mathbf{r})} - \frac{\delta C}{\delta P_k(\mathbf{r})} g^{kl} \nabla_l \frac{\delta B}{\delta \rho(\mathbf{r})} \right] \right) d\mathbf{r}. \quad (3.2.110)$$

This term will more precisely vanish under the cyclic summation of the mixed bracket  $\{A, \{B, C\}_{\rho}\}_{\mathbf{P}} + \{A, \{B, C\}_{\mathbf{P}}\}_{\rho}$  with a sub-term of  $-\int_D \rho \nabla_l \left( \frac{\delta A}{\delta \rho} \right) g^{lk} \frac{\delta \{B, C\}_{\rho}}{\delta P_k} d\mathbf{r}$ .  $\square$

### 3.2.4 GENERIC formulation for the Allen-Cahn/Cahn-Hilliard coupled with Navier-Stokes model.

The following example is an extension of the framework presented above for the classical hydrodynamics, to a more complex system and follows the general lines of the article on the application of GENERIC to the classical phase-field/Navier-Stokes formulation by A. Jelic, P. Ilg and H. C. Öttinger [43] in which they consider the following coupled system (Model H):

$$\begin{cases} \partial_t \rho = -(\mathbf{v} \cdot \nabla) \rho, \\ \partial_t c = -(\mathbf{v} \cdot \nabla) c + m \Delta \mu, \\ \partial_t \mathbf{P} = -(\mathbf{v} \cdot \nabla) \mathbf{P} + \operatorname{div}(\boldsymbol{\Sigma}), \end{cases} \quad (3.2.111)$$

where  $\mathbf{P} := \rho \mathbf{v}$  stands for the momentum density and  $m$  represents the elastic relaxation time of the system. The model is also supplemented with the incompressibility condition  $\operatorname{div}(\mathbf{v}) = 0$ , which actually implies the reduction of the original terms  $\operatorname{div}(\mathbf{v} z_i)$  to  $(\mathbf{v} \cdot \nabla) z_i$  where  $z_i \in \{\rho, c, \mathbf{P}\}$  in the corresponding constitutive equations. In addition, the quantity  $\boldsymbol{\Sigma}$  corresponds to the total stress tensor, which can be defined by the sum the incompressible hydrodynamic stress tensor  $\boldsymbol{\Pi} = -p\mathbb{I} + \eta \dot{\gamma}$  defined earlier and an extra elastic stress contribution due to the coupling with the phase-field dynamics, as follows:

$$\begin{aligned} \boldsymbol{\Sigma} &:= \boldsymbol{\Pi} - \lambda^2 (\nabla c \otimes \nabla c) + w(c) \mathbb{I} \\ &= -p \mathbb{I} + \eta \dot{\gamma} - \lambda^2 (\nabla c \otimes \nabla c) + w(c) \mathbb{I}. \end{aligned} \quad (3.2.112)$$

Moreover,  $w(c)$  denotes the elastic (mixing) free energy density defined by  $w(c) := f_L(c) + \lambda^2 |\nabla c|^2 / 2$ . The term  $-\lambda^2 (\nabla c \otimes \nabla c)$  corresponds to the extra elastic surface stress induced by the microscopic internal energy. This tensor can be considered as a generator of momentum related to the interface of the phase field [315]. Finally, function  $\mu$  represents the classical Cahn-Hilliard chemical potential as usual, i.e.,

$$\mu := \mu(c) := \nabla_c^L w(c) = f_L'(c) - \lambda^2 \Delta c. \quad (3.2.113)$$

Furthermore, from the definition of the Helmholtz free energy, the following relation between the bulk contribution to the chemical potential and the entropy density holds:  $f_L'(c) := \mu_b(c) = -\Theta \partial_c s$ . In the problem we additionally impose initial conditions  $\mathbf{v}_0, c_0$  at time  $t = 0$  and appropriate periodic boundary conditions and assuming solution  $\mathbf{v}$  and  $c \in H_{(0)}^2(D)$ ,

where we can define the space  $H_{(0)}^2(D)$  as the space of periodic functions  $c$  such that:

$$H_{(0)}^2(D) := \left\{ c \in H^2(D), \int_D c d\mathbf{r} = 0 \right\}. \quad (3.2.114)$$

Furthermore since  $c \in H_{(0)}^2(D)$ , by assumption the following identity holds (see [327]):

$$\operatorname{div}(\nabla c \otimes \nabla c) = \nabla \left( \frac{1}{2} |\nabla c|^2 \right) + \Delta c \nabla c. \quad (3.2.115)$$

The phase field model for a fluid mixture consists of separate hydrodynamic system of each component, together with the free interface that separates them. The interfacial dynamics in the mixture of different fluids, solids or gas has been of interest for many years. Many surface properties, such as capillarity, are associated with the surface tension through special boundary conditions on the interfaces. In order to obtain a model equations, we use energetic variations following the papers of C. Liu, M. H. Giga, Y. Hyon and other [317–319], in combination with the classical approach that already discussed in the previous subsection for the mass balance (3.2.29), (3.2.30) and the gradient flow derivation of the Cahn-Hilliard equation, see Theorem 1.2.1 and Theorem 1.2.2.

The Energetic Variational Approach, which is motivated by the earlier work by L. Onsager on the reciprocal relationships, that combined in a unique way the fluxes and the forces in a thermodynamical system [33, 34]. The method comprises of the Principle of Least Action which determines the Hamiltonian contribution to the model and the Maximum Dissipation Principle provides the dissipative part.

**Lemma 3.2 (Dissipation of energy in simple fluids).** *Based on the standard definition for the dissipation  $\mathcal{D}$  of the total energy of a system, i.e.,  $dE_{\text{total}}/dt = -\mathcal{D}$ , the following energy law dictates a simple fluid,*

$$\frac{d}{dt} \int_D \frac{1}{2} \rho |\mathbf{v}|^2 d\mathbf{r} = - \int_D \eta |\nabla \mathbf{v}|^2 d\mathbf{r}, \quad (3.2.116)$$

where the flow is governed by the classical incompressible Navier-Stokes equations (3.2.30), (3.2.37). The term on the right (with opposite sign), is known as the dissipation of the energy (left term)  $\mathcal{D} := \int_D \eta |\nabla \mathbf{v}|^2 d\mathbf{r}$ .

*Proof.* The proof is straightforward from the mass balance  $\partial_t \rho = -\nabla \cdot (\rho \mathbf{v})$  and if we multiply by  $\mathbf{v}$  and then apply Green's first identity, to the following momentum balance with  $\operatorname{div}(\mathbf{v}) = 0$  and homogeneous Neumann boundary conditions:

$$\rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) + \nabla p = \eta \Delta \mathbf{v}. \quad (3.2.117)$$

Note that the terms  $\rho(\mathbf{v} \cdot \nabla \mathbf{v}) \cdot \mathbf{v}$  and  $\nabla p \cdot \mathbf{v}$  which arise after the multiplication by  $\mathbf{v}$ , disappear after the integration by parts.  $\square$

**Definition 3.11 (Action functional).** *Subsequently, we are able to define the simplest form for the action functional which comes up from the Navier-Stokes kinetic energy, as follows:*

$$\mathcal{A}(\mathbf{r}) := \int_{D_T} \frac{1}{2} \rho |\mathbf{v}|^2 - w(\rho(\mathbf{r}, t)) d\mathbf{r} dt, \quad (3.2.118)$$

in which  $w$  stands for the internal energy density, or equivalently in terms of the Eulerian description in which we pull back from the current domain  $D$ , to a reference domain  $D_0$  (see eq. (3.2.123)) and we obtain,

$$\mathcal{A}(\mathbf{r}) := \int_{(D_0)_t} \left( \frac{1}{2J} \rho_0(\mathbf{R}) |\partial_t \mathbf{r}|^2 - w(J^{-1} \rho_0(\mathbf{R})) \right) J d\mathbf{R} dt, \quad (3.2.119)$$

where  $\rho_0(\mathbf{R}) = \rho(\mathbf{R}, t)|_{t=0}$  stands for the initial mass of the fluid contained in the reference volume and we additionally denoted the determinant of the deformation defined in (3.2.121) by  $J = \det(Q)$  and therefore we can identify  $\rho(\mathbf{r}(\mathbf{R}, t), t) = J^{-1} \rho_0(\mathbf{R})$ .

**Remark 3.17 (Flow maps).** We define the Eulerian flow map  $\mathbf{r}(\mathbf{R}, t)$  in terms of the the Lagrangian (initial) material coordinate  $\mathbf{R}$ , from the reference volume  $D_0$  to the deformed volume over some time  $D$  as a trajectory such that

$$\partial_t \mathbf{r}(\mathbf{R}, t) = \mathbf{v}(\mathbf{r}(\mathbf{R}, t), t) \text{ with } \mathbf{r}(\mathbf{R}, 0) = \mathbf{R}. \quad (3.2.120)$$

We additionally define the related deformation gradient tensor of the trajectory, which describes the motion in the neighbourhood of a point, as follows:

$$Q(\mathbf{r}(\mathbf{R}, t), t) = \frac{\partial \mathbf{r}(\mathbf{R}, t)}{\partial \mathbf{R}}, \quad (3.2.121)$$

and satisfies the following equation

$$Q_t + \mathbf{v} \cdot \nabla_{\mathbf{r}} Q = (\nabla_{\mathbf{r}} \mathbf{v}) Q. \quad (3.2.122)$$

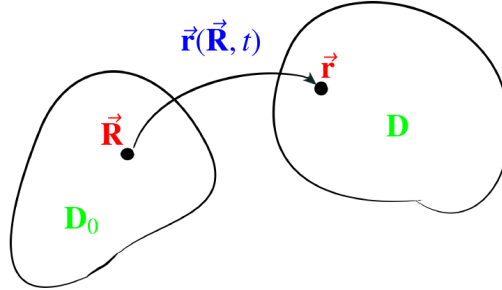


Figure 3.2: Flow map from the reference domain  $D_0$  to the current  $D$ .

**Lemma 3.3 (The Euler's equation).** The first variation of the Eulerian action functional (3.2.119) is equal to zero according to the Least Action Principle and together with the incompressibility condition  $J := \det(Q) = 1$ , provides the following Euler equation:

$$\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla \tilde{p}, \text{ with } \operatorname{div}(\mathbf{v}) = 0. \quad (3.2.123)$$

*Proof.* The first variation  $\delta_{\mathbf{r}}^{L^2} \mathcal{A}(\mathbf{r}) := \langle \nabla_{\mathbf{r}}^{L^2} \mathcal{A}(\mathbf{r}), \mathbf{y} \rangle_{L^2(D)}$  of the action functional can be evaluated with the help of a test function  $\mathbf{y} := \mathbf{y}(\mathbf{R}, t) = \tilde{\mathbf{y}}(\mathbf{r}(\mathbf{R}, t), t) \in L^2(0, T; C_c^\infty(D))_d$ , as follows (see [305, 320, 321] for more details): We first consider the classical definition of the Gâteaux differential by

$$\begin{aligned}
 \langle \nabla_{\mathbf{r}}^{L^2} \mathcal{A}(\mathbf{r}, \mathbf{y}) \rangle_{L^2} &= \lim_{k \rightarrow 0} k^{-1} \int_{(D_0)_T} \frac{1}{2} \rho_0(\mathbf{R}) \left( |\partial_t \mathbf{r} + k \partial_t \mathbf{y}|^2 - |\partial_t \mathbf{r}|^2 \right) d\mathbf{R} dt \\
 &\quad - \lim_{k \rightarrow 0} k^{-1} \int_{(D_0)_T} w \left( \left[ \det \left( \frac{\partial(\mathbf{r} + k\mathbf{y})}{\partial \mathbf{R}} \right) \right]^{-1} \rho_0(\mathbf{R}) \right) \det \left( \frac{\partial(\mathbf{r} + k\mathbf{y})}{\partial \mathbf{R}} \right) d\mathbf{R} dt \\
 &\quad + \lim_{k \rightarrow 0} k^{-1} \int_{(D_0)_T} w \left( \left[ \det \left( \frac{\partial \mathbf{r}}{\partial \mathbf{R}} \right) \right]^{-1} \rho_0(\mathbf{R}) \right) \det \left( \frac{\partial \mathbf{r}}{\partial \mathbf{R}} \right) d\mathbf{R} dt, \tag{3.2.124}
 \end{aligned}$$

which is equivalent to

$$\begin{aligned}
 \langle \nabla_{\mathbf{r}}^{L^2} \mathcal{A}(\mathbf{r}, \mathbf{y}) \rangle_{L^2} &= \lim_{k \rightarrow 0} k^{-1} \int_{(D_0)_T} \frac{1}{2} \rho_0(\mathbf{R}) \left( 2k(\partial_t \mathbf{r} \cdot \partial_t \mathbf{y}) + k^2 |\partial_t \mathbf{y}|^2 \right) d\mathbf{R} dt \\
 &\quad - \lim_{k \rightarrow 0} k^{-1} \int_{(D_0)_T} w \left( \left[ \det \left( \frac{\partial(\mathbf{r} + k\mathbf{y})}{\partial \mathbf{R}} \right) \right]^{-1} \rho_0(\mathbf{R}) \right) \det \left( \frac{\partial \mathbf{r}}{\partial \mathbf{R}} \right) d\mathbf{R} dt \\
 &\quad + \lim_{k \rightarrow 0} k^{-1} \int_{(D_0)_T} w \left( \left[ \det \left( \frac{\partial \mathbf{r}}{\partial \mathbf{R}} \right) \right]^{-1} \rho_0(\mathbf{R}) \right) \det \left( \frac{\partial \mathbf{r}}{\partial \mathbf{R}} \right) d\mathbf{R} dt \\
 &\quad - \lim_{k \rightarrow 0} k^{-1} \int_{(D_0)_T} w \left( \left[ \det \left( \frac{\partial \mathbf{r}}{\partial \mathbf{R}} \right) \right]^{-1} \rho_0(\mathbf{R}) \right) \det \left( \frac{\partial(\mathbf{r} + k\mathbf{y})}{\partial \mathbf{R}} \right) d\mathbf{R} dt \\
 &= \int_{(D_0)_T} \rho_0(\mathbf{R}) (\partial_t \mathbf{r} \cdot \partial_t \mathbf{y}) - w(J^{-1} \rho_0(\mathbf{R})) \operatorname{tr} \left( \frac{\partial \mathbf{R}}{\partial \mathbf{r}} \frac{\partial \mathbf{y}}{\partial \mathbf{R}} \right) J d\mathbf{R} dt \\
 &\quad + \int_{(D_0)_T} J(J^{-2} \rho_0(\mathbf{R})) w_\rho(J^{-1} \rho_0(\mathbf{R})) \operatorname{tr} \left( \frac{\partial \mathbf{R}}{\partial \mathbf{r}} \frac{\partial \mathbf{y}}{\partial \mathbf{R}} \right) J d\mathbf{R} dt, \tag{3.2.125}
 \end{aligned}$$

where we denoted by  $w_\rho$  the following special first variation of  $w$  with respect to  $\rho$ ,

$$w_\rho := \lim_{k \rightarrow 0} k^{-1} \left\{ w \left( \left[ \det \left( \frac{\partial(\mathbf{r} + k\mathbf{y})}{\partial \mathbf{R}} \right) \right]^{-1} \rho_0(\mathbf{R}) \right) - w \left( \left[ \det \left( \frac{\partial \mathbf{r}}{\partial \mathbf{R}} \right) \right]^{-1} \rho_0(\mathbf{R}) \right) \right\}. \tag{3.2.126}$$

provided that  $\rho(\mathbf{r}(\mathbf{R}, t), t) = J^{-1} \rho_0(\mathbf{R})$ ,  $\forall \mathbf{R} \in D_0, t \geq 0$ . In the last two lines of the derivation above, we make use of the following remark for the identification of the determinant's time derivative:

**Lemma 3.4.** *Let  $\mathcal{T} : \mathbb{R}_0^+ \rightarrow GL(d, \mathbb{R}) \subset \mathbb{R}^{d \times d}$  be a time dependent differentiable field of invertible matrices and let  $\det : \mathbb{R}^{d \times d} \rightarrow \mathbb{R}$  be the determinant, then*

$$\frac{d}{dt} \det(\mathcal{T}) = \det(\mathcal{T}) \operatorname{tr} \left( \mathcal{T}^{-1} \frac{d}{dt} \mathcal{T} \right), \tag{3.2.127}$$

for the proof and more details we refer to ([305, 320]).

**Remark 3.18.** *The following formulas involving the deformation with respect to a variation of the flow field, i.e.,  $Q^\varepsilon(\mathbf{R}, t) := \partial(\mathbf{r} + \varepsilon \mathbf{y}) / \partial \mathbf{R}$  for all  $\mathbf{y} \in L^2(0, T; C_c^\infty(D))_d$ , are useful for the calculations of the related action functionals:*

$$\left\{ \begin{array}{l} \delta_{\mathbf{r}}^{L^2} \det(Q^\varepsilon(\mathbf{R}, t)) := \langle \nabla_{\mathbf{r}}^{L^2} \det(Q^\varepsilon)(\mathbf{r}, \mathbf{y}) \rangle_{L^2(D)} = \det(Q) \operatorname{tr} \left( \frac{\partial \mathbf{y}(\mathbf{R}, t)}{\partial \mathbf{R}} Q^{-1} \right), \\ \delta_{\mathbf{r}}^{L^2} (Q^\varepsilon)^{-1}(\mathbf{R}, t) := \langle \nabla_{\mathbf{r}}^{L^2} (Q^\varepsilon)^{-1}(\mathbf{r}, \mathbf{y}) \rangle_{L^2(D)} = -Q^{-1} \frac{\partial \mathbf{y}(\mathbf{R}, t)}{\partial \mathbf{R}} Q^{-1}, \\ \delta_{\mathbf{r}}^{L^2} Q^\varepsilon(\mathbf{R}, t) := \langle \nabla_{\mathbf{r}}^{L^2} Q^\varepsilon(\mathbf{r}, \mathbf{y}) \rangle_{L^2(D)} = \frac{\partial \mathbf{y}(\mathbf{R}, t)}{\partial \mathbf{R}}. \end{array} \right. \tag{3.2.128}$$

For the proof and more details of the above identities (see also [305, 322]).

Therefore by changing from the Lagrangian to Eulerian setting and integrate by parts over time, we obtain from the least action principle and the incompressibility assumption the following identity:

$$0 = \int_{D_T} -\rho(\mathbf{r}, t) \frac{d}{dt} (\mathbf{v}(\mathbf{r}, t)) \cdot \tilde{\mathbf{y}} + (w_\rho(\rho(\mathbf{r}, t))\rho(\mathbf{r}, t) - w(\rho(\mathbf{r}, t))) \operatorname{div}_{\mathbf{r}}(\tilde{\mathbf{y}}) \, d\mathbf{r} \, dt. \quad (3.2.129)$$

By integrating by parts and identifying the pressure by the basic thermodynamic relationship of state, i.e.,  $\tilde{p}(\mathbf{r}, t) := w_\rho(\rho(\mathbf{r}, t))\rho(\mathbf{r}, t) - w(\rho(\mathbf{r}, t))$ , subsequently provides the weak Euler equation for the momentum balance:

$$\delta_{\tilde{\mathbf{r}}}^{L^2} \mathcal{A}(\mathbf{r}) = - \int_{D_T} \left[ \rho(\mathbf{r}, t) (\partial_t \mathbf{v}(\mathbf{r}, t) + (\mathbf{v}(\mathbf{r}, t) \cdot \nabla_{\mathbf{r}}) \mathbf{v}(\mathbf{r}, t)) + \nabla_{\mathbf{r}} \tilde{p}(\mathbf{r}, t) \right] \cdot \tilde{\mathbf{y}} \, d\mathbf{r} \, dt = 0, \quad (3.2.130)$$

which is equivalent to (3.2.123) and the proof is completed.  $\square$

We additionally consider to include dissipation in the flow field which is mainly caused by the flow viscosity  $\eta$ , which can be assumed to be constant in this particular case.

**Lemma 3.5 (Stokes equation).** *The maximum dissipation principle applied to the dissipation functional  $\mathcal{D}(\mathbf{v}) := \int_D \eta |\nabla \mathbf{v}|^2 \, dx$ , provides the following incompressible Stokes part of the momentum balance*

$$\eta \Delta \mathbf{v} = -\nabla p, \text{ with } \operatorname{div}(\mathbf{v}) = 0. \quad (3.2.131)$$

*Proof.* We shall evaluate the variation with respect to the velocity field  $\mathbf{v}$ , in the direction of a vector valued divergence free test function, i.e.,  $\mathbf{y} \in L^2(0, T; H_{\operatorname{div}}^1(D))_d$ ,  $\mathbf{y} \cdot \mathbf{n} = 0$  on  $\partial D$ :

$$\begin{aligned} \delta_{\mathbf{v}}^{L^2} \mathcal{D}(\mathbf{v}) &:= \langle \nabla_{\mathbf{v}}^{L^2} \mathcal{D}(\mathbf{v}), \mathbf{y} \rangle_{L^2} := \lim_{k \rightarrow 0} k^{-1} \int_D \eta (|\nabla(\mathbf{v} + k\mathbf{y})|^2 - |\nabla \mathbf{v}|^2) \, d\mathbf{r} \\ &= \int_D 2\eta \nabla \mathbf{v} : \nabla \mathbf{y} \, d\mathbf{r} \\ &= -2\eta \langle \Delta \mathbf{v}, \mathbf{y} \rangle_{L^2(D)}. \end{aligned} \quad (3.2.132)$$

Therefore, the least action principle then implies that  $\delta_{\mathbf{v}}^{L^2} \mathcal{D}(\mathbf{v}) = 0$ . At this point we will make use of the Helmholtz-Weyl's decomposition statement for a vector field, which can be summarised in the following remark (see also [320, 323, 324] and [325, Chap. III.1]):

**Remark 3.19.** *An arbitrary vector field  $\mathbf{u} \in L^2(D)_d$ , can be uniquely expressed as the sum*

$$\mathbf{u} = \mathbf{w} + \nabla p, \quad (3.2.133)$$

where  $p \in \mathcal{H}^{1,2}(D) := \{p \in L_{\operatorname{loc}}^2(D), \nabla p \in L^2(D)_d\}$  and  $\mathbf{w} \in \mathcal{H}_2(D) := \{\mathbf{w} \in L^2(D)_d : \operatorname{div}(\mathbf{w}) = 0 \text{ in } D, \mathbf{w} \cdot \mathbf{n} \text{ on } \partial D\}$ . Hence, for given  $\mathbf{u} \in L^2(D)_d$ , there exists  $p \in \mathcal{H}^{1,2}(D)$  unique up to additive constants, such that  $\mathbf{u} - \nabla p \in \mathcal{H}_2(D)$ , or equivalently

$$\int_D (\nabla p - \mathbf{u}) \cdot \nabla \varphi \, d\mathbf{r} = 0, \text{ for all } \varphi \in \mathcal{H}^{1,2}(D), \quad (3.2.134)$$

that is,  $p$  is a weak solution of the following Neumann problem

$$\begin{cases} \Delta p = \operatorname{div}(\mathbf{u}) & \text{in } D, \\ \partial_{\mathbf{n}} p = \mathbf{u} \cdot \mathbf{n} & \text{on } \partial D. \end{cases} \quad (3.2.135)$$

This remark implies that the dissipative part reads in the form of the Stokes equation, i.e.,  $-\nabla \cdot (\eta \nabla \mathbf{v}) = \nabla p$  or equivalently for constant  $\eta$  provides (3.2.131) and the proof of Lemma 3.5 is completed.  $\square$

As a result, by combining Euler's (3.2.123) and Stokes equations (3.2.131) according to the equivalence law of force balance, i.e., that the dissipative force is equal to the conservative, provides the full incompressible Navier-Stokes momentum equation

$$\rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla \hat{p} + \eta \Delta \mathbf{v}, \text{ with } \operatorname{div}(\mathbf{v}) = 0, \quad (3.2.136)$$

in which we identified the new pressure  $\hat{p}$ , by the following difference  $\hat{p} := \bar{p} - p$ .

**Remark 3.20.** *The Euler equation can be also obtained as a result of the Least Action Principle applied to the simple action functional  $A(\mathbf{r}) := \frac{1}{2} \int_{(D_0)_T} \rho_0(\mathbf{R}) |\partial_t \mathbf{r}|^2 J d\mathbf{R} dt$  (kinetic energy), in combination with remark 3.19 and the incompressibility assumption ( $J = 1$ ).*

**Remark 3.21.** *The conservation of mass  $\rho_t = \operatorname{div}(\mathbf{v}\rho)$  can be derived directly from the first variation over time, of the mass functional in the Lagrangian setting, i.e.,*

$$m(t) := \int_{D_0} \rho(\mathbf{r}(\mathbf{R}, t), t) \det(Q) d\mathbf{R}, \quad (3.2.137)$$

with the help of lemma 3.4. Therefore a system is dictated by the conservation of mass, if and only if  $\rho(\mathbf{r}(\mathbf{R}, t), t) = \rho_0(\mathbf{R}) / \det(Q)$ ,  $\forall \mathbf{R} \in D_0$ ,  $t \geq 0$  [305, 320].

The coupling model of study is an extension of the classical Model H (3.2.111) presented above, motivated by the articles of C. Liu, J. Shen, X. Yang, Z. Guo and P. Lin[316, 326–328] and consists of an incompressible Navier-Stokes momentum balance coupled with an Allen-Cahn/Cahn-Hilliard evolution for the phase field  $c := c(\mathbf{r}, t)$ . As previously discussed we shall use the same notation, so the variable  $\mathbf{v} := \mathbf{v}(\mathbf{r}, t)$  represents the velocity field and  $u := u(\mathbf{r}, t)$  is the internal energy density of the system. Finally, we additionally impose to the system the influence of some external forcing (usually gravity) and hence, the full system reads in the form:

$$\begin{cases} \partial_t \rho = -(\mathbf{v} \cdot \nabla) \rho, \\ \partial_t c = -(\mathbf{v} \cdot \nabla) c + m \Delta \mu(c) - \mu(c), \\ \partial_t \mathbf{P} = -(\mathbf{v} \cdot \nabla) \mathbf{P} + \operatorname{div}(\boldsymbol{\Sigma}) - \rho g \hat{\mathbf{z}}, \end{cases} \quad (3.2.138)$$

in light of the definition  $\boldsymbol{\Sigma} := -p\mathbb{I} + \eta \dot{\gamma} - \lambda^2 (\nabla c \otimes \nabla c) + w(c)\mathbb{I}$  and supplemented with the incompressibility condition  $\operatorname{div}(\mathbf{v}) = 0$ . As noted, the several parameters appearing in (3.2.138) are interpreted as for the system (3.2.111), with the same notation. In addition, the vector  $\rho g \hat{\mathbf{z}}$  denotes the density of a constant external gravitation forcing with  $\hat{\mathbf{z}}$  being the unit vector of upward direction.



**Remark 3.22 (Principle of Virtual Work).** *It is worth mentioning that the term  $\lambda^2(\nabla c \otimes \nabla c) - w(c)\mathbb{I}$  that appears in the momentum balance (3.2.138), can be derived also based on the following statement: Given a free energy functional  $w := w(c, \nabla c)$ , all the solutions of the Euler–Lagrangian equation*

$$-\nabla \cdot \left( \frac{\partial w(c, \nabla c)}{\partial \nabla c} \right) + \frac{\partial w(c, \nabla c)}{\partial c} = 0, \quad (3.2.139)$$

satisfy the following equation

$$\nabla \cdot \left( \frac{\partial w(c, \nabla c)}{\partial \nabla c} \otimes \nabla c - w(c, \nabla c)\mathbb{I} \right) = 0, \quad (3.2.140)$$

which corresponds to the related elastic stress tensor term in the momentum balance. For the proof of the Principle of Virtual Work and more details, we refer to [329].

**Theorem 3.2.2 (Tensor representation with GENERIC).** *Let the set of representative state variables to be chosen as  $\mathbf{z} = [\rho, c, \mathbf{P}, u]^T \in \mathcal{Z}^{4z}(D)$ ,  $D \subset \mathbb{R}^3$ , then the above Allen-Cahn/Cahn-Hilliard coupled with Navier-Stokes system (3.2.138), satisfies GENERIC and can be compactly presented with the help of six different tensors, as follows: The Poisson and friction tensors for the bulk part (assumption for isolated system) with the help of the related degeneracy requirements are shown to be:*

$$\mathbb{L}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} 0 & 0 & \rho(\mathbf{r}')\partial_{\mathbf{r}'}\delta & 0 \\ 0 & 0 & -c(\mathbf{r}')\partial_{\mathbf{r}'}\delta & 0 \\ -\partial_{\mathbf{r}}\delta\rho(\mathbf{r}) & -c(\mathbf{r})\partial_{\mathbf{r}}\delta & \mathbf{P}(\mathbf{r}')\partial_{\mathbf{r}}\delta - \partial_{\mathbf{r}}\delta\mathbf{P}(\mathbf{r}) & -\partial_{\mathbf{r}}\delta p(\mathbf{r}') - \partial_{\mathbf{r}}\delta u(\mathbf{r}) \\ 0 & 0 & u(\mathbf{r}')\partial_{\mathbf{r}'}\delta + p(\mathbf{r})\partial_{\mathbf{r}'}\delta & 0 \end{pmatrix}, \quad (3.2.141)$$

in which we remind that we set  $\delta := \delta(\mathbf{r} - \mathbf{r}')$  for simplicity and similarly

$$\mathbb{M}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \mathbb{M}^{cc}(\mathbf{r}, \mathbf{r}') & 0 & \mathbb{M}^{cu}(\mathbf{r}, \mathbf{r}') \\ 0 & 0 & \mathbb{M}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') & \mathbb{M}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') \\ 0 & \mathbb{M}^{uc}(\mathbf{r}, \mathbf{r}') & \mathbb{M}^{u\mathbf{P}}(\mathbf{r}, \mathbf{r}') & \mathbb{M}^{uu}(\mathbf{r}, \mathbf{r}') \end{pmatrix}, \quad (3.2.142)$$

where the related elements are given by

$$\mathbb{M}^{cc}(\mathbf{r}, \mathbf{r}') = \Theta(\mathbf{r}')\delta(\mathbf{r}' - \mathbf{r}) - m\partial_{\mathbf{r}}\delta\Theta(\mathbf{r}')\partial_{\mathbf{r}'} \text{ and } \mathbb{M}^{cu}(\mathbf{r}, \mathbf{r}') = -m\lambda^2\partial_{\mathbf{r}}\delta\Theta(\mathbf{r}')\partial_{\mathbf{r}'} \left( \partial_{\mathbf{r}'}^2 c(\mathbf{r}') - m^{-1}c(\mathbf{r}') \right). \quad (3.2.143)$$

Furthermore  $\mathbb{M}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') = (\partial_{\mathbf{r}'}\partial_{\mathbf{r}} + \mathbf{1}\partial_{\mathbf{r}'} \cdot \partial_{\mathbf{r}})\eta\Theta(\mathbf{r}')\delta$ ,  $\mathbb{M}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') = \eta\partial_{\mathbf{r}}\delta \cdot \Theta(\mathbf{r}')\dot{\gamma}(\mathbf{r}')$  and

$$\begin{aligned} \mathbb{M}^{uu}(\mathbf{r}, \mathbf{r}') &= -m\lambda^2\partial_{\mathbf{r}}^2 c(\mathbf{r})\partial_{\mathbf{r}}\delta\Theta(\mathbf{r}')\partial_{\mathbf{r}'}\Delta c(\mathbf{r}') + \lambda^2 c(\mathbf{r})\partial_{\mathbf{r}}\delta\Theta(\mathbf{r}')\partial_{\mathbf{r}'}\Delta c(\mathbf{r}') \\ &\quad + \eta\Theta(\mathbf{r}')\dot{\gamma}(\mathbf{r}) \cdot \partial_{\mathbf{r}'}\delta\mathbf{v}(\mathbf{r}') - \partial_{\mathbf{r}}\delta(k^q\Theta^2)(\mathbf{r}')\partial_{\mathbf{r}'} \end{aligned} \quad (3.2.144)$$

Finally, the last two non zero elements are expressed in the following forms:

$$\mathbb{M}^{u\mathbf{P}}(\mathbf{r}, \mathbf{r}') = \eta\Theta(\mathbf{r}')\dot{\gamma}(\mathbf{r}) \cdot \partial_{\mathbf{r}'}\delta \text{ and } \mathbb{M}^{uc}(\mathbf{r}, \mathbf{r}') = -m\lambda^2\partial_{\mathbf{r}}^2 c(\mathbf{r})\partial_{\mathbf{r}}\delta\Theta(\mathbf{r}')\partial_{\mathbf{r}'} + \lambda^2 c(\mathbf{r})\partial_{\mathbf{r}}\delta\Theta(\mathbf{r}')\partial_{\mathbf{r}'} \quad (3.2.145)$$

In addition, for the related boundary contributions we obtain the Poisson part on the boundary, i.e.,

$$\mathbb{L}_{\partial}(\mathbf{r}) = \begin{pmatrix} 0 & 0 & \rho(\mathbf{r})\mathbf{n} & 0 \\ 0 & 0 & 0 & 0 \\ 0 & c(\mathbf{r})\mathbf{n} & \mathbf{P}(\mathbf{r}) \cdot \mathbf{n} & 0 \\ 0 & 0 & (p(\mathbf{r}) + u(\mathbf{r}))\mathbf{n} & 0 \end{pmatrix} \text{ and } \mathbb{L}_{\partial T}(\mathbf{r}) = \begin{pmatrix} 0 & \mathbf{n}c(\mathbf{r}) & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \mathbf{n}\rho(\mathbf{r}) & 0 & \mathbf{n} \cdot \mathbf{P}(\mathbf{r}) & \mathbf{n}(p(\mathbf{r}) + u(\mathbf{r})) \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

In the same way for the friction tensor we can deduce that,

$$\mathbb{M}_{\partial}(\mathbf{r}) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \eta\Theta(\mathbf{r})((\mathbf{n}\partial_{\mathbf{r}})^T + \mathbf{n} \cdot \partial_{\mathbf{r}}\mathbf{1}) + \mathbf{n}\rho g(\mathbf{r}) & -(\eta\Theta(\mathbf{r})\dot{\gamma}(\mathbf{r}) + \rho g\mathbf{v}(\mathbf{r})) \cdot \mathbf{n} \\ 0 & 0 & 0 & k^q\Theta^2(\mathbf{r})\mathbf{n} \cdot \partial_{\mathbf{r}} \end{pmatrix},$$

$$\mathbb{M}_{\partial^T}(\mathbf{r}) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \eta\Theta(\mathbf{r})((\mathbf{n}\partial_{\mathbf{r}})^T + \mathbf{n} \cdot \partial_{\mathbf{r}}\mathbf{1}) + \mathbf{n}\rho g(\mathbf{r}) & 0 \\ 0 & 0 & -\mathbf{n} \cdot (\eta\Theta(\mathbf{r})\dot{\gamma}(\mathbf{r}) + \rho g\mathbf{v}(\mathbf{r})) & \mathbf{n} \cdot \partial_{\mathbf{r}}(k^q\Theta^2(\mathbf{r})) \end{pmatrix}. \quad (3.2.146)$$

*Proof.* Following the previous example for the classical hydrodynamic equations via the GENERIC formalism principles, one can identify the total energy and entropy functionals as follows

$$\mathcal{E}(\mathbf{z}) := \int_D e(\rho, \mathbf{P}, c) d\mathbf{r} = \int_D \left( \frac{\mathbf{P}^2}{2\rho} + w(c) \right) d\mathbf{r} \text{ and } \mathcal{S}(\mathbf{z}) := \int_D s(u, c) d\mathbf{r}. \quad (3.2.147)$$

The formulation is slightly different if one introduces the internal energy density variable and hence in view of a recent work by A. Onuki [330], we can express the total energy and entropy in the following forms:

$$\mathcal{E}(\mathbf{z}) := \int_D e(\rho, \mathbf{P}, u, c) d\mathbf{r} := \int_D \left( \frac{\mathbf{P}^2}{2\rho} + u + \frac{\lambda^2 |\nabla c|^2}{2} \right) d\mathbf{r} \quad (3.2.148)$$

and

$$\mathcal{S}(\mathbf{z}) := \int_D s(u, c) d\mathbf{r} := \int_D \left( s_1(u, c) - \frac{\lambda^2 |\nabla c|^2}{2} \right) d\mathbf{r}, \quad (3.2.149)$$

where we assumed for simplicity (since the exact form is not required in the derivation by GENERIC), that the entropy density is just a function  $s(u, c)$ . As a result and in light of the definition  $\mathbf{P} := \rho\mathbf{v}$ , the functional derivatives with respect to the set of state functions  $\mathbf{z} := [\rho, c, \mathbf{P}, u]^T$  imply

$$\partial_{\mathbf{z}} s = (\partial_{\rho} s, \partial_c s, 0, \Theta^{-1})^T, \quad \partial_{\mathbf{z}} e = \left( -\frac{\mathbf{v}^2}{2}, -\lambda^2 \Delta c, \mathbf{v}, 1 \right)^T. \quad (3.2.150)$$

Based on the formulation for open systems, we first consider to apply GENERIC to the bulk contribution (as an isolated system) in which we assume no influence of the external forcing  $\rho g \hat{\mathbf{z}}$ . The contribution of the external force will be added at a later stage in the pure boundary evolution accounting for exchange and interaction with the environment, i.e.,

$$\int_{\partial D} \sum_{j=1}^4 (\mathbb{L}_{\partial}^{z_i z_j} + \mathbb{L}_{\partial^T}^{z_i z_j})(\mathbf{r}) \partial_{z_j} e(\mathbf{z}(\mathbf{r})) + (\mathbb{M}_{\partial}^{z_i z_j} - \mathbb{M}_{\partial^T}^{z_i z_j})(\mathbf{r}) \partial_{z_j} s(\mathbf{z}(\mathbf{r})) d^2 r, \quad i, j \in \{1, 2, 3, 4\}, \quad (3.2.151)$$

supplemented with the special degeneracy requirements for  $\mathbb{L}_{\partial}, \mathbb{M}_{\partial}$  (3.2.23). The elements of the Poisson and friction tensors  $\mathbb{L}, \mathbb{M}$  can be evaluated as in the previously discussed

application (see Theorem 3.2.1), based on the general evolution equation

$$\partial_t z_i(\mathbf{r}) = \int_D \sum_{j=1}^4 \mathbb{L}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j(\mathbf{r}')} e(\mathbf{z}) d\mathbf{r}' + \int_D \sum_{j=1}^4 \mathbb{M}^{z_i z_j}(\mathbf{r}, \mathbf{r}') \partial_{z_j(\mathbf{r}')} s(\mathbf{z}) d\mathbf{r}', \quad i, j \in \{1, 2, 3, 4\}, \quad (3.2.152)$$

for each state variable  $z_1 := \rho$ ,  $z_2 := c$ ,  $z_3 := \mathbf{P}$ ,  $z_4 := u$ . Starting from (3.2.152) and in light of the derivatives over the different fields (3.2.150), one obtains for the phase-field balance  $\partial_t c = -(\mathbf{v} \cdot \nabla)c + m\Delta\mu(c) - \mu(c)$  from (3.2.138), that

$$\begin{aligned} & -(\mathbf{v} \cdot \nabla)c - m\Delta(\lambda^2 \Delta c - f'_L(c)) + (\lambda^2 \Delta c - f'_L(c)) \\ & = \int_D -\mathbb{L}^{c\rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}')/2 - \mathbb{L}^{cc}(\mathbf{r}, \mathbf{r}') \lambda^2 \Delta c(\mathbf{r}') + \mathbb{L}^{c\mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') + \mathbb{L}^{cu}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \\ & + \int_D \mathbb{M}^{c\rho}(\mathbf{r}, \mathbf{r}') \partial_\rho s(\mathbf{r}') + \mathbb{M}^{cc}(\mathbf{r}, \mathbf{r}') \partial_c s(\mathbf{r}') + \mathbb{M}^{cu}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') d\mathbf{r}'. \end{aligned} \quad (3.2.153)$$

On the other hand the degeneracy requirements imply for each of the fields  $z_i \in \{\rho, c, \mathbf{P}, u\}$  separately that

$$\begin{aligned} & \int_D \mathbb{L}^{z_i \rho}(\mathbf{r}, \mathbf{r}') \partial_\rho s(\mathbf{r}') + \mathbb{L}^{z_i c}(\mathbf{r}, \mathbf{r}') \partial_c s(\mathbf{r}') + \mathbb{L}^{z_i u}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') d\mathbf{r}' = 0 \\ \text{and } & \int_D -\mathbb{M}^{z_i \rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}')/2 - \mathbb{M}^{z_i c}(\mathbf{r}, \mathbf{r}') \lambda^2 \Delta c(\mathbf{r}') + \mathbb{M}^{z_i \mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') + \mathbb{M}^{z_i u}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 0. \end{aligned} \quad (3.2.154)$$

Therefore, with the help of the Dirac delta identities (3.2.68), from the advective Cahn-Hilliard part of the system using the identification  $f'_L(c) = -\Theta \partial_c s$  and in light of the incompressibility assumption, by matching the first term on the left-hand side of (3.2.153) with the first four terms on the right-hand side, i.e.,

$$-\int_D \mathbf{v}(\mathbf{r}) \partial_r \delta(\mathbf{r} - \mathbf{r}') c(\mathbf{r}') d\mathbf{r} = \int_D -\mathbb{L}^{c\rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}')/2 - \mathbb{L}^{cc}(\mathbf{r}, \mathbf{r}') \lambda^2 \Delta c(\mathbf{r}') + \mathbb{L}^{c\mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') + \mathbb{L}^{cu}(\mathbf{r}, \mathbf{r}') d\mathbf{r}'. \quad (3.2.155)$$

Hence, we can identify the element  $\mathbb{L}^{c\mathbf{P}}(\mathbf{r}, \mathbf{r}')$  which dictates the convection of the configurational variable  $c$  by

$$-\int_D \mathbf{v}(\mathbf{r}) \partial_r \delta(\mathbf{r} - \mathbf{r}') c(\mathbf{r}') d\mathbf{r} = \int_D \mathbb{L}^{c\mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') d\mathbf{r}, \quad (3.2.156)$$

which implies  $\mathbb{L}^{c\mathbf{P}}(\mathbf{r}, \mathbf{r}') = -c(\mathbf{r}') \partial_r \delta(\mathbf{r} - \mathbf{r}')$  due to the incompressibility condition  $\text{div}(\mathbf{v}) = 0$ . Moreover, the above choice of  $\mathbb{L}^{c\mathbf{P}}(\mathbf{r}, \mathbf{r}')$  in (3.2.155), i.e.,  $0 = -\mathbb{L}^{c\rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}')/2 - \mathbb{L}^{cc}(\mathbf{r}, \mathbf{r}') \lambda^2 \Delta c(\mathbf{r}') + \mathbb{L}^{cu}(\mathbf{r}, \mathbf{r}')$  and the degeneracy requirement

$$\int_D \mathbb{L}^{c\rho}(\mathbf{r}, \mathbf{r}') \partial_\rho s(\mathbf{r}') + \mathbb{L}^{cc}(\mathbf{r}, \mathbf{r}') \partial_c s(\mathbf{r}') d\mathbf{r}' = - \int_D \mathbb{L}^{cu}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') d\mathbf{r}', \quad (3.2.157)$$

necessarily implies  $\mathbb{L}^{c\rho}(\mathbf{r}, \mathbf{r}') = \mathbb{L}^{cc}(\mathbf{r}, \mathbf{r}') = \mathbb{L}^{cu}(\mathbf{r}, \mathbf{r}') = 0$ . As result, we obtained the first row of the Poisson tensor:

$$\mathbb{L}^{c\rho}(\mathbf{r}, \mathbf{r}') = \mathbb{L}^{cc}(\mathbf{r}, \mathbf{r}') = \mathbb{L}^{cu}(\mathbf{r}, \mathbf{r}') = 0 \text{ and } \mathbb{L}^{c\mathbf{P}}(\mathbf{r}, \mathbf{r}') = -c(\mathbf{r}') \partial_r \delta. \quad (3.2.158)$$

Here and over the rest of this subsection, we introduce the simplified notation  $\delta := \delta(\mathbf{r} - \mathbf{r}')$ . The irreversible effects which are introduced by the chemical potential, are assumed to be summarised in the friction tensor and hence the elements  $\mathbb{M}^{cc}(\mathbf{r}, \mathbf{r}')$ ,  $\mathbb{M}^{cu}(\mathbf{r}, \mathbf{r}')$  can be

derived by matching the remaining terms, according to the relations:

$$\begin{cases} m\Delta f'_L(c) - f'_L(c) = m \int_D \partial_{\mathbf{r}} \delta \partial_{\mathbf{r}'} f'_L(c(\mathbf{r}')) d\mathbf{r}' - \int_D f'_L(c(\mathbf{r}')) \delta(\mathbf{r}' - \mathbf{r}) d\mathbf{r}' = \int_D \mathbb{M}^{cc}(\mathbf{r}, \mathbf{r}') \partial_{c,s}(\mathbf{r}') d\mathbf{r}', \\ -m\lambda^2 \Delta^2 c + \lambda^2 \Delta c = -m\lambda^2 \int_D \partial_{\mathbf{r}} \delta \partial_{\mathbf{r}'} (\partial_{\mathbf{r}'}^2 c(\mathbf{r}')) d\mathbf{r}' + \lambda^2 \int_D \partial_{\mathbf{r}} \delta \partial_{\mathbf{r}'} c(\mathbf{r}') d\mathbf{r}' = \int_D \mathbb{M}^{cu}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') d\mathbf{r}'. \end{cases} \quad (3.2.159)$$

We next apply the properties of the Dirac delta function these relations are simplified to

$$\mathbb{M}^{cc}(\mathbf{r}, \mathbf{r}') = \Theta(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}) - m \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} \text{ and } \mathbb{M}^{cu}(\mathbf{r}, \mathbf{r}') = -m\lambda^2 \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} (\partial_{\mathbf{r}'}^2 c(\mathbf{r}') - m^{-1} c(\mathbf{r}')). \quad (3.2.160)$$

From the degeneracy requirement for  $\mathbb{M}$  we get  $\mathbb{M}^{c\rho}(\mathbf{r}, \mathbf{r}') = \mathbb{M}^{c\mathbf{P}}(\mathbf{r}, \mathbf{r}') = 0$ . Following the same procedure, and by the consideration of (3.2.115) which implies  $\mu(c) \nabla c = \text{div}(w(c) \mathbb{I} - \lambda^2 (\nabla c \otimes \nabla c))$ , the divergence free momentum balance if the system was isolated, i.e.,

$$\partial_t \mathbf{P} = -(\mathbf{v} \cdot \nabla) \mathbf{P} + \eta \nabla^2 \mathbf{v} - \nabla p + \mu(c) \nabla c, \quad (3.2.161)$$

can be rewritten in terms of (3.2.152), as follows:

$$\begin{aligned} & -(\mathbf{v} \cdot \nabla) \mathbf{P} + \eta \nabla^2 \mathbf{v} - \nabla p + \mu(c) \nabla c \\ &= \int_D -\mathbb{L}^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}') / 2 - \mathbb{L}^{\mathbf{P}c}(\mathbf{r}, \mathbf{r}') \lambda^2 \Delta c(\mathbf{r}') + \mathbb{L}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') \mathbf{v}(\mathbf{r}') + \mathbb{L}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \\ &+ \int_D \mathbb{M}^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') \partial_{\rho s}(\mathbf{r}') + \mathbb{M}^{\mathbf{P}c}(\mathbf{r}, \mathbf{r}') \partial_{c,s}(\mathbf{r}') + \mathbb{M}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') d\mathbf{r}'. \end{aligned} \quad (3.2.162)$$

Consequently by matching terms, one can derive the elements

$$\begin{aligned} \mathbb{L}^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') &= -\partial_{\mathbf{r}} \delta \rho(\mathbf{r}), \quad \mathbb{L}^{\mathbf{P}c}(\mathbf{r}, \mathbf{r}') = -c(\mathbf{r}) \partial_{\mathbf{r}} \delta \text{ and} \\ \mathbb{L}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') &= \mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta - \partial_{\mathbf{r}} \delta \mathbf{P}(\mathbf{r}), \quad \mathbb{L}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') = -\partial_{\mathbf{r}} \delta p(\mathbf{r}') - \partial_{\mathbf{r}} \delta u(\mathbf{r}). \end{aligned} \quad (3.2.163)$$

For the above choice of elements, the following fundamental thermodynamic identity  $w(c(\mathbf{r})) = -p(\mathbf{r}) + c(\mathbf{r}) \partial_c w(c(\mathbf{r}))$ , has been also taken into account, which can be found in any classical book about thermodynamics such as for example [280] and also in [15, 331]. We remind that the quantity  $w(c)$  denotes the Cahn-Hilliard free energy, i.e.,  $w(c) := f_L(c) + \lambda^2 |\nabla c|^2 / 2$ .

The proof of the satisfaction of the Jacoby identity and the Leibniz rule follows exactly the same arguments as in subsection 3.2.3 and therefore we skip this part. Finally, the remaining terms and the degeneracy requirement for the friction tensor provide the elements

$$\mathbb{M}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') = \eta \partial_{\mathbf{r}} \delta \cdot \Theta(\mathbf{r}') \dot{\gamma}(\mathbf{r}'), \quad \mathbb{M}^{\mathbf{P}c}(\mathbf{r}, \mathbf{r}') = \mathbb{M}^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') = 0. \quad (3.2.164)$$

Note that we used the rate of strain tensor  $\dot{\gamma} := \nabla \mathbf{v} + (\nabla \mathbf{v})^T$  in the related elements, which provides the diffusion term  $\Delta \mathbf{v}$  after applying the partial derivative, due to the incompressibility condition  $\text{div}(\mathbf{v}) = 0$ . Moreover, in view of incompressibility we deduce also that  $\text{tr}(\dot{\gamma}) = 2 \text{div}(\mathbf{v}) = 0$ . Using the antisymmetry property of the Poisson tensor we are able to choose the last row of the elements, as follows:  $\mathbb{L}^{uc}(\mathbf{r}, \mathbf{r}') = 0$ ,  $\mathbb{L}^{u\mathbf{P}}(\mathbf{r}, \mathbf{r}') = u(\mathbf{r}') \partial_{\mathbf{r}'} \delta + p(\mathbf{r}) \partial_{\mathbf{r}} \delta$ .

Similarly for the friction tensor we obtain

$$\mathbb{M}^{u\mathbf{P}}(\mathbf{r}, \mathbf{r}') = \eta \Theta(\mathbf{r}) \dot{\gamma}(\mathbf{r}) \cdot \partial_{\mathbf{r}'} \delta \text{ and } \mathbb{M}^{uc}(\mathbf{r}, \mathbf{r}') = -m\lambda^2 \partial_{\mathbf{r}'}^2 c(\mathbf{r}) \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} + \lambda^2 c(\mathbf{r}) \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} \quad (3.2.165)$$

By the degeneracy requirement for the friction tensor in combination with the obtained forms for the elements  $\mathbb{M}^{u\rho}, \mathbb{M}^{\mathbf{P}c}, \mathbb{M}^{\mathbf{P}u}$ , we can deduce that,

$$\mathbb{M}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') = (\partial_{\mathbf{r}'} \partial_{\mathbf{r}} + \mathbf{1} \partial_{\mathbf{r}'} \cdot \partial_{\mathbf{r}}) \eta \Theta(\mathbf{r}') \delta. \quad (3.2.166)$$

Symmetry reasons allow us to define the coupling of elements  $\mathbb{L}^{\rho z_i}, \mathbb{M}^{\rho z_i}$  and  $\mathbb{L}^{u z_i}, \mathbb{M}^{u z_i}$  for  $z_i \in \{\rho, c, \mathbf{P}, u\}$ , which will later lead to the formulation of the internal energy balance. Hence we obtain  $\mathbb{L}^{\rho\mathbf{P}}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') \partial_{\mathbf{r}'} \delta$ ,  $\mathbb{L}^{\rho c}(\mathbf{r}, \mathbf{r}') = 0$ , which together with the degeneracy requirement for  $\mathbb{L}$  provide the following relationships, under the assumption  $\text{div}(\mathbf{v}) = 0$ ,

$$\begin{aligned} -(\mathbf{v} \cdot \nabla) \rho &= \int_D -\mathbb{L}^{\rho\rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}') / 2 + \rho(\mathbf{r}') \partial_{\mathbf{r}'} \delta \mathbf{v}(\mathbf{r}') + \mathbb{L}^{\rho u}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \\ &+ \int_D \mathbb{M}^{\rho\rho}(\mathbf{r}, \mathbf{r}') \partial_{\rho s}(\mathbf{r}') + \mathbb{M}^{\rho\mathbf{P}}(\mathbf{r}, \mathbf{r}') \partial_{c s}(\mathbf{r}') + \mathbb{M}^{\rho u}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') d\mathbf{r}'. \end{aligned} \quad (3.2.167)$$

Moreover, the degeneracy requirements imply

$$\int_D \mathbb{L}^{\rho\rho}(\mathbf{r}, \mathbf{r}') \partial_{\rho s}(\mathbf{r}') + \mathbb{L}^{\rho u}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') d\mathbf{r}' = 0 \text{ and } \int_D -\mathbb{M}^{\rho\rho}(\mathbf{r}, \mathbf{r}') \mathbf{v}^2(\mathbf{r}') / 2 + \mathbb{M}^{\rho u}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 0, \quad (3.2.168)$$

from which we obtain  $\mathbb{L}^{\rho\rho}(\mathbf{r}) = \mathbb{L}^{\rho u}(\mathbf{r}, \mathbf{r}') = \mathbb{L}^{u\rho}(\mathbf{r}, \mathbf{r}') = 0$  and also  $\mathbb{M}^{\rho\rho}(\mathbf{r}, \mathbf{r}') = \mathbb{M}^{\rho c}(\mathbf{r}, \mathbf{r}') = \mathbb{M}^{\rho u}(\mathbf{r}, \mathbf{r}') = \mathbb{M}^{u\rho}(\mathbf{r}, \mathbf{r}') = 0$ . In addition, the degeneracy requirements related to the internal energy balance implies the following constraint  $\int_D \mathbb{L}^{uu}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') d\mathbf{r}' = 0$  and also,

$$\int_D \left( m\lambda^2 \partial_{\mathbf{r}'}^2 c(\mathbf{r}) \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} \lambda^2 \Delta c(\mathbf{r}') + \lambda^2 c(\mathbf{r}) \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} - \eta \Theta(\mathbf{r}) \dot{\gamma}(\mathbf{r}) \cdot \partial_{\mathbf{r}'} \delta \mathbf{v}(\mathbf{r}') + \mathbb{M}^{uu}(\mathbf{r}, \mathbf{r}') \right) d\mathbf{r}' = 0, \quad (3.2.169)$$

which finally gives

$$\begin{aligned} \mathbb{M}^{uu}(\mathbf{r}, \mathbf{r}') &= -m\lambda^2 \partial_{\mathbf{r}'}^2 c(\mathbf{r}) \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} \Delta c(\mathbf{r}') + \lambda^2 c(\mathbf{r}) \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} \Delta c(\mathbf{r}') \\ &+ \eta \Theta(\mathbf{r}) \dot{\gamma}(\mathbf{r}) \cdot \partial_{\mathbf{r}'} \delta \mathbf{v}(\mathbf{r}') - \partial_{\mathbf{r}} \delta (k^q \Theta^2)(\mathbf{r}') \partial_{\mathbf{r}'} \end{aligned} \quad (3.2.170)$$

and  $\mathbb{L}^{uu}(\mathbf{r}, \mathbf{r}') = 0$ , where the last term enters by the entropy production principle as stated in the previous example for the classical Navier-Stokes and we let  $k^q$  to represent the thermal conductivity. As a result, we are able to formulate the internal energy balance as follows:

$$\begin{aligned} \partial_t u &= \int_D (u(\mathbf{r}') \partial_{\mathbf{r}'} \delta + p(\mathbf{r}) \partial_{\mathbf{r}'} \delta) \mathbf{v}(\mathbf{r}') d\mathbf{r} - m\lambda^2 \int_D \partial_{\mathbf{r}'}^2 c(\mathbf{r}) \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} \partial_{c s}(\mathbf{r}') d\mathbf{r}' \\ &- \int_D \left( \lambda^2 c(\mathbf{r}) \partial_{\mathbf{r}} \delta \Theta(\mathbf{r}') \partial_{\mathbf{r}'} \partial_{c s}(\mathbf{r}') - \mathbb{M}^{uu}(\mathbf{r}, \mathbf{r}') \Theta^{-1}(\mathbf{r}') \right) d\mathbf{r}' \\ &= \mathbf{v} \cdot \nabla u - m\lambda^2 \Delta c \text{div}(\Theta \partial_{\mathbf{r}} \partial_{c s}) - \lambda^2 c(\mathbf{r}) \text{div}(\Theta \partial_{\mathbf{r}} \partial_{c s}) - m\lambda^2 \Delta c \partial_{\mathbf{r}} \Delta c - \eta \dot{\gamma} : (\nabla \mathbf{v})^T + \text{div}(k^q \nabla \Theta), \end{aligned} \quad (3.2.171)$$

which holds due to the incompressibility condition  $\text{div}(\mathbf{v}) = 0$ . The properties of antisymmetry and symmetry respectively, are satisfied.

Let us consider now the full case where the system interacts with its surroundings, in which the boundary contribution to the evolution is given by (3.2.151). We can then obtain the elements of  $\mathbb{L}^\partial$  and  $\mathbb{M}^\partial$ , based on the already deduced elements of  $\mathbb{L}, \mathbb{M}$ , the related degeneracy requirements and Green's first identity. The boundary degeneracy requirements imply for each field  $z_i \in \{\rho, c, \mathbf{P}, u\}$ :

$$\int_{\partial D} \mathbb{L}_{\partial}^{z_i \rho}(\mathbf{r}) \partial_{\rho} s(\mathbf{r}) + \mathbb{L}_{\partial}^{z_i c}(\mathbf{r}) \partial_c s(\mathbf{r}) + \mathbb{L}_{\partial}^{z_i u}(\mathbf{r}) \Theta^{-1}(\mathbf{r}) d^2 r = 0,$$

$$\text{and } \int_{\partial D} -\mathbb{M}_{\partial}^{z_i \rho}(\mathbf{r}) \mathbf{v}^2(\mathbf{r})/2 - \mathbb{M}_{\partial}^{z_i c}(\mathbf{r}) \lambda \Delta c(\mathbf{r}) + \mathbb{M}_{\partial}^{z_i \mathbf{P}}(\mathbf{r}) \mathbf{v}(\mathbf{r}) + \mathbb{M}_{\partial}^{z_i u}(\mathbf{r}) d^2 r = 0 \quad (3.2.172)$$

and with the help of the elements of  $\mathbb{L}$  that are previously derived, we find that,  $\mathbb{L}_{\partial}^{\rho c}(\mathbf{r}) = \mathbb{L}_{\partial r}^{\rho c}(\mathbf{r}) = \mathbb{L}_{\partial r}^{cc}(\mathbf{r}) = \mathbb{L}_{\partial}^{cu}(\mathbf{r}) = \mathbb{L}_{\partial r}^{uc}(\mathbf{r}) = 0$  and  $\mathbb{L}_{\partial}^{c\rho}(\mathbf{r}) = c(\mathbf{r})\mathbf{n}$ ,  $\mathbb{L}_{\partial r}^{\rho c}(\mathbf{r}) = \mathbf{n}c(\mathbf{r})$ , where  $\mathbf{n}$  is the outwardly directed unit normal vector on  $\partial D$ . Similarly the related elements of  $\mathbb{L}_{\partial}$  associated with the momentum balance can be chosen as follows:

$$\begin{cases} \mathbb{L}_{\partial}^{\mathbf{P}\rho}(\mathbf{r}) = 0, \mathbb{L}_{\partial r}^{\mathbf{P}\rho}(\mathbf{r}) = \rho(\mathbf{r})\mathbf{n} \text{ and } \mathbb{L}_{\partial}^{\mathbf{P}\mathbf{P}}(\mathbf{r}) = \mathbf{P}(\mathbf{r}) \cdot \mathbf{n}, \mathbb{L}_{\partial r}^{\mathbf{P}\mathbf{P}}(\mathbf{r}) = \mathbf{n} \cdot \mathbf{P}(\mathbf{r}), \\ \mathbb{L}_{\partial}^{u\mathbf{P}}(\mathbf{r}) = (p(\mathbf{r}) + u(\mathbf{r}))\mathbf{n} \text{ and } \mathbb{L}_{\partial r}^{u\mathbf{P}}(\mathbf{r}) = \mathbf{n}(p(\mathbf{r}) + u(\mathbf{r})). \end{cases} \quad (3.2.173)$$

The influence of the external forcing will be added in the friction boundary tensors, to one of the elements associated with the momentum balance according to the related degeneracy requirements, namely

$$\begin{cases} \mathbb{M}_{\partial}^{\mathbf{P}u}(\mathbf{r}) = -(\eta\Theta(\mathbf{r})\dot{\gamma}(\mathbf{r}) + \rho g\mathbf{v}(\mathbf{r})) \cdot \mathbf{n}, \mathbb{M}_{\partial r}^{\mathbf{P}\mathbf{P}}(\mathbf{r}) = -\mathbf{n} \cdot (\eta\Theta(\mathbf{r})\dot{\gamma}(\mathbf{r}) + \rho g\mathbf{v}(\mathbf{r})) \text{ and } \mathbb{M}_{\partial}^{\mathbf{P}c} = \mathbb{M}_{\partial r}^{\mathbf{P}c}(\mathbf{r}) = 0, \\ \mathbb{M}_{\partial}^{\mathbf{P}\rho}(\mathbf{r}) = \mathbb{M}_{\partial r}^{\mathbf{P}\rho}(\mathbf{r}) = 0 \text{ and } \mathbb{M}_{\partial}^{\mathbf{P}\mathbf{P}}(\mathbf{r}) = \mathbb{M}_{\partial r}^{\mathbf{P}\mathbf{P}}(\mathbf{r}) = \eta\Theta(\mathbf{r})((\mathbf{n}\partial_{\mathbf{r}})^T + \mathbf{n} \cdot \partial_{\mathbf{r}}\mathbf{1}) + \mathbf{n}\rho g(\mathbf{r}). \end{cases} \quad (3.2.174)$$

□

**Remark 3.23.** We can deduce for the bulk contribution of the Poisson bracket  $\{\mathcal{A}_1, \mathcal{A}_2\}_{bulk}$  for all  $\mathcal{A}_1, \mathcal{A}_2 \in C^\infty(\mathcal{Z}^{4z})$  in terms of only one space argument  $\mathbf{r}$  that

$$\begin{aligned} \{\mathcal{A}_1, \mathcal{A}_2\}_{bulk} := & \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} d\mathbf{r} - \int_D \rho(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r})} d\mathbf{r} \\ & + \int_D \mathbf{P}(\mathbf{r}) \cdot \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} d\mathbf{r} - \int_D \mathbf{P}(\mathbf{r}) \cdot \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta \rho(\mathbf{r})} d\mathbf{r} \\ & + \int_D u(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta u(\mathbf{r})} d\mathbf{r} - \int_D u(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r})} d\mathbf{r} \\ & + \int_D p(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta u(\mathbf{r})} d\mathbf{r} - \int_D p(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r})} d\mathbf{r} \\ & + \int_D c(\mathbf{r}) \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_1}{\delta c(\mathbf{r})} d\mathbf{r} - \int_D c(\mathbf{r}) \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \nabla \right) \frac{\delta \mathcal{A}_2}{\delta c(\mathbf{r})} d\mathbf{r}. \end{aligned} \quad (3.2.175)$$

In the same way, the bulk part of the dissipative bracket reads

$$\begin{aligned}
 & [\mathcal{A}_1, \mathcal{A}_2]_{bulk} \\
 & := \int_D \eta \Theta(\mathbf{r}) \left( \nabla \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma}(\mathbf{r}) \frac{\delta \mathcal{A}_1}{\delta u(\mathbf{r})} \right) : \left( \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} + \left[ \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right]^T - \dot{\gamma}(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r})} \right) d\mathbf{r} \\
 & + \int_D \bar{k} \Theta(\mathbf{r}) \operatorname{div} \left( \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \right) \operatorname{div} \left( \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right) d\mathbf{r} + \int_D k^q \Theta^2(\mathbf{r}) \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_1}{\delta u(\mathbf{r})} \right) \cdot \nabla \left( \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r})} \right) d\mathbf{r} \\
 & + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta c(\mathbf{r})} \mathbb{M}^{cc}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta c(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta c(\mathbf{r})} \mathbb{M}^{cu}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\
 & + \int_{D \times D} \frac{\delta \mathcal{A}_1}{\delta u(\mathbf{r})} \mathbb{M}^{uu}(\mathbf{r}, \mathbf{r}') \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r}')} d\mathbf{r} d\mathbf{r}'. \tag{3.2.176}
 \end{aligned}$$

Moreover, the boundary contributions to the brackets analogously read

$$\begin{aligned}
 \{\mathcal{A}_1, \mathcal{A}_2\}_{boundary} & := \int_{\partial D} \left( \frac{\delta \mathcal{A}_1}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) + \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \mathbf{P}(\mathbf{r}) + \frac{\delta \mathcal{A}_1}{\delta u(\mathbf{r})} [u(\mathbf{r}) + p(\mathbf{r})] \right) \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \mathbf{n} d^2 r \\
 & + \int_{\partial D} \frac{\delta \mathcal{A}_1}{\delta c(\mathbf{r})} c(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta c(\mathbf{r})} \cdot \mathbf{n} d^2 r. \tag{3.2.177}
 \end{aligned}$$

Similarly for the dissipative boundary contribution bracket we deduce

$$\begin{aligned}
 [\mathcal{A}_1, \mathcal{A}_2]_{boundary} & := \int_{\partial D} \eta \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \left( \left( \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right)^T + \nabla \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \right) \cdot \mathbf{n} d^2 r \\
 & + \int_{\partial D} \eta \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot (\rho g)(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta \mathbf{P}(\mathbf{r})} \cdot \mathbf{n} d^2 r + \int_{\partial D} \frac{\delta \mathcal{A}_1}{\delta u(\mathbf{r})} k^q \Theta^2(\mathbf{r}) \left( \nabla \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r})} \right) \cdot \mathbf{n} d^2 r \\
 & - \int_{\partial D} \eta \Theta(\mathbf{r}) \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot \dot{\gamma}(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r})} \cdot \mathbf{n} d^2 r + \int_{\partial D} \frac{\delta \mathcal{A}_1}{\delta \mathbf{P}(\mathbf{r})} \cdot (\rho g \mathbf{v})(\mathbf{r}) \frac{\delta \mathcal{A}_2}{\delta u(\mathbf{r})} \cdot \mathbf{n} d^2 r. \tag{3.2.178}
 \end{aligned}$$

**Remark 3.24.** The derived form for the Poisson tensor (3.2.141) for the system (3.2.138), is exactly the same as the one derived in [43] for the model  $H$  (3.2.111). The difference appears in the frictions tensors and more precisely in the forms of the elements  $\mathbb{M}^{cu}$  and  $\mathbb{M}^{uc}$  because of the presence of the extra chemical potential term as well as the extra four boundary tensors, arising due to the influence of the external forcing.

### 3.2.5 The equations of hydrodynamics and coarse-graining

The specific example is an overview of the derivation of the macroscopic GENERIC hydrodynamic equations by coarse graining in terms of bridging time and length scales between levels of description, based on the articles by M. Hütter, J. Brader and A. Trevoort [42, 300]. We more precisely consider the case of non-isothermal flow of a compressible single component fluid. The non-local correlation effects, arising from a spherical symmetric, long range interaction potential, i.e., a potential of the simple form  $V(\mathbf{r}_{kl}) = C_V / |\mathbf{r}_{kl}|$ , where  $C_V$  is a constant expressed as the product of particle quantities such masses or alternatively charges. In addition  $|\mathbf{r}_{kl}| = |\mathbf{r}_k - \mathbf{r}_l|$  denotes the length of the particle distance vectors, where  $\mathbf{r}_{kl}$  is directed from particle  $l$  towards particle  $k$ . Non-local effects occur due to the phenomenon of entanglement, whereby particles that interact with each other become correlated for all times, or dependent on each others states and properties, in order to gradually behave as a single substance. Therefore, non locality literally indicates the ability of particles to instantly know about each other state, even there is a large distance between them.

In order to describe the flow from a continuum scale point of view, one needs to take into account that the thermodynamics and motion of any fluid is described by the classical hydrodynamic equations. Consequently, one needs to consider the velocity field  $\mathbf{v}$  as a first variable, but in general is not convenient to use it as a dynamic variable since, it is not the density of a conserved quantity and it may lead to a much more complicated expression for the Poisson tensor  $\mathbb{L}$ . Furthermore, since we deal with a compressible fluid one must take into account the changes in the mass density  $\rho$  and due to the fact that we are examining an non isothermal process, it is necessary to involve in the procedure a state variable such as the internal energy density  $u$ ,

**Assumption 3.1 (Microscopic dynamical functions).** *Under the above considerations, the best choice of the state variables defined for all times, in this case is  $\mathbf{z} = [\rho, \mathbf{P}, u]^T \in \mathcal{Z}^{3z}(D)$ ,  $D \subset \mathbb{R}^3$ . Furthermore the microscopic dynamical functions  $\Pi_{z_i}$  of  $\mathbf{P}, \rho, u$  in terms of  $r_k$  and  $\mathbf{p}_k$ , are given as follows:*

$$\left\{ \begin{array}{l} \Pi_\rho(\mathbf{x}, \mathbf{r}) = \sum_{k=1}^N m_k \delta(\mathbf{r} - \mathbf{r}_k), \quad \Pi_{\mathbf{P}}(\mathbf{x}, \mathbf{r}) = \sum_{i=k}^N \mathbf{p}_k \delta(\mathbf{r} - \mathbf{r}_k) \text{ and} \\ \Pi_u(\mathbf{x}, \mathbf{r}) = \sum_{k=1}^N \left( \frac{m_k}{2} \bar{\mathbf{p}}_k^2 + \frac{1}{2} \sum_l V(\mathbf{r}_{kl}) \right) \delta(\mathbf{r} - \mathbf{r}_k), \text{ where } \mathbf{r}_{kl} = \mathbf{r}_k - \mathbf{r}_l, \end{array} \right. \quad (3.2.179)$$

where the summation runs over all the particles and we defined

$$\bar{\mathbf{p}}_k(\mathbf{r}) = \mathbf{p}_k / m_k - \mathbf{v}(\mathbf{r}), \quad (3.2.180)$$

as the peculiar momenta, i.e., the momenta with respect to the macroscopic velocity field  $\mathbf{v}$ , which leads to non-vanishing internal energy, even in the case of an ideal gas ( $V(\mathbf{r}_{kl}) = 0$ ).

**Lemma 3.6 (Total energy and entropy).** *In light of the Assumption 3.1 and the ensemble average of the microscopic dynamical functions, i.e.,  $z_i := \langle \Pi_{z_i}(\mathbf{x}, \mathbf{r}) \rangle_{\mathbf{z}}$ , the total energy of the system can be found to be of the form*

$$\mathcal{E}(\mathbf{z}) := \int_D e(\mathbf{r}) d\mathbf{r} = \int_D \left( \mathbf{P}^2(\mathbf{r}) / 2\rho(\mathbf{r}) + u(\mathbf{r}) \right) d\mathbf{r}, \quad D \subseteq \mathbb{R}^3 \quad (3.2.181)$$

by averaging over the macrostate  $\mathbf{z}$ , the corresponding microscopic Hamiltonian defined by

$$\mathcal{H} := \int_D \sum_{l=1}^N \left( \frac{m_l (\bar{\mathbf{p}}_l(\mathbf{r}) + \mathbf{v}(\mathbf{r}))^2}{2} + \frac{1}{2} \sum_{l \neq k=1}^N V(\mathbf{r}_{kl}) \right) \delta(\mathbf{r} - \mathbf{r}_l) d\mathbf{r}, \quad (3.2.182)$$

in terms of the peculiar momenta given in (3.2.180). Moreover, we define the total entropy functional of the system by

$$\mathcal{S}(\mathbf{r}) = \int_D s(\rho(\mathbf{r}), u(\mathbf{r})) d\mathbf{r}, \quad D \subseteq \mathbb{R}^3. \quad (3.2.183)$$

*Proof.* Since the total energy can be defined as an ensemble average and the microscopic Hamiltonian (3.2.182), we obtain



$$\begin{aligned}
 \mathcal{E}(\mathbf{z}) := \langle \mathcal{H} \rangle_{\mathbf{z}} &:= \int_D \left\langle \sum_{l=1}^N \left( \frac{m_l (\tilde{\mathbf{p}}_l(\mathbf{r}) + \mathbf{v}(\mathbf{r}))^2}{2} + \frac{1}{2} \sum_{l \neq k=1}^N V(\mathbf{r}_{kl}) \right) \delta(\mathbf{r} - \mathbf{r}_l) \right\rangle_{\mathbf{z}} d\mathbf{r} \\
 &\stackrel{(3.2.180)}{=} \int_D \left\langle \sum_{l=1}^N \left( m_l (\mathbf{p}_l/m_l - \mathbf{v}(\mathbf{r})) \cdot \mathbf{v}(\mathbf{r}) + \frac{m_l \mathbf{v}^2(\mathbf{r})}{2} + \left[ \frac{m_l}{2} \tilde{\mathbf{p}}_l^2(\mathbf{r}) + \frac{1}{2} \sum_{l \neq k=1}^N V(\mathbf{r}_{kl}) \right] \right) \delta(\mathbf{r} - \mathbf{r}_l) \right\rangle_{\mathbf{z}} d\mathbf{r} \\
 &= \int_D \left\langle \sum_{l=1}^N \mathbf{p}_l \delta(\mathbf{r} - \mathbf{r}_l) \right\rangle_{\mathbf{z}} \mathbf{v}(\mathbf{r}) d\mathbf{r} - \int_D \left\langle \sum_{l=1}^N m_l \delta(\mathbf{r} - \mathbf{r}_l) \right\rangle_{\mathbf{z}} \frac{\mathbf{v}^2(\mathbf{r})}{2} d\mathbf{r} \\
 &\quad + \int_D \left\langle \sum_{l=1}^N \left[ \frac{m_l}{2} \tilde{\mathbf{p}}_l^2(\mathbf{r}) + \frac{1}{2} \sum_{l \neq k=1}^N V(\mathbf{r}_{kl}) \right] \delta(\mathbf{r} - \mathbf{r}_l) \right\rangle_{\mathbf{z}} d\mathbf{r} \\
 &=: \int_D \langle \Pi_{\mathbf{P}}(\mathbf{x}, \mathbf{r}) \rangle_{\mathbf{z}} \mathbf{v}(\mathbf{r}) d\mathbf{r} - \int_D \langle \Pi_{\rho}(\mathbf{x}, \mathbf{r}) \rangle_{\mathbf{z}} \frac{\mathbf{v}^2(\mathbf{r})}{2} d\mathbf{r} + \int_D \langle \Pi_u(\mathbf{x}, \mathbf{r}) \rangle_{\mathbf{z}} d\mathbf{r} \\
 &= \int_D \left( (\mathbf{P} \otimes \mathbf{v})(\mathbf{r}) - \rho(\mathbf{r}) \frac{\mathbf{v}^2(\mathbf{r})}{2} + u(\mathbf{r}) \right) d\mathbf{r} \\
 &= \int_D \left( \mathbf{P}^2(\mathbf{r})/2\rho(\mathbf{r}) + u(\mathbf{r}) \right) d\mathbf{r}, \text{ since } \mathbf{P}(\mathbf{r}) := (\rho\mathbf{v})(\mathbf{r}) \\
 &=: \int_D e(\mathbf{r}) d\mathbf{r}, \tag{3.2.184}
 \end{aligned}$$

due to the definitions (3.2.179).  $\square$

In order to obtain the time evolution equations, the next step is to evaluate the functional derivatives  $\partial_{\mathbf{z}e}$  and  $\partial_{\mathbf{z}s}$ . It is clear that  $\partial_{\mathbf{z}e}$  is a 3x1 column vector with components the partial derivatives with respect to each state variable  $\rho, \mathbf{P}, u$  and in the same way  $\partial_{\mathbf{z}s}$  is again a 3x1 column vector with components the partial derivatives with respect to each state variable. Thus, we deduce

$$\begin{cases} \partial_{\mathbf{P}e} = \frac{\partial(\mathbf{P}^2(\mathbf{r})/2\rho(\mathbf{r}))}{\partial \mathbf{P}(\mathbf{r})} = \frac{\mathbf{P}(\mathbf{r})}{\rho(\mathbf{r})} = \mathbf{v}(\mathbf{r}), \\ \partial_{\rho e} = \frac{\partial(\mathbf{P}^2(\mathbf{r})/2\rho(\mathbf{r}))}{\partial \rho(\mathbf{r})} = \frac{-\mathbf{P}^2(\mathbf{r})}{2\rho^2(\mathbf{r})} = \frac{-\mathbf{v}^2(\mathbf{r})}{2}, \\ \partial_{ue} = \frac{\partial u(\mathbf{r})}{\partial u(\mathbf{r})} = 1. \end{cases} \tag{3.2.185}$$

As a result, we deduce  $\partial_{\mathbf{z}e} = (-\mathbf{v}^2(\mathbf{r})/2, \mathbf{v}(\mathbf{r}), 1)^T$  and in a similar way, since the entropy density is only a functional of  $u, \rho$ , one obtains  $\partial_{\mathbf{z}s} = (\partial_{\rho}s, 0, \partial_u s)^T$ . Using the basic identities involving the Dirac delta functions (3.2.68), the elements of the Poisson tensor can be evaluated by the formulas (3.2.25) and (3.2.27), applied to the expressions (3.2.179). Following the work by Irving and Kirkwood [332], one can derive the element  $\mathbb{L}^{\rho c}$  as follows:

$$\begin{aligned}
 \mathbb{L}^{\rho \mathbf{P}}(\mathbf{r}, \mathbf{r}') &= \langle \{ \Pi_{\rho}, \Pi_{\mathbf{P}} \} \rangle_{\mathbf{z}} = \sum_{k=1}^N \left\langle \frac{\partial \Pi_{\rho}(\mathbf{x}, \mathbf{r})}{\partial \mathbf{r}_k} \cdot \frac{\partial \Pi_{\mathbf{P}}(\mathbf{x}, \mathbf{r}')}{\partial p_k} - \frac{\partial \Pi_{\rho}(\mathbf{x}, \mathbf{r})}{\partial p_k} \cdot \frac{\partial \Pi_{\mathbf{P}}(\mathbf{x}, \mathbf{r}')}{\partial \mathbf{r}_k} \right\rangle_{\mathbf{z}} \\
 &\stackrel{(3.2.179)}{=} \sum_{k=1}^N \left\langle m_k \frac{\partial \delta(\mathbf{r} - \mathbf{r}_k)}{\partial \mathbf{r}_k} \cdot \mathbf{1} \delta(\mathbf{r}' - \mathbf{r}_k) \right\rangle_{\mathbf{z}} \\
 &= \sum_{k=1}^N \left\langle m_k \delta(\mathbf{r}' - \mathbf{r}_k) \right\rangle_{\mathbf{z}} \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} = \rho(\mathbf{r}') \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'}. \tag{3.2.186}
 \end{aligned}$$

Following the same procedure for the  $\mathbb{L}^{\rho c}$  element we deduce

$$\begin{aligned}
 \mathbb{L}^{\mathbf{P}\rho}(\mathbf{r}, \mathbf{r}') &= \langle \{\Pi_{\mathbf{p}}, \Pi_{\rho}\} \rangle_{\mathbf{z}} \stackrel{(3.2.179)}{=} - \sum_k^N \langle \mathbf{1} \delta(\mathbf{r} - \mathbf{r}_k) \cdot m_k \frac{\partial \delta(\mathbf{r}' - \mathbf{r}_k)}{\partial \mathbf{r}_k} \rangle_{\mathbf{z}} \\
 &= - \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} \sum_k^N \langle m_k \delta(\mathbf{r} - \mathbf{r}_k) \rangle_{\mathbf{z}} = - \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} \rho(\mathbf{r}), \quad (3.2.187)
 \end{aligned}$$

which is an obvious in some sense result for this element, since the Poisson operator is antisymmetric. In addition, for the element  $\mathbb{L}^{\rho\rho}$  we obtain

$$\mathbb{L}^{\rho\rho}(\mathbf{r}, \mathbf{r}') = \langle \{\Pi_{\rho}, \Pi_{\rho}\} \rangle_{\mathbf{z}} = 0, \quad (3.2.188)$$

since the partial derivatives of the instantaneous value of the particle density  $\Pi_{\rho}$  with respect to the momentum  $\mathbf{p}_k$  of each particle are zero. It is easy to check that the elements  $\mathbb{L}^{\rho\mathbf{P}}$  and  $\mathbb{L}^{\mathbf{P}\rho}$  are also equal to zero:  $\mathbb{L}^{\rho u} = \mathbb{L}^{u\rho} = 0$ , since both the partial derivative of  $\Pi_{\rho}$  with respect to the momentum  $\mathbf{p}_k$  of each particle is zero and the partial derivative of  $\Pi_u$  with respect to  $\mathbf{p}_k$  is zero as well. At this stage, there are three elements remaining to be determined. The element  $\mathbb{L}^{\mathbf{P}\mathbf{P}}$  can be evaluated as follows:

$$\begin{aligned}
 \mathbb{L}^{\mathbf{P}\mathbf{P}}(\mathbf{r}, \mathbf{r}') &= \langle \{\Pi_{\mathbf{p}}, \Pi_{\mathbf{p}}\} \rangle_{\mathbf{z}} \stackrel{(3.2.179)}{=} \sum_{k=1}^N \langle \mathbf{p}_k \frac{\partial \delta(\mathbf{r} - \mathbf{r}_k)}{\partial \mathbf{r}_k} \delta(\mathbf{r}' - \mathbf{r}_k) - \delta(\mathbf{r} - \mathbf{r}_k) \frac{\partial \delta(\mathbf{r}' - \mathbf{r}_k)}{\partial \mathbf{r}_k} \mathbf{p}_k \rangle_{\mathbf{z}} \\
 &= \sum_{k=1}^N \langle \mathbf{p}_k \delta(\mathbf{r}' - \mathbf{r}_k) \rangle_{\mathbf{z}} \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} - \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} \sum_{k=1}^N \langle \mathbf{p}_k \delta(\mathbf{r} - \mathbf{r}_k) \rangle_{\mathbf{z}} \\
 &= \mathbf{P}(\mathbf{r}') \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} - \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} \mathbf{P}(\mathbf{r}). \quad (3.2.189)
 \end{aligned}$$

For the elements  $\mathbb{L}^{\mathbf{P}u}$  and  $\mathbb{L}^{u\mathbf{P}}$  we deduce

$$\begin{aligned}
 \mathbb{L}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') &= \langle \{\Pi_{\mathbf{p}}, \Pi_u\} \rangle_{\mathbf{z}} \\
 &= \sum_k \left\langle \frac{\partial \Pi_{\mathbf{p}}(\mathbf{x}, \mathbf{r})}{\partial \mathbf{r}_k} \frac{\partial \Pi_u(\mathbf{x}, \mathbf{r}')}{\partial \mathbf{p}_k} - \frac{\partial \Pi_u(\mathbf{x}, \mathbf{r})}{\partial \mathbf{p}_k} \frac{\partial \Pi_{\mathbf{p}}(\mathbf{x}, \mathbf{r}')}{\partial \mathbf{r}_k} \right\rangle_{\mathbf{z}} \\
 &\stackrel{(3.2.179)}{=} - \frac{\partial}{\partial \mathbf{r}} \langle \sum_k \mathbf{p}_k \tilde{\mathbf{p}}_k \delta(\mathbf{r} - \mathbf{r}_k) \rangle_{\mathbf{z}} \delta(\mathbf{r}' - \mathbf{r}) + \langle \Pi_u \rangle_{\mathbf{z}} \frac{\partial}{\partial \mathbf{r}'} \delta(\mathbf{r}' - \mathbf{r}) \\
 &\quad - \sum_{k,l} \left\langle \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} \delta(\mathbf{r}' - \mathbf{r}_k) \right\rangle_{\mathbf{z}} \delta(\mathbf{r}' - \mathbf{r}_l) \\
 &= - \frac{\partial}{\partial \mathbf{r}} \langle \sum_k m_k \tilde{\mathbf{p}}_k^2 \delta(\mathbf{r} - \mathbf{r}_k) \rangle_{\mathbf{z}} \delta(\mathbf{r}' - \mathbf{r}) - u(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \delta(\mathbf{r}' - \mathbf{r}) \\
 &\quad - \frac{1}{2} \sum_{k,l} \left\langle \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} (\delta(\mathbf{r}' - \mathbf{r}_k) - \delta(\mathbf{r}' - \mathbf{r}_l)) \right\rangle_{\mathbf{z}} \delta(\mathbf{r}' - \mathbf{r}) \\
 &= - \frac{\partial}{\partial \mathbf{r}} \langle \sum_k m_k \tilde{\mathbf{p}}_k^2 \delta(\mathbf{r} - \mathbf{r}_k) \rangle_{\mathbf{z}} \delta(\mathbf{r}' - \mathbf{r}) - u(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \delta(\mathbf{r}' - \mathbf{r}) \\
 &\quad - \frac{1}{2} \sum_{k,l} \left\langle \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} \frac{\partial}{\partial \mathbf{r}'} \cdot (\mathbf{r}_{kl} W_{ij} \delta(\mathbf{r}' - \mathbf{r}_l)) \right\rangle_{\mathbf{z}} \delta(\mathbf{r}' - \mathbf{r}). \quad (3.2.190)
 \end{aligned}$$

Where  $\mathbf{r}_{kl} = \mathbf{r}_l - \mathbf{r}_k$  and we used the following expansion :

$$\delta(\mathbf{r}' - \mathbf{r}_k) = \delta((\mathbf{r}' - \mathbf{r}_l) + (\mathbf{r}_l - \mathbf{r}_k)) = \delta(\mathbf{r}' - \mathbf{r}_l) - \mathbf{r}_{kl} \cdot \frac{\partial}{\partial \mathbf{r}_l} \delta(\mathbf{r}' - \mathbf{r}_l) + \frac{1}{2} + \mathbf{r}_{kl} \mathbf{r}_{kl} \cdot \frac{\partial^2}{\partial \mathbf{r}_l^2} \delta(\mathbf{r}' - \mathbf{r}_l). \quad (3.2.191)$$

Hence, we can equivalently obtain,

$$\delta(\mathbf{r}' - \mathbf{r}_k) - \delta(\mathbf{r}' - \mathbf{r}_l) = \frac{\partial}{\partial \mathbf{r}'} \cdot (\mathbf{r}_{kl} W_{kl} \delta(\mathbf{r}' - \mathbf{r}_l)), \text{ where: } W_{kl} = 1 - \frac{1}{2} \mathbf{r}_{kl} \cdot \frac{\partial}{\partial \mathbf{r}'} + \dots + \frac{1}{a!} (-\mathbf{r}_{kl} \cdot \frac{\partial}{\partial \mathbf{r}'})^{a-1}.$$

**Remark 3.25.** Note that one can define the  $n$ -th partial derivative of the delta function  $\delta(\mathbf{r})$  appearing in the Taylor expansion, with the help of an arbitrary real valued test function  $\varphi(\mathbf{r})$ , by the following fundamental relationship (see also [311, p. 694-696]):

$$\int_D \mathbf{r}^n \varphi(\mathbf{r}) \frac{\partial^n}{\partial \mathbf{r}^n} \delta(\mathbf{r}) d\mathbf{r} = (-1)^n \int_D \frac{\partial^n (\mathbf{r} \varphi(\mathbf{r}))}{\partial \mathbf{r}^n} \delta(\mathbf{r}) d\mathbf{r}. \quad (3.2.192)$$

As a result, one deduces the form for the element  $\mathbb{L}^{\mathbf{P}u}$ ,

$$\mathbb{L}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') = -u(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}'} \delta(\mathbf{r}' - \mathbf{r}) + \delta(\mathbf{r} - \mathbf{r}') \frac{\partial}{\partial \mathbf{r}'} \cdot \mathbf{\Pi}(\mathbf{r}'), \quad (3.2.193)$$

where the quantity  $\mathbf{\Pi}(\mathbf{r}')$ , is defined by

$$\mathbf{\Pi}(\mathbf{r}') = \langle \mathbf{\Pi}_{\mathbf{\Pi}} \rangle_{\mathbf{z}} = -\langle \sum_l m_l \dot{\mathbf{p}}_l^2 \delta(\mathbf{r}' - \mathbf{r}_l) \rangle_{\mathbf{z}} + \frac{1}{2} \langle \sum_{k,l} \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_l} \mathbf{r}_{kl} W_{kl} \delta(\mathbf{r}' - \mathbf{r}_l) \rangle_{\mathbf{z}} \quad (3.2.194)$$

and denotes an average stress tensor consisted of two parts. The left term in the above sum, is a consequence of particle motion and the second exists due to particle interactions. According to the property of antisymmetry of the Poisson operator we obtain

$$\mathbb{L}^{u\mathbf{P}}(\mathbf{r}, \mathbf{r}') = u(\mathbf{r}') \frac{\partial}{\partial \mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{\Pi}(\mathbf{r}). \quad (3.2.195)$$

If one make the identification using the hydrostatic pressure  $p(\mathbf{r})$  that  $\mathbf{\Pi}(\mathbf{r}) = p(\mathbf{r})\mathbf{1}$ , then one can rewrite the elements  $\mathbb{L}^{\mathbf{P}u}$  and  $\mathbb{L}^{u\mathbf{P}}$ , as follows:

$$\begin{cases} \mathbb{L}^{u\mathbf{P}}(\mathbf{r}, \mathbf{r}') = u(\mathbf{r}') \frac{\partial}{\partial \mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') + p(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}'), \\ \mathbb{L}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') = -u(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') - \frac{\partial}{\partial \mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') p(\mathbf{r}'). \end{cases} \quad (3.2.196)$$

As a consequence, similarly as in [42],[28] and according to the result we obtained for the elements above the Poisson tensor can be written in the following form for  $\delta := \delta(\mathbf{r} - \mathbf{r}')$ :

$$\mathbb{L}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} 0 & \rho(\mathbf{r}') \partial_{\mathbf{r}'} \delta & 0 \\ -\partial_{\mathbf{r}} \delta \rho(\mathbf{r}) & \mathbf{P}(\mathbf{r}') \partial_{\mathbf{r}'} \delta - \partial_{\mathbf{r}} \delta \mathbf{P}(\mathbf{r}) & \mathbb{L}^{\mathbf{P}u}(\mathbf{r}, \mathbf{r}') \\ 0 & \mathbb{L}^{u\mathbf{P}}(\mathbf{r}, \mathbf{r}') & 0 \end{pmatrix}. \quad (3.2.197)$$

In order to obtain an expression for the friction matrix  $\mathbb{M}$  of the problem we shall use the formula given in (3.2.26). Let  $\mathbb{P}$  denote the projector acting on phase space functions. Here, the explicit form of  $\mathbb{P}$  is not needed. We only require that  $\mathbb{P}\Pi_{z_i} = \Pi_{z_i}$ . This could be achieved by applying the projection operator  $\mathbb{P}' = 1 - \mathbb{P}$ , which is orthogonal to the slow variables  $\Pi_{z_i}(\mathbf{x}(t), \mathbf{r})$ , which means  $\mathbb{P}'\Pi_{z_i}(\mathbf{x}(t), \mathbf{r}) = 0$ . The fast time rate of change of the macroscopic variables leads to relation  $\mathbb{P}'\dot{\Pi}_{z_i} = \dot{\Pi}_{z_i}^f$ , as it is explained in the subsection (4.3). One obtains due to the definitions of  $\Pi_{\rho}(\mathbf{x}, \mathbf{r})$  from Assumption 3.1, that

$$\dot{\Pi}_{\rho}(\mathbf{x}, \mathbf{r}) = \sum_l m_l \dot{\mathbf{r}}_l \frac{\partial}{\partial \mathbf{r}_l} \delta(\mathbf{r} - \mathbf{r}_l) = \sum_l \mathbf{p}_l \frac{\partial}{\partial \mathbf{r}_l} \delta(\mathbf{r} - \mathbf{r}_l) = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{\Pi}_{\mathbf{P}}, \quad (3.2.198)$$

using the Hamilton's equation of motion. Furthermore, since  $\mathbb{P}'\Pi_{\mathbf{p}} = 0$ , it follows that

$$\dot{\Pi}_{\mathbf{p}}^f = \mathbb{P}'\dot{\Pi}_{\mathbf{p}} = 0. \quad (3.2.199)$$

Using a similar calculation, we obtain

$$\dot{\Pi}_{\mathbf{p}}(\mathbf{x}, \mathbf{r}) = \sum_l \left( \dot{\mathbf{p}}_l \delta(\mathbf{r} - \mathbf{r}_l) + \mathbf{p}_l \dot{\mathbf{r}}_l \frac{\partial}{\partial \mathbf{r}_l} \delta(\mathbf{r} - \mathbf{r}_l) \right). \quad (3.2.200)$$

The  $N$  particles of the fluid interact via the usual microscopic Hamiltonian of the system which can be written in the following form (see Definition 3.3 in section 3.1):

$$\mathcal{H}(\mathbf{p}, \mathbf{r}) = \sum_{l=1}^N \left( \frac{\mathbf{p}_l^2}{2m_l} + \frac{1}{2} \sum_{k=1}^N V(\mathbf{r}_{kl}) \right), \text{ where } \mathbf{r}_{kl} := \mathbf{r}_k - \mathbf{r}_l. \quad (3.2.201)$$

The Hamilton's equations of motion, as stated in Remark 3.1 of section 3.1, can be expressed for the  $j$ -th particle in the form

$$\begin{cases} \dot{\mathbf{r}}_l = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_l} = \mathbf{p}_l / m_l, \\ \dot{\mathbf{p}}_k = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_k} = -\frac{1}{2} \sum_{k \neq l=1}^N \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k}. \end{cases} \quad (3.2.202)$$

Plugging this expressions into the form (3.2.200) we deduce

$$\begin{aligned} \dot{\Pi}_{\mathbf{p}}(\mathbf{x}, \mathbf{r}) &= \sum_l \left( -\frac{1}{2} \sum_k \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} \delta(\mathbf{r} - \mathbf{r}_l) + \frac{\mathbf{p}_l^2}{m_l} \frac{\partial}{\partial \mathbf{r}_l} \delta(\mathbf{r} - \mathbf{r}_l) \right) \\ &= -\sum_l \left( \frac{1}{2} \sum_k \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} \frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{r}_{kl} W_{ij} \delta(\mathbf{r} - \mathbf{r}_l)) + \frac{\mathbf{p}_k^2}{m_l} \frac{\partial}{\partial \mathbf{r}_l} \delta(\mathbf{r} - \mathbf{r}_l) \right) \\ &= \frac{\partial}{\partial \mathbf{r}} \cdot \left( \sum_l \left( \frac{1}{2} \sum_k \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_l} \mathbf{r}_{kl} W_{kl} \delta(\mathbf{r} - \mathbf{r}_l) - m_l \tilde{\mathbf{p}}_l^2 \delta(\mathbf{r} - \mathbf{r}_l) \right) \right) \\ &=: \frac{\partial}{\partial \mathbf{r}} \cdot \Pi_{\Pi}(\mathbf{x}, \mathbf{r}). \end{aligned} \quad (3.2.203)$$

Thus, by applying the projection operator  $\mathbb{P}'$  to  $\dot{\Pi}_{\mathbf{p}}$ , one obtains the fast fluctuation

$$\dot{\Pi}_{\mathbf{p}}^f(\mathbf{x}, \mathbf{r}) = \frac{\partial}{\partial \mathbf{r}} \cdot \mathbb{P}' \Pi_{\Pi}(\mathbf{x}, \mathbf{r}) = \frac{\partial}{\partial \mathbf{r}} \cdot \Pi^f(\mathbf{x}, \mathbf{r}), \quad (3.2.204)$$

where we denoted with  $\Pi^f$  the rapidly fluctuating contribution to  $\Pi_{\Pi}$ . Furthermore for the evolution of the instantaneous values of the internal energy density, in the same way as for  $\dot{\Pi}_{\mathbf{p}}$  using again Hamilton's equation, one has

$$\begin{aligned} \dot{\Pi}_u(\mathbf{x}, \mathbf{r}) &= \sum_k \left( \frac{m_k}{2} \dot{\tilde{\mathbf{p}}}_k^2 + \frac{1}{2} \sum_l V(\mathbf{r}_{kl}) \right) \frac{\mathbf{p}_k}{m_k} \cdot \frac{\partial}{\partial \mathbf{r}_k} \delta(\mathbf{r} - \mathbf{r}_k) + \sum_k m_k \tilde{\mathbf{p}}_k \cdot \dot{\tilde{\mathbf{p}}}_k \delta(\mathbf{r} - \mathbf{r}_k) \\ &\quad + \frac{1}{2} \sum_{k,l} \left( \frac{\mathbf{p}_k}{m_k} \cdot \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} + \frac{\mathbf{p}_l}{m_l} \cdot \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_l} \right) \delta(\mathbf{r} - \mathbf{r}_k) \\ &= -\frac{\partial}{\partial \mathbf{r}} \cdot \left( \sum_k \left( \frac{m_k}{2} \tilde{\mathbf{p}}_k^2 + \frac{1}{2} \sum_l V(\mathbf{r}_{kl}) \right) \tilde{\mathbf{p}}_k \delta(\mathbf{r} - \mathbf{r}_k) - \sum_{kl} \frac{1}{2} \tilde{\mathbf{p}}_k \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} \mathbf{r}_{kl} W_{kl} \delta(\mathbf{r} - \mathbf{r}_k) \right) \\ &\quad + \left( -\sum_k m_k \tilde{\mathbf{p}}_k^2 \delta(\mathbf{r} - \mathbf{r}_k) + \frac{1}{2} \sum_{kl} \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} \mathbf{r}_{kl} W_{kl} \delta(\mathbf{r} - \mathbf{r}_k) \right) : \frac{\partial \mathbf{v}(\mathbf{r})}{\partial \mathbf{r}} \\ &= -\frac{\partial}{\partial \mathbf{r}} \cdot \Pi_h + \Pi_{\Pi} : \frac{\partial \mathbf{v}(\mathbf{r})}{\partial \mathbf{r}}, \end{aligned} \quad (3.2.205)$$

where we defined the heat flux by

$$\mathbf{J}^q = \langle \Pi \mathbf{J}^q \rangle_{\mathbf{z}} = \left\langle \sum_k \left( \frac{m_i}{2} \tilde{\mathbf{p}}_k^2 + \frac{1}{2} \sum_l V(\mathbf{r}_{kl}) \right) \tilde{\mathbf{p}}_k \delta(\mathbf{r} - \mathbf{r}_k) - \sum_{kl} \frac{1}{2} \tilde{\mathbf{p}}_k \frac{\partial V(\mathbf{r}_{kl})}{\partial \mathbf{r}_k} \mathbf{r}_{kl} W_{kl} \delta(\mathbf{r} - \mathbf{r}_k) \right\rangle_{\mathbf{z}}, \quad (3.2.206)$$

represents the heat flux vector. As a result by applying again the projection operator, we obtain fluctuations for the internal energy in the following form:

$$\dot{\Pi}_u^f = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbb{P}' \Pi_h + \mathbb{P}' \Pi_\Pi : \frac{\partial \mathbf{v}(\mathbf{r})}{\partial \mathbf{r}} = -\frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{J}^q)^f + \mathbf{\Pi}^f : \frac{\partial \mathbf{v}(\mathbf{r})}{\partial \mathbf{r}}, \quad (3.2.207)$$

where  $\partial \mathbf{v} / \partial \mathbf{r}$  denotes the transposition of the velocity gradient and it is a tensor quantity.

At this stage, one is able to deduce the friction tensor elements which are combinations of the state variables  $\mathbf{P}$  and  $\rho$ . For the element  $M_{\rho\rho}$  one deduces

$$\mathbb{M}^{\rho\rho}(\mathbf{r}, \mathbf{r}') = (k_B)^{-1} \int_0^\tau \langle \dot{\Pi}_\rho^f \dot{\Pi}_\rho^f \rangle_{\mathbf{z}} dt = 0. \quad (3.2.208)$$

In the same way, it is obvious that the elements  $\mathbb{M}^{\rho\mathbf{P}}$ ,  $\mathbb{M}^{\mathbf{P}\rho}$ ,  $\mathbb{M}^{u\rho}$  and  $\mathbb{M}^{\rho u}$ , are equal to zero as well. Furthermore, in order to specify a form for each of the non-zero elements. In the specific problem we will consider absence of cross correlations of the fluctuations, which means that the integral over the time interval  $[0, \tau]$ , involving combination of the heat flux fluctuating part  $(\mathbf{J}^q)^f$  and that of the stress tensor  $\mathbf{\Pi}^f$  are zero. Since the expression for the remaining elements might be more complicated, we will use Einstein tensor index notation, to avoid misunderstanding, in some parts. The element  $\mathbb{M}^{\mathbf{P}\alpha\mathbf{P}\beta}$  can be evaluated as follows (the subscripts  $\alpha, \beta, \dots$ , imply contractions with some vectors  $A_\alpha, A_\beta, \dots$ , multiply form the left or the right, depended on the specific case):

$$\mathbb{M}^{\mathbf{P}\alpha\mathbf{P}\gamma}(\mathbf{r}, \mathbf{r}') = (k_B)^{-1} \int_0^\tau \langle \dot{\Pi}_{\mathbf{P}\alpha}^f \dot{\Pi}_{\mathbf{P}\gamma}^f \rangle_{\mathbf{z}} dt = \frac{\partial}{\partial \mathbf{r}_\mu} \frac{\partial}{\partial \mathbf{r}'_\nu} \left( (k_B)^{-1} \int_0^\tau \langle \Pi_{\alpha\mu}^f(\mathbf{x}(t), \mathbf{r}) \Pi_{\nu\gamma}^f(\mathbf{x}(0), \mathbf{r}') \rangle_{\mathbf{z}} dt \right). \quad (3.2.209)$$

Furthermore,

$$\begin{aligned} \mathbb{M}^{uu}(\mathbf{r}, \mathbf{r}') &= (k_B)^{-1} \int_0^\tau \langle \dot{\Pi}_u^f \dot{\Pi}_u^f \rangle_{\mathbf{z}} dt = \frac{\partial \mathbf{v}_\mu(\mathbf{r})}{\partial \mathbf{r}_\alpha} \frac{\partial \mathbf{v}_\nu(\mathbf{r}')}{\partial \mathbf{r}'_\gamma} \left( (k_B)^{-1} \int_0^\tau \langle \Pi_{\alpha\mu}^f(\mathbf{x}(t), \mathbf{r}) \Pi_{\nu\gamma}^f(\mathbf{x}(0), \mathbf{r}') \rangle_{\mathbf{z}} dt \right) \\ &\quad + \frac{\partial}{\partial \mathbf{r}_\mu} \frac{\partial}{\partial \mathbf{r}'_\nu} \left( (k_B)^{-1} \int_0^\tau \langle (\mathbf{J}^q)_\mu^f(\mathbf{x}(t), \mathbf{r}) (\mathbf{J}^q)_\nu^f(\mathbf{x}(0), \mathbf{r}') \rangle_{\mathbf{z}} dt \right). \end{aligned} \quad (3.2.210)$$

Finally for the elements  $\mathbb{M}^{\mathbf{P}\alpha u}$  and  $\mathbb{M}^{u\mathbf{P}\gamma}$ , one can easily deduce that:

$$\mathbb{M}^{\mathbf{P}\alpha u}(\mathbf{r}, \mathbf{r}') = (k_B)^{-1} \int_0^\tau \langle \dot{\Pi}_{\mathbf{P}\alpha}^f \dot{\Pi}_u^f \rangle_{\mathbf{z}} dt = \frac{\partial}{\partial \mathbf{r}_\mu} \frac{\partial \mathbf{v}_\nu(\mathbf{r}')}{\partial \mathbf{r}'_\gamma} \left( (k_B)^{-1} \int_0^\tau \langle \Pi_{\alpha\mu}^f(\mathbf{x}(t), \mathbf{r}) \Pi_{\nu\gamma}^f(\mathbf{x}(0), \mathbf{r}') \rangle_{\mathbf{z}} dt \right) \quad (3.2.211)$$

and similarly,

$$\mathbb{M}^{u\mathbf{P}\gamma}(\mathbf{r}, \mathbf{r}') = (k_B)^{-1} \int_0^\tau \langle \dot{\Pi}_u^f \dot{\Pi}_{\mathbf{P}\gamma}^f \rangle_{\mathbf{z}} dt = \frac{\partial \mathbf{v}_\mu(\mathbf{r})}{\partial \mathbf{r}_\alpha} \frac{\partial}{\partial \mathbf{r}'_\gamma} \left( (k_B)^{-1} \int_0^\tau \langle \Pi_{\alpha\mu}^f(\mathbf{x}(t), \mathbf{r}) \Pi_{\nu\gamma}^f(\mathbf{x}(0), \mathbf{r}') \rangle_{\mathbf{z}} dt \right). \quad (3.2.212)$$

The stress tensor correlation integral, has the form of a fourth order tensorial kernel ("viscosity kernel") and can be denoted by

$$\eta^{\gamma\nu\alpha\mu}(\mathbf{r}, \mathbf{r}') := (k_B \Theta)^{-1} \int_0^\tau \langle \Pi_{\alpha\mu}^f(\mathbf{x}(t), \mathbf{r}) \Pi_{\nu\gamma}^f(\mathbf{x}(0), \mathbf{r}') \rangle_{\mathbf{z}} dt. \quad (3.2.213)$$

In general, the correlation functions should be finite for values of  $|\mathbf{r} - \mathbf{r}'|$  smaller than the interaction range and therefore following the paper by P. Español and A. Donev [333] one

can obtain a local approximation, such that  $\eta^{\gamma\alpha\mu}(\mathbf{r}, \mathbf{r}')_{local} \approx \eta^{\gamma\alpha\mu}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$ . Using similar arguments and the Fourier's law (see Remark 3.26) for the heat flux correlation one can have the local approximation of the integral [333–335]:

$$-k_{\mu\nu}^q \partial_{\mathbf{r}_\nu} \Theta(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}') = k_{\mu\nu}^q(\mathbf{r}) \Theta^2(\mathbf{r}) \partial_{\mathbf{r}_\nu} \Theta^{-1}(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}') \approx (k_B)^{-1} \int_0^\tau \langle (\mathbf{J}^q)_\mu^f(\mathbf{x}(t), \mathbf{r}) (\mathbf{J}^q)_\nu^f(\mathbf{x}(0), \mathbf{r}') \rangle_z dt, \quad (3.2.214)$$

where  $k_{\mu\nu}^q := k_{\mu\nu}^q(\mathbf{r})$  denotes the thermal conductivity tensor. As a result, similarly as in [42] and [28], the friction tensor can be written as

$$\mathbb{M}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mathbb{M}^{\mathbf{P}\alpha\mathbf{P}\gamma}(\mathbf{r}, \mathbf{r}') & \mathbb{M}^{\mathbf{P}\alpha u}(\mathbf{r}, \mathbf{r}') \\ 0 & \mathbb{M}^{u\mathbf{P}\gamma}(\mathbf{r}, \mathbf{r}') & \mathbb{M}^{uu}(\mathbf{r}, \mathbf{r}') \end{pmatrix}. \quad (3.2.215)$$

Similarly as in [42], the full set of evolution equation using the forms we have already deduced for the friction and Poisson tensors and for the derivatives  $\partial_{ze}$ ,  $\partial_{zs}$ . Thus, for the time evolution of the mass density  $\rho$  one obtains using the equation (3.2.21) and the identities for involving the Dirac delta (3.2.68)

$$\frac{\partial \rho(\mathbf{r})}{\partial t} = - \int_D \rho(\mathbf{r}') \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}') d\mathbf{r}' = -\text{div}[(\rho \mathbf{v})](\mathbf{r}). \quad (3.2.216)$$

Equation (3.2.216) is the well known continuity equation in hydrodynamics for a system, which is in a steady state (does not change its behaviour over time) and indicates that the importing rate of mass in the system, is equal to the rate at which mass leaves the system. Simply put, equation (3.2.216) expresses conservation of mass. Similarly using again the equation (3.2.21), one deduces for the momentum density  $\mathbf{P} := \rho \mathbf{v}$

$$\begin{aligned} \frac{\partial \mathbf{P}(\mathbf{r})}{\partial t} &= - \int_D \mathbf{P}(\mathbf{r}') \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}') d\mathbf{r}' - \int_D \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}} \mathbf{P}(\mathbf{r}') \cdot \mathbf{v}(\mathbf{r}') d\mathbf{r}' \\ &\quad + \int_D \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}} \rho(\mathbf{r}') \frac{\mathbf{v}^2(\mathbf{r}')}{2} d\mathbf{r}' + \int_D (\mathbb{L}^{\mathbf{P}u} + \mathbb{M}^{\mathbf{P}u} \partial_{us}) d\mathbf{r}' \\ &= -\text{div}[(\mathbf{P} \otimes \mathbf{v})](\mathbf{r}) - \int_D u(\mathbf{r}') \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}} d\mathbf{r}' - \int_D \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}} p(\mathbf{r}') d\mathbf{r}' + \int_D \mathbb{M}^{\mathbf{P}u} \partial_{us} d\mathbf{r}'. \end{aligned} \quad (3.2.217)$$

The tensor quantity  $\mathbf{P} \otimes \mathbf{v}$  is the momentum flux, that is, the momentum crossing the surface per unit area and per unit time. Finally a similar calculation leads to the internal energy balance, that is

$$\frac{\partial u(\mathbf{r})}{\partial t} = - \int_D u(\mathbf{r}') \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}') d\mathbf{r}' - \int_D p(\mathbf{r}') \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}'} \cdot \mathbf{v}(\mathbf{r}') d\mathbf{r}' + \int_D \mathbb{M}^{uu} \partial_{us} d\mathbf{r}'. \quad (3.2.218)$$

Finally, using the approximations (3.2.214) and (3.2.213) and the fundamental thermodynamic relationships (3.1.51), one obtains the forms for the momentum density and internal energy density balance, as follows:

$$\begin{aligned} \frac{\partial u(\mathbf{r})}{\partial t} &= - \int_D u(\mathbf{r}') \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}') d\mathbf{r}' - \int_D p(\mathbf{r}') \frac{\partial \delta(\mathbf{r}-\mathbf{r}')}{\partial \mathbf{r}'} \cdot \mathbf{v}(\mathbf{r}') d\mathbf{r}' \\ &\quad + \int_D \frac{\partial \mathbf{v}_\mu(\mathbf{r})}{\partial \mathbf{r}_\alpha} \frac{\partial \mathbf{v}_\nu(\mathbf{r}')}{\partial \mathbf{r}'_\gamma} \eta^{\gamma\alpha\mu}(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}') d\mathbf{r}' + \int_D \frac{\partial}{\partial \mathbf{r}_\mu} \frac{\partial}{\partial \mathbf{r}'_\nu} \lambda_{\mu\nu}(\mathbf{r}) T(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}') d\mathbf{r}' \\ &=: -\text{div}(u\mathbf{v}) - \mathbf{\Pi} : (\partial_{\mathbf{r}} \mathbf{v})^T - \text{div}(\mathbf{J}_\mu^q) \end{aligned} \quad (3.2.219)$$

and similarly

$$\begin{aligned}
 \frac{\partial \mathbf{P}(\mathbf{r})}{\partial t} &= -\frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{P}(\mathbf{r})\mathbf{v}(\mathbf{r})) - \int_D u(\mathbf{r}) \frac{\partial \delta(\mathbf{r}' - \mathbf{r})}{\partial \mathbf{r}} d\mathbf{r}' \\
 &\quad - \int_D \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} p(\mathbf{r}') d\mathbf{r}' + \int_D \frac{\partial}{\partial \mathbf{r}_\mu} \frac{\partial \mathbf{v}_\nu(\mathbf{r}')}{\partial \mathbf{r}'_\gamma} \eta^{\gamma\alpha\mu}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \\
 &=: -\operatorname{div}(\mathbf{P} \otimes \mathbf{v}) - \operatorname{div}(\mathbf{\Pi}).
 \end{aligned} \tag{3.2.220}$$

**Remark 3.26 (Newton's and Fourier's Laws).** *The results above are obtained with the help of Newton's law  $\tau_{\gamma\nu} = \eta^{\gamma\alpha\mu} \partial_{\mathbf{r}'_\mu} v_\alpha(\mathbf{r}')$ , as well as the Fourier's law for heat conduction  $\mathbf{J}_\mu^q = -k_{\mu\nu}^q \partial_{\mathbf{r}_\nu} \Theta$  [42] and the Dirac identities (3.2.68).*

Finally, It may be of interest to investigate how this procedure can be applied in order to derive the coupling of Navier-Stokes with the Cahn-Hilliard model, where the definition of the microscopic dynamical function of the phase-field needs to be considered in a different way than the one for the fluid density. To the best of our knowledge a first step towards this direction has been taken by P. Español et al in [333, 334], but we shall leave any further considerations and more details on this topic, as a possible direction for the future.

## Chapter 4

# Further applications of Cahn-Hilliard/Navier-Stokes couplings.

### 4.1 A Cahn-Hilliard/Navier-Stokes system for the dynamics of adsorption.

The Cahn-Hilliard coupled with Navier-Stokes system discussed earlier in the subsection (3.2.4), can be extended for different types of chemical potentials corresponding to different types of free energies. In this chapter, we consider a specific form of free energy which has been first introduced by H. Diamant, D. Andelman et al. [336] and also discussed by P. Gosselin and H. Mohrbach [337] and Y. Hirose et al [338], to describe the kinetics of adsorption of surfactant mixtures. The molecules from a gas or liquid, or a dissolved solid adhere to an interface and in this way a thin film of the adsorbate on the surface of the adsorbent, is created. Adsorption, due to the electrochemical interaction between the particles of a system and a surface, is considered in many experiments, such as for example the adsorption of a perfect gas on a surface or of charged particles in an electrolytes [339], [340]. This phenomenon is a consequence of surface energy and is very important in several industrial applications such as the stabilization of foams, the formulation of nano-porous materials, drug delivery, etc. [341–343].

Let us consider the case of a mixture of different types of particles. This requires a dynamic description of the interfacial tension due to interactions between the various types of particles involved, especially if one considers surfactants. Starting from the basic definitions and notions of microscopic surface tension  $\sigma$ , which describes a particle-free interface, as well as the macroscopic surface tension  $\sigma_A$ , which depends on the local volume fraction  $c := c(\mathbf{r}, t) : D_T \rightarrow \mathbb{R}$  of adsorbed particles, i.e., we can write the surface pressure  $P_s(\phi, c)$  in the more general form (see [46, 344]):

$$P_s(\phi, c) = \sigma - \sigma_A = - \int_D m(\lambda) f_L(\phi) f_I(\phi, c) d\mathbf{r}, \quad D \subset \mathbb{R}^d, \quad (4.1.1)$$



where  $f_L(c) := \frac{1}{4}(1-\phi^2)^2$  denotes the homogeneous free energy density and the function  $f_I(\phi, c)$  can be explicitly defined by

$$f_I(\phi, c) := \left( k_B \Theta \left[ c \log c + \frac{|\phi|+1}{2} \log \left( \frac{|\phi|+1}{2} \right) \right] - \alpha c - \beta c^2 - \mu_I c \right) / a^2, \quad (4.1.2)$$

and expresses a specific interfacial free energy density, in which the first term is due to the mixing entropy and the second accounts for the energetic preference of the surfactants to lie at the interface. Moreover,  $m(\lambda)$  represents a scaling factor which depends on the parameter  $\lambda$ , i.e.,  $m(\lambda) := 3\sqrt{2}/\lambda$ , and weights the gradient penalty term and  $\alpha$  represents a surface activity parameter (surfactant molecular dimension) and is typically of order  $10\Theta$ , where  $\Theta$  denotes the temperature which is considered to be constant in the specific case (adsorption isotherms). In addition,  $\beta$  is the lateral interaction parameter and is realistically a few  $\Theta$  as well [344]. Finally  $a > 0$  represents the molecular dimension of particles. The quantity  $\mu_I := \lim_{\mathbf{r} \rightarrow 0} \mu(\mathbf{r})$  represents the chemical potential of the solution next to the interface. The phase field order parameter  $\phi := \phi(\mathbf{r}, t) : D_T \rightarrow \mathbb{R}$ ,  $D \subset \mathbb{R}^d$  is such that  $\phi(\mathbf{r}, t) \in (-1, 1)$ , for all times  $0 \leq t \leq T$  and needs to be considered independently of the local volume fraction of particles in the immiscible two-phase fluid  $c := c(\mathbf{r}, t) > 0$ , despite the constraint  $2(1-c) = |\phi|+1$ . Hence, due to this constraint the volume fraction takes the values  $c(\mathbf{r}, t) \in (0, 1)$ .

The system is characterised by the following total free energy functional

$$\mathcal{F}_{ads}(c, \phi) := \int_D f_\lambda(c, \phi) d\mathbf{r} := \int_D w(\phi) + m(\lambda) f_L(\phi) f_I(\phi, c) + \chi_1(\phi) f_b^{ex}(c) d\mathbf{r} \geq 0, \quad (4.1.3)$$

where  $\chi_1(\phi) := (\phi+1)/2$  is an approximation of the characteristic function corresponding to phase  $\phi = 1$ . Moreover, the function  $w(\phi)$  denotes the classical Cahn-Hilliard free energy density term defined by

$$w(\phi) := f_L(\phi) + \frac{\lambda^2}{2} |\nabla \phi|^2 := \phi^2(1-\phi)^2 + \frac{\lambda^2}{2} |\nabla \phi|^2 \quad (4.1.4)$$

and the quantity

$$f_b^{ex}(c) := (k_B \Theta [c(\log c - 1) - c_b(\log c_b - 1)] - \mu_b(c - c_b)) / a^3, \quad (4.1.5)$$

stands for the excess in bulk grand canonical free energy density in the absence of gradient terms (associated with the grand canonical ensemble). This is simply defined by the ideal entropy of mixing [345, 346], in contact with a reservoir. The density  $c_b := \lim_{\mathbf{r} \rightarrow \infty} c(\mathbf{r})$  stands for the bulk equilibrium density of particles. In addition,  $\mu_b := \lim_{\mathbf{r} \rightarrow \infty} \mu(\mathbf{r}) = k_B \Theta \log c_b$ , represents the bulk equilibrium chemical potential.

**Remark 4.1.** *In thermodynamic equilibrium the chemical potential is the same through the entire system and more precisely  $\mu_I = \mu_b$  [46, 336]. In addition, the first variation of  $f_b^{ex}(c)$  with respect to  $c$ , i.e.,  $df_b^{ex}(c)/dc = 0$ , implies the equilibrium profile  $\log c = (k_B \Theta)^{-1} \mu_b$ , i.e.,  $c(\mathbf{r}) = c_b$ ,  $\mathbf{r} > 0$ .*

#### 4.1.1 Derivation of the equations of motion.

Equilibrium relations can be straightforwardly deduced, by setting the first variation of the free energy density with respect to  $\phi$  and  $c$  is equal to zero: namely  $\partial_z f_\lambda|_{z=\phi, c} = 0$ .

**Theorem 4.1.1 (Gradient flow equations).** *The following system of evolution equations of the densities  $c$  and  $\phi$ :*

$$\begin{cases} \partial_t c = m(\lambda) M_c \operatorname{div}(c \nabla (f_L(\phi) \partial_c f_I(\phi, c)) + M_c \operatorname{div}(c \nabla (\chi_1(\phi) \mu_b^{\text{ex}}(c))), \\ \partial_t \phi = m(\lambda) M_\phi \Delta (f_L'(\phi) f_I(\phi, c) + f_L(\phi) \partial_\phi f_I) + M_\phi \Delta (f_b^{\text{ex}}(c) \chi_1'(\phi)) + M_\phi \Delta \mu(\phi), \end{cases} \quad (4.1.6)$$

where  $\mu(\phi) := f_L'(\phi) - \lambda^2 \Delta \phi$  stands for the Cahn-Hilliard chemical potential. In addition, homogeneous Neumann and no-flux boundary conditions, i.e.,  $\partial_{\mathbf{n}} z = \hat{M}_z \partial_{\mathbf{n}} \partial_z f_\lambda = 0$ ,  $z \in (\phi, c)$ , are imposed. This particular system can be formally obtained from the adsorption free energy  $\mathcal{F}_{\text{ads}}$  defined in (4.1.3) and in combination with (4.1.4), (4.1.5), via the following gradient flow formulation: For  $z \in (\phi, c)$  the gradient flow of  $\mathcal{F}_{\text{ads}}$  in a weak form, is given by

$$\langle \partial_t z, v \rangle_{L^2(D)} = - \langle \hat{M}_z \nabla_z^\mathcal{X} \mathcal{F}_{\text{ads}}(z), v \rangle_{\mathcal{Z}(D)}, \quad (4.1.7)$$

for all  $v \in \mathcal{X}(D) \subseteq \mathcal{Z}(D)$ . The mobility coefficient  $\hat{M}_z$  is set to be a constant  $M_z$  for  $z = \phi$  and as a function  $M(z) := z M_z$  if  $z = c$ .

*Proof.* The evolution equation for the volume fraction  $c$  and the order parameter  $\phi$  can be obtained as result of the functional gradient of the free energy  $\mathcal{F}_{\text{ads}}(c, \phi)$ , which is well defined using the "Gateaux derivative of  $\mathcal{F}_{\text{ads}}$  at  $z$ , from the general relationship

$$\delta_z^\mathcal{X} \mathcal{F}_{\text{ads}}(z) := \lim_{k \rightarrow 0} \frac{\mathcal{F}_{\text{ads}}(z + kv) - \mathcal{F}_{\text{ads}}(z)}{k} = \langle \nabla_z^\mathcal{X} \mathcal{F}_{\text{ads}}(z), v \rangle_{\mathcal{Z}(D)}, \quad \forall v \in \mathcal{X}(D) \subseteq \mathcal{Z}(D), \quad (4.1.8)$$

where we consider each time one of the two variables  $c, \phi$  to be constant with respect to the differentiation of  $\mathcal{F}_{\text{ads}}$  over the other, namely

$$\begin{aligned} \langle \nabla_c^\mathcal{X} \mathcal{F}_{\text{ads}}(\phi, c), v_c \rangle_{L^2(D)} &:= \lim_{k \rightarrow 0} \int_D \left( m(\lambda) f_L(\phi) k_B T a^{-2} k^{-1} c \log(1 + \varepsilon v_c / c) \right) d\mathbf{r} \\ &+ \lim_{k \rightarrow 0} \int_D k^{-1} m(\lambda) f_L(\phi) a^{-2} k_B T v_c \log(c + k v_c) d\mathbf{r} \\ &- \lim_{k \rightarrow 0} \int_D \left( m(\lambda) f_L(\phi) v_c \alpha a^{-2} - 2m(\lambda) f_L(\phi) c a^{-2} v_c \beta \right) d\mathbf{r} \\ &- \lim_{k \rightarrow 0} \int_D \left( \beta a^{-2} k v_c^2 m(\lambda) f_L(\phi) - \mu_I v_c \alpha^{-2} m(\lambda) f_L(\phi) \right) d\mathbf{r} \\ &- \lim_{k \rightarrow 0} \int_D \left( \mu_b \chi_1(\phi) a^{-3} v_c + \chi_1(\phi) k_B T a^{-3} k^{-1} c \log(1 + k v_c / c) \right) d\mathbf{r} \\ &- \lim_{k \rightarrow 0} \int_D \left( \chi_1(\phi) k_B T a^{-3} v_c + \chi_1(\phi) k_B T a^{-3} v_c \log(c + k v_c) \right) d\mathbf{r}. \end{aligned} \quad (4.1.9)$$

Therefore by taking the limit  $\varepsilon$  to zero inside the integral, one deduces

$$\begin{aligned} \langle \nabla_c^\mathcal{X} \mathcal{F}_{\text{ads}}(\phi, c), v_c \rangle_{L^2(D)} &= \int_D \left( m(\lambda) f_L(\phi) k_B T a^{-2} v_c + m(\lambda) f_L(\phi) a^{-2} k_B T v_c \log(c) \right) d\mathbf{r} \\ &- \int_D \left( m(\lambda) f_L(\phi) v_c \alpha a^{-2} - 2m(\lambda) f_L(\phi) c^{-2} v_c \beta - \mu_I v_c a^{-2} m(\lambda) f_L(\phi) \right) d\mathbf{r} \\ &- \int_D \left( \mu_b \chi_1(\phi) a^{-3} v_c + \chi_1(\phi) k_B T a^{-3} v_c \right) d\mathbf{r} \\ &- \int_D \left( \chi_1(\phi) k_B T a^{-3} v_c + \chi_1(\phi) k_B T a^{-3} v_c \log(c) \right) d\mathbf{r} \end{aligned}$$

In the form of the usual  $L^2$ -inner product the above integral can be rewritten as follows:

$$\begin{aligned}
 \langle \nabla_c^X \mathcal{F}_{ads}(\phi, c), v_c \rangle_{L^2(D)} &= \langle m(\lambda) f_L(\phi) k_B T a^{-2} + m(\lambda) f_L(\phi)^{-2} k_B T \log(c), v_c \rangle_{L^2(D)} \\
 &\quad - \langle m(\lambda) f_L(\phi) \alpha a^{-2} - 2m(\lambda) f_L(\phi) c a^{-2} \beta - \mu_1 a^{-2} m(\lambda) f_L(\phi), v_c \rangle_{L^2(D)} \\
 &\quad - \langle \mu_b \chi_1(\phi) a^{-3} + \chi_1(\phi) k_B T a^{-3} \log(c), v_c \rangle_{L^2(D)} \\
 &= -\langle m(\lambda) f_L(\phi) \partial_c f_I(\phi, c), v_c \rangle_{L^2} - \langle \chi_1 \mu_b^{ex}, v_c \rangle_{L^2(D)},
 \end{aligned}$$

where  $\mu_b^{ex}(c) := \partial_c f_b^{ex} = a^{-3}(-\mu_b + k_B T \log c)$ . In order to get a weak (gradient flow) formulation of the above functional with respect to both  $\phi$  and  $c$  one needs to consider first the semi-inner product:

$$\langle u, v \rangle_{H_0^1(D)} := \langle \nabla u, \nabla v \rangle_{L^2(D)} \quad (4.1.10)$$

and the associate  $v_{c^*}$  of  $v_c$ , namely

$$\begin{cases} \Delta v_{c^*} = v_c, \\ \nabla v_{c^*} \cdot \mathbf{n} = 0. \end{cases} \quad (4.1.11)$$

As a consequence, one obtains the related gradient flow equation by using the scalar product:

$$\langle u, v \rangle_{H^{-1}(D)} := \langle \nabla u^*, \nabla v^* \rangle_{L^2(D)}, \quad \forall u, v \in H^{-1}(D). \quad (4.1.12)$$

Using the associate  $v_{c^*}$ , the above sum of inner products is equal to

$$\begin{aligned}
 &m(\lambda) \langle c M_c \nabla(f_L(\phi) \partial_c f_I), \nabla v_{c^*} \rangle_{L^2(D)} + \langle c M_c \nabla(\chi_1 \mu_b^{ex}), \nabla v_{c^*} \rangle_{L^2(D)} \\
 &= m(\lambda) \langle c M_c \Delta(f_L(\phi) \partial_c f_I), \Delta v_{c^*} \rangle_{H^{-1}(D)} + \langle c M_c \Delta(\chi_1 \mu_b^{ex}), \Delta v_{c^*} \rangle_{H^{-1}(D)}, \text{ by (4.1.12)} \\
 &= -m(\lambda) \langle c M_c \nabla(f_L(\phi) \partial_c f_I), \nabla v_c \rangle_{H^{-1}(D)} + \langle c M_c \nabla(\chi_1 \mu_b^{ex}), \nabla v_c \rangle_{H^{-1}(D)}, \text{ by (4.1.11)} \\
 &= -m(\lambda) \langle c M_c \nabla f_L(\phi) \partial_c f_I + c M_c f_L(\phi) \nabla \partial_c f_I, \nabla v_c \rangle_{H^{-1}(D)} - \langle c M_c \nabla(\chi_1 \mu_b^{ex}), \nabla v_c \rangle_{H^{-1}(D)}.
 \end{aligned}$$

As a result one can derive a first form of the  $H^{-1}$ -gradient flow of  $\mathcal{F}_{ads}$ , with respect to  $c$ :

$$\langle \partial_t c, v_c \rangle_{L^2(D)} + m(\lambda) \langle c M_c \nabla f_L(\phi) \partial_c f_I + c M_c f_L(\phi) \nabla \partial_c f_I, \nabla v_c \rangle_{H^{-1}(D)} + \langle c M_c \nabla(\chi_1 \mu_b^{ex}), \nabla v_c \rangle_{H^{-1}(D)} = 0. \quad (4.1.13)$$

This can be also expanded using the analytic form for the  $f_I$ , as follows:

$$\begin{aligned}
 \langle \partial_t c, v_c \rangle_{L^2(D)} &= -m(\lambda) \langle c M_c \nabla f_L(\phi) (k_B T \log\left(\frac{2c}{(|\phi|+1)}\right) - \alpha - 2\beta c - \mu_1) / a^2, \nabla v_c \rangle_{H^{-1}(D)} \\
 &\quad - \langle c M_c \nabla(\chi_1 \mu_b^{ex}), \nabla v_c \rangle_{H^{-1}(D)} - m(\lambda) \langle 2f_L(\phi) \beta a^{-2} c M_c \nabla c, \nabla v_c \rangle_{H^{-1}(D)} \\
 &\quad - m(\lambda) \langle c M_c f_L(\phi) k_B T a^{-2} (\partial_\phi \log c \nabla \phi + \partial_c \log c \nabla c), \nabla v_c \rangle_{H^{-1}(D)}.
 \end{aligned} \quad (4.1.14)$$

The constraint between  $c$  and  $\phi$  and the analytic form for  $\partial_c f_I$ , was used in the above derivation. As a result, we can deduce that

$$\begin{aligned}
 \langle \partial_t c, v_c \rangle_{L^2(D)} &= -m(\lambda) \langle (c M_c \nabla f_L(\phi) (k_B T \log\left(\frac{2c}{(|\phi|+1)}\right) - \alpha - 2\beta c - \mu_1) / a^2, \nabla v_c \rangle_{H^{-1}(D)} \\
 &\quad - \langle c M_c \nabla(\chi_1 \mu_b^{ex}), \nabla v_c \rangle_{H^{-1}(D)} - m(\lambda) \langle 2f_L(\phi) \beta a^{-2} c M_c \nabla c, \nabla v_c \rangle_{H^{-1}(D)} \\
 &\quad - m(\lambda) \langle M_c f_L(\phi) k_B T a^{-2} (c \phi [|\phi|(|\phi|+1)]^{-1} \nabla \phi + \nabla c), \nabla v_c \rangle_{H^{-1}(D)}.
 \end{aligned} \quad (4.1.15)$$

Similarly we can obtain the directional derivative at point  $\phi$  in the direction of  $v_\phi \in X(D) = C_0^\infty(D)$ :

$$\begin{aligned}\nabla_\phi^X \mathcal{F}(\phi, c) &:= \lim_{k \rightarrow 0} \int_D k^{-1} (f_\lambda(\phi + kv_\phi, c) - f_\lambda(\phi, c)) d\mathbf{r} \\ &= m(\lambda) \langle \partial_\phi (f_L(\phi) f_I(\phi, c)), v_\phi \rangle_{L^2(D)} + \langle f_b^{ex}(c) \chi_1'(\phi), v_\phi \rangle_{L^2(D)} \\ &\quad + \langle f_L'(\phi), v_\phi \rangle_{L^2(D)} + \langle 2\nabla\phi, \nabla v_\phi \rangle_{L^2(D)}.\end{aligned}$$

Therefore, by applying integration by parts in the last inner product we deduce that

$$\begin{aligned}\nabla_\phi^X \mathcal{F}(\phi, c) &= m(\lambda) \langle \partial_\phi (f_L(\phi) f_I(\phi, c)), v_\phi \rangle_{L^2(D)} + \langle f_b^{ex}(c) \partial_\phi \chi_1(\phi), v_\phi \rangle_{L^2(D)} + \langle f_L'(\phi) - 2\Delta\phi, v_\phi \rangle_{L^2(D)} \\ &= m(\lambda) \langle f_L'(\phi) f_I(\phi, c) + f_L(\phi) \partial_\phi f_I(\phi, c), v_\phi \rangle_{L^2(D)} \\ &\quad + \langle f_b^{ex}(c) \partial_\phi \chi_1(\phi), v_\phi \rangle_{L^2(D)} + \langle \mu(\phi), v_\phi \rangle_{L^2(D)},\end{aligned}\tag{4.1.16}$$

where  $\mu_\phi := f_L'(\phi) - 2\Delta\phi$  is the chemical potential. Applying similar arguments, the related Gradient flow reads (with the help of the associates as before):

$$\begin{aligned}\langle \partial_t \phi, v_\phi \rangle_{L^2} &= m(\lambda) \langle M_\phi \nabla (f_L'(\phi) f_I(\phi, c) + f_L(\phi) \partial_\phi f_I(\phi, c)), \nabla v_\phi^* \rangle_{L^2(D)} \\ &\quad + \langle M_\phi \nabla \mu(\phi), \nabla v_\phi^* \rangle_{L^2(D)} + \langle M_\phi \nabla (f_b^{ex}(c) \partial_\phi \chi_1(\phi)), \nabla v_\phi^* \rangle_{L^2(D)}\end{aligned}\tag{4.1.17}$$

$$\begin{aligned}&= m(\lambda) \langle M_\phi \Delta (f_L'(\phi) f_I(\phi, c) + f_L(\phi) \partial_\phi f_I(\phi, c)), \Delta v_\phi^* \rangle_{H^{-1}(D)} \\ &\quad + \langle M_\phi \Delta \mu(\phi), \Delta v_\phi^* \rangle_{H^{-1}(D)} + \langle M_\phi \Delta (f_b^{ex}(c) \partial_\phi \chi_1(\phi)), \Delta v_\phi^* \rangle_{H^{-1}(D)}.\end{aligned}\tag{4.1.18}$$

Thus, the resulting weak formulation for  $\phi$  is

$$\begin{aligned}\langle \partial_t \phi, v_\phi \rangle_{L^2(D)} &= m(\lambda) \langle M_\phi \Delta (f_L'(\phi) f_I(\phi, c) + f_L(\phi) \partial_\phi f_I(\phi, c)), v_\phi \rangle_{H^{-1}(D)} \\ &\quad + \langle M_\phi \Delta (f_b^{ex}(c) \partial_\phi \chi_1(\phi)), v_\phi \rangle_{H^{-1}(D)} + \langle M_\phi \Delta \mu(\phi), v_\phi \rangle_{H^{-1}(D)}.\end{aligned}\tag{4.1.19}$$

As a result, we obtain the evolution equation for the composition  $\phi$ , i.e.,

$$\partial_t \phi = m(\lambda) M_\phi \Delta (f_L'(\phi) f_I(\phi, c) + f_L(\phi) \partial_\phi f_I(\phi, c)) + M_\phi \Delta (f_b^{ex}(c) \partial_\phi \chi_1(\phi)) + M_\phi \Delta \mu(\phi)\tag{4.1.20}$$

and this completes the derivation.  $\square$

**Remark 4.2 (Conservation of mass).** *Conservation of mass for the system (4.1.6) is straightforward, namely:*

$$\begin{cases} \frac{d}{dt} \int_D c d\mathbf{r} = \int_D \partial_t c d\mathbf{r} = M_c \int_D \operatorname{div}(c \nabla \partial_c f_\lambda) d\mathbf{r} = M_c \int_{\partial D} c \nabla \partial_c f_\lambda \cdot \mathbf{n} ds = 0, \\ \frac{d}{dt} \int_D \phi d\mathbf{r} = \int_D \partial_t \phi d\mathbf{r} = M_\phi \int_D \Delta \partial_\phi f_\lambda d\mathbf{r} = M_\phi \int_{\partial D} \nabla \partial_\phi f_\lambda \cdot \mathbf{n} ds = 0, \end{cases}\tag{4.1.21}$$

which hold both by assumption for the boundary conditions.

The coupling to fluid flow for incompressible fluids  $\operatorname{div}(\mathbf{v}) = 0$ , can be derived by adding an additional convection term to each of the evolution equations (4.1.6), as follows:

$$\begin{cases} \partial_t c + \mathbf{v} \cdot \nabla c = M_c \operatorname{div}(c \nabla \partial_c f_\lambda) := m(\lambda) M_c \operatorname{div}(c \nabla (f_L(\phi) \partial_c f_I(\phi, c))) + M_c \operatorname{div}(c \nabla (\chi_1(\phi) \mu_b^{ex}(c))), \\ \partial_t \phi + \mathbf{v} \cdot \nabla \phi = M_\phi \Delta \partial_\phi f_\lambda := m(\lambda) M_\phi \Delta (f_L'(\phi) f_I(\phi, c) + f_L(\phi) \partial_\phi f_I(\phi, c)) + M_\phi \Delta (f_b^{ex}(c) \chi_1'(\phi)) + M_\phi \Delta \mu(\phi). \end{cases}\tag{4.1.22}$$

In order to obtain a form for the momentum balance we shall follow the classical Energetic Variational Approach introduced in the previous section (3.2.4). The result can be summarised in the following theorem:

**Theorem 4.1.2.** *The Least Action Principle for the first variation of the following action functional*

$$\begin{aligned} \mathcal{A}(\mathbf{r}(\mathbf{R}, t)) &:= \int_{(D_0)_T} \left( \frac{1}{2} |\partial_t \mathbf{r}(\mathbf{R}, t)|^2 - f_L(\phi(\mathbf{r}(\mathbf{R}, t), t)) - \frac{\lambda^2}{2} |\nabla_{\mathbf{r}} \phi(\mathbf{r}(\mathbf{R}, t), t)|^2 \right) d\mathbf{R} dt \\ &\quad - \int_{(D_0)_T} m(\lambda) f_L(\phi(\mathbf{r}(\mathbf{R}, t), t)) f_I(\phi(\mathbf{r}(\mathbf{R}, t), t), c(\mathbf{r}(\mathbf{R}, t), t)) d\mathbf{R} dt \\ &\quad - \int_{(D_0)_T} \chi_1(\phi(\mathbf{r}(\mathbf{R}, t), t)) f_b^{ex}(c(\mathbf{r}(\mathbf{R}, t), t)) d\mathbf{R} dt, \end{aligned} \quad (4.1.23)$$

with respect to the flow map  $\mathbf{r}(\mathbf{R}, t)$ , namely  $\delta \mathcal{A}(\mathbf{r}) / \delta \mathbf{r} = 0$ , together with the maximum dissipation principle [285], subject to incompressibility, implies the following incompressible phase-field-Navier-Stokes momentum equation (see [46, 319] for more details):

$$\begin{aligned} \partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v} - \Delta \mathbf{v} + \nabla p &= -\partial_\phi f_\lambda(\phi, c) \nabla \phi - \partial_c f_\lambda(\phi, c) \nabla c \\ &:= -\operatorname{div}(\lambda^2 (\nabla \phi \otimes \nabla \phi) + w(\phi) \mathbf{I}) - m(\lambda) \nabla (f_L(\phi) f_I(\phi, c)) - \nabla (\chi_1(\phi) f_b^{ex}(c)). \end{aligned} \quad (4.1.24)$$

*Proof.* We aim to follow similar arguments as for the classical Navier-Stokes discussed in lemma 3.3 and thus we consider the first variation  $\delta_{\mathbf{r}}^{L^2} \mathcal{A}(\mathbf{r}) := \langle \nabla_{\mathbf{r}}^{L^2} \mathcal{A}(\mathbf{r}), \mathbf{y} \rangle_{L^2}$  of the action functional can be evaluated with the help of a test function  $\mathbf{y} := \mathbf{y}(\mathbf{R}, t) = \tilde{\mathbf{y}}(\mathbf{r}(\mathbf{R}, t), t) \in L^2(0, T; C_c^\infty(D))_d$  (with  $\mathbf{y}(\mathbf{R}, 0) = \mathbf{y}(\mathbf{R}, T)$ ) for all  $\mathbf{R} \in D_0$ ) and more precisely we consider a one parameter family of maps, i.e.,  $d_\varepsilon \mathbf{r}^\varepsilon = \mathbf{y}$  with  $\mathbf{r}^0 := \mathbf{r}(\mathbf{R}, t)$  and  $\operatorname{div}_{\mathbf{r}}(\mathbf{y}) = 0$  due to incompressibility condition. Hence, we are going to obtain the first variation with respect to  $\varepsilon$ , of each of the following functionals, separately.

$$\begin{aligned} \mathcal{A}_1(\mathbf{r}) &:= \int_{(D_0)_T} \left( \frac{1}{2} |\partial_t \mathbf{r}(\mathbf{R}, t)|^2 - f_L(\phi(\mathbf{r}(\mathbf{R}, t), t)) - \frac{\lambda^2}{2} |\nabla_{\mathbf{r}} \phi(\mathbf{r}(\mathbf{R}, t), t)|^2 \right) d\mathbf{R} dt, \\ \mathcal{A}_2(\mathbf{r}) &:= - \int_{(D_0)_T} m(\lambda) f_L(\phi(\mathbf{r}(\mathbf{R}, t), t)) f_I(\phi(\mathbf{r}(\mathbf{R}, t), t), c(\mathbf{r}(\mathbf{R}, t), t)) d\mathbf{R} dt \\ &\quad - \int_{(D_0)_T} \chi_1(\phi(\mathbf{r}(\mathbf{R}, t), t)) f_b^{ex}(c(\mathbf{r}(\mathbf{R}, t), t)) d\mathbf{R} dt, \end{aligned} \quad (4.1.25)$$

and evaluate the first variation of each one separately. The first term in  $\mathcal{A}_1$  provides the Euler equation part in the momentum balance, as discussed in lemma 3.3 For the remaining terms following [327], we obtain the first variation as follows:

$$\begin{aligned} \delta_{\mathbf{r}}^{L^2} \mathcal{A}_1(\mathbf{r}) &= -\frac{d}{dk} \Big|_{k=0} \int_{(D_0)_T} f_L(\phi(\mathbf{r}^k(\mathbf{R}, t), t)) d\mathbf{R} dt - \frac{d}{dk} \Big|_{k=0} \int_{(D_0)_T} \frac{\lambda^2}{2} |\nabla_{\mathbf{r}^k} \phi(\mathbf{r}^k(\mathbf{R}, t), t)|^2 d\mathbf{R} dt \\ &= - \int_{(D_0)_T} f'_L(\phi) \nabla_{\mathbf{r}}^j \phi \mathbf{y}^j d\mathbf{R} dt - \int_{(D_0)_T} \lambda^2 \nabla_{\mathbf{r}}^i \phi \frac{d}{dk} \Big|_{k=0} (\nabla_{\mathbf{r}^k}^j \phi(\mathbf{r}^k, t) \nabla_{\mathbf{r}^k}^i \mathbf{r}^j) d\mathbf{R} dt \\ &= - \int_{(D_0)_T} f'_L(\phi) \nabla_{\mathbf{r}}^j \phi \mathbf{y}^j d\mathbf{R} dt - \int_{(D_0)_T} \lambda^2 \nabla_{\mathbf{r}}^i \phi \nabla_{\mathbf{r}}^j \nabla_{\mathbf{r}}^i \phi(\mathbf{r}, t) \mathbf{y}^j d\mathbf{R} dt \\ &\quad + \int_{(D_0)_T} \lambda^2 \nabla_{\mathbf{r}}^i \phi(\mathbf{r}, t) \nabla_{\mathbf{r}}^j \phi(\mathbf{r}, t) \nabla_{\mathbf{r}}^i \mathbf{y}^j d\mathbf{R} dt \end{aligned} \quad (4.1.26)$$

Moreover, the variation of the second part reads

$$\begin{aligned}
 \delta_{\mathbf{r}}^{L^2} \mathcal{A}_2(\mathbf{r}) = & - \int_{(D_0)_T} m(\lambda) \frac{d}{dk} \Big|_{k=0} f_L(\phi(\mathbf{r}^k(\mathbf{R}, t), t)) f_I(\phi(\mathbf{r}(\mathbf{R}, t), t), c(\mathbf{r}(\mathbf{R}, t), t)) d\mathbf{R} dt \\
 & - \int_{(D_0)_T} m(\lambda) f_L(\phi(\mathbf{r}(\mathbf{R}, t), t)) \frac{d}{dk} \Big|_{k=0} f_I(\phi(\mathbf{r}^k(\mathbf{R}, t), t), c(\mathbf{r}^k(\mathbf{R}, t), t)) d\mathbf{R} dt \\
 & - \int_{(D_0)_T} \frac{d}{dk} \Big|_{k=0} \chi_1(\phi(\mathbf{r}^k(\mathbf{R}, t), t)) f_b^{ex}(c(\mathbf{r}(\mathbf{R}, t), t)) d\mathbf{R} dt, \\
 & - \int_{(D_0)_T} \chi_1(\phi(\mathbf{r}(\mathbf{R}, t), t)) \frac{d}{dk} \Big|_{k=0} f_b^{ex}(c(\mathbf{r}^k(\mathbf{R}, t), t)) d\mathbf{R} dt, \tag{4.1.27}
 \end{aligned}$$

or equivalently

$$\begin{aligned}
 \delta_{\mathbf{r}}^{L^2} \mathcal{A}_2(\mathbf{r}) = & - \int_{(D_0)_T} m(\lambda) f_L'(\phi) \nabla_{\mathbf{r}}^j \phi \mathbf{y}^j f_I(\phi(\mathbf{r}, t), c(\mathbf{r}, t)) d\mathbf{R} dt \\
 & - \int_{(D_0)_T} m(\lambda) f_L(\phi) \partial_{\phi} f_I(\phi(\mathbf{r}, t), c(\mathbf{r}, t)) \nabla_{\mathbf{r}}^j \phi \mathbf{y}^j d\mathbf{R} dt \\
 & - \int_{(D_0)_T} m(\lambda) f_L(\phi) \partial_c f_I(\phi(\mathbf{r}, t), c(\mathbf{r}, t)) \nabla_{\mathbf{r}}^j c \mathbf{y}^j d\mathbf{R} dt \\
 & - \int_{(D_0)_T} \chi_1'(\phi(\mathbf{r}, t)) \nabla_{\mathbf{r}}^j \phi \mathbf{y}^j f_b^{ex}(c(\mathbf{r}, t)) d\mathbf{R} dt, \\
 & - \int_{(D_0)_T} \chi_1(\phi(\mathbf{r}(\mathbf{R}, t), t)) f_b^{ex}(c(\mathbf{r}, t)) \nabla_{\mathbf{r}}^j c \mathbf{y}^j d\mathbf{R} dt. \tag{4.1.28}
 \end{aligned}$$

Hence, by adding the two variations and by considering the fact that  $\mathbf{y}$  is arbitrary and divergence free, we deduce by the Least Action Principle, i.e.,  $\delta_{\mathbf{r}}^{L^2} \mathcal{A}(\mathbf{r}) = 0$ , the balance

$$\begin{aligned}
 \partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v} = & -\lambda^2 \operatorname{div}(\nabla \phi \otimes \nabla \phi) - \mu(\phi) \nabla \phi - m(\lambda) \nabla(f_L(\phi) f_I(\phi, c)) - \nabla(\chi_1(\phi) f_b^{ex}(c)) \\
 = & -\lambda^2 \operatorname{div}(\nabla \phi \otimes \nabla \phi) - \nabla(f_L(\phi) + \frac{\lambda^2}{2} |\nabla \phi|^2) - m(\lambda) \nabla(f_L(\phi) f_I(\phi, c)) - \nabla(\chi_1(\phi) f_b^{ex}(c)) \\
 = & -\nabla(f_L(\phi) + \frac{\lambda^2}{2} |\nabla \phi|^2) - m(\lambda) \nabla(f_L(\phi) f_I(\phi, c)) - \nabla(\chi_1(\phi) f_b^{ex}(c)) \\
 = & -\nabla f_{\lambda}(\phi, c), \tag{4.1.29}
 \end{aligned}$$

where the elastic surface stress term  $-\lambda^2 \operatorname{div}(\nabla \phi \otimes \nabla \phi)$  is neglected by a simple algebraic calculation by taking into account the identity  $\operatorname{div}(\nabla \phi \otimes \nabla \phi) = \frac{1}{2} \nabla |\nabla \phi|^2 + \Delta \phi \nabla \phi$  (see [316] for the proof), i.e.,

$$\begin{aligned}
 -\lambda^2 \operatorname{div}(\nabla \phi \otimes \nabla \phi) + \nabla(f_L(\phi) + \frac{\lambda^2}{2} |\nabla \phi|^2) = & -\frac{\lambda^2}{2} \nabla |\nabla \phi|^2 - \lambda^2 \Delta \phi \nabla \phi + \nabla(f_L(\phi) + \frac{\lambda^2}{2} |\nabla \phi|^2) \\
 = & -\frac{\lambda^2}{2} \nabla |\nabla \phi|^2 - \lambda^2 \Delta \phi \nabla \phi + f_L'(\phi) \nabla \phi - \lambda^2 \Delta \phi \nabla \phi \\
 =: & \mu(\phi) \nabla \phi. \tag{4.1.30}
 \end{aligned}$$

It is worth mentioning that the term on the right hand side of (4.1.29) can be directly derived, as a consequence of the Principle of Virtual Work (see Remark 3.22). Finally, the remaining terms  $-\Delta \mathbf{v} + \nabla p$  enter the momentum balance (4.1.24), due to the Maximum Dissipation Principle from Lemma 3.5 and by Remark 3.19 (Weyl's decomposition).  $\square$

Alternatively, we can consider the dissipation functional in the diffuse interface approach and the related principle to be summarised in the following lemma.

**Lemma 4.1 (Maximum Dissipation Principle).** *The dissipation  $\mathcal{D}$ , can be derived from the time rate of change in the total energy for the whole coupled system according to the law  $\frac{dE_{total}}{dt} = -\mathcal{D}$ . Consequently if we consider the total energy functional of the system to be given by*

$$E_{total}(\mathbf{v}, \phi, c) := E_{kinetic}(\mathbf{v}) + \mathcal{F}_{ads}(\phi, c) := \int_D \frac{1}{2} |\mathbf{v}|^2 + \lambda^2 f_\lambda(\phi, c) \, d\mathbf{r}, \quad (4.1.31)$$

*we can evaluate the maximum value for the dissipation (first variation over  $\mathbf{v}$ ) from the following dissipation functional in the diffusive interface approach, which includes the contribution of the related potentials, i.e.,*

$$\mathcal{D}(\mathbf{v}, \phi, c) := -\frac{dE_{total}}{dt} = \int_D |\nabla \mathbf{v}|^2 \, d\mathbf{r} + \lambda^2 M_c \int_D c |\nabla F_c|^2 \, d\mathbf{r} + \lambda^2 M_\phi \int_D |\nabla F_\phi|^2 \, d\mathbf{r}, \quad (4.1.32)$$

*where we denoted the related chemical potentials as  $F_\phi := \partial_\phi f_\lambda$  and analogously  $F_c := \partial_c f_\lambda$ , with  $f_\lambda := f_\lambda(\phi, c)$  to be the adsorption free energy density defined in (4.1.3).*

*Proof.* The form (4.1.32) for the dissipation can be obtained using the definition of the total energy (4.1.31), lemma 3.2 and the advective Cahn-Hilliard flow equations (4.1.22), as follows:

$$\begin{aligned} \mathcal{D}(\mathbf{v}, \phi, c) &:= -\frac{dE_{total}}{dt} := -\frac{d}{dt} \left( \int_D \frac{1}{2} |\mathbf{v}|^2 + \lambda^2 f_\lambda(\phi, c) \, d\mathbf{r} \right) \\ &= \int_D |\nabla \mathbf{v}|^2 \, d\mathbf{r} - \lambda^2 \int_D (F_\phi \partial_t \phi + F_c \partial_t c) \, d\mathbf{r} \\ &= \int_D |\nabla \mathbf{v}|^2 \, d\mathbf{r} - \lambda^2 \int_D (M_\phi F_\phi \Delta F_\phi + M_c F_c \operatorname{div}(c \nabla F_c)) \, d\mathbf{r} + \lambda^2 \int_D \mathbf{v} \cdot (F_\phi \nabla \phi + F_c \nabla c) \, d\mathbf{r} \\ &= \int_D |\nabla \mathbf{v}|^2 \, d\mathbf{r} + \lambda^2 M_\phi \int_D |\nabla F_\phi|^2 \, d\mathbf{r} + \lambda^2 M_c \int_D c |\nabla F_c|^2 \, d\mathbf{r} + \lambda^2 \int_D \mathbf{v} \cdot \nabla f_\lambda(\phi, c) \, d\mathbf{r} \\ &= \int_D |\nabla \mathbf{v}|^2 \, d\mathbf{r} + \lambda^2 M_\phi \int_D |\nabla F_\phi|^2 \, d\mathbf{r} + \lambda^2 M_c \int_D c |\nabla F_c|^2 \, d\mathbf{r}, \end{aligned} \quad (4.1.33)$$

where the last term vanished after integration by parts, due to the incompressibility constraint  $\operatorname{div}(\mathbf{v}) = 0$ . The variation  $\delta_{\mathbf{v}}^{L^2} \mathcal{D}(\mathbf{v}, \phi, c)$  in the direction of an arbitrary vector valued divergence free test function, e.g.,  $\mathbf{y} \in L^2(0, T; H_{div}^1(D))_d$ ,  $\mathbf{y} \cdot \mathbf{n} = 0$  on  $\partial D$ . Since in the diffusive interface method can be applied by an additional dissipation term, which corresponds to relaxation and implies Allen-Cahn type equations and hence we can evaluate the variation as follows:

$$\begin{aligned} \delta_{\mathbf{v}}^{L^2} \mathcal{D}(\mathbf{v}, \phi, c) &= \lim_{\varepsilon \rightarrow 0} 2 \int_D (\nabla \mathbf{v} + \varepsilon \nabla \mathbf{y}) : \nabla \mathbf{y} \, d\mathbf{r} + \lim_{\varepsilon \rightarrow 0} 2\lambda^2 M_\phi^{-1} \int_D [\partial_t \phi + (\mathbf{v} + \varepsilon \mathbf{y}) \cdot \nabla \phi] \mathbf{y} \cdot \nabla \phi \, d\mathbf{r} \\ &\quad + \lim_{\varepsilon \rightarrow 0} 2\lambda^2 M_c^{-1} \int_D [\partial_t c + (\mathbf{v} + \varepsilon \mathbf{y}) \cdot \nabla c] \mathbf{y} \cdot \nabla c \, d\mathbf{r} \\ &= -2 \int_D (\Delta \mathbf{v} - \lambda^2 M_c^{-1} (\partial_t c + \mathbf{v} \cdot \nabla c) \cdot \nabla c - \lambda^2 M_\phi^{-1} (\partial_t \phi + \mathbf{v} \cdot \nabla \phi) \cdot \nabla \phi) \cdot \mathbf{y} \, d\mathbf{r} = 0, \end{aligned} \quad (4.1.34)$$

which follows after integration by parts applied to the first term. Therefore, by Weyl's decomposition, we obtain the following system with dissipative force for incompressible flow, i.e.,

$$\Delta \mathbf{v} - \lambda^2 M_\phi^{-1} (\partial_t \phi + \mathbf{v} \cdot \nabla \phi) \cdot \nabla \phi - \lambda^2 M_c^{-1} (\partial_t c + \mathbf{v} \cdot \nabla c) \cdot \nabla c = \nabla \tilde{p}. \quad (4.1.35)$$

Combining with the Euler equation part obtained from the Least Action Principle, we

can deduce the following momentum balance

$$\Delta \mathbf{v} - \lambda^2 M_\phi^{-1} (\partial_t \phi + \mathbf{v} \cdot \nabla \phi) \cdot \nabla \phi - \lambda^2 M_c^{-1} (\partial_t c + \mathbf{v} \cdot \nabla c) \cdot \nabla c = \nabla p + \partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}. \quad (4.1.36)$$

Hence, the above result suggests that the sum of the dissipative terms  $-\lambda^2 M_\phi^{-1} (\partial_t \phi + \mathbf{v} \cdot \nabla \phi) \cdot \nabla \phi - \lambda^2 M_c^{-1} (\partial_t c + \mathbf{v} \cdot \nabla c) \cdot \nabla c$ , is equivalent to the conservative term  $-\lambda^2 \operatorname{div}(\nabla \phi \otimes \nabla \phi) - \nabla(f_L(\phi) + \frac{\lambda^2}{2} |\nabla \phi|^2) - m(\lambda) \nabla(f_L(\phi) f_I(\phi, c)) - \nabla(\chi_1(\phi) f_b^{ex}(c))$  in (4.1.29), derived by the Least Action Principle earlier. For more details on the Maximum Dissipation Principle and variational modelling of complex flows, see also [316, 317].  $\square$

## 4.2 The Poisson-Nerst-Planck/Navier-Stokes system.

In this thesis, we have so far provided an overview of the mathematical framework in the context of phase separating complex fluid mixtures. Roughly speaking, we reviewed the already existing framework and took another step forward to the variational modelling and analysis of the various aspects related to the physics, the mathematical derivation and analysis as well as numerics for the binary and ternary Cahn-Hilliard type dynamics, in homogeneous and periodically perforated domains. We have also considered the extension to the coupling to the Navier-Stokes equations. Moreover, thermodynamically consistent modelling in the context of GENERIC formalism, as we observed, forms another interesting and still challenging part in the general research area of complex fluids. Furthermore, we deeply investigated the application of formal homogenization arguments to microscopic models, aiming to provide convergence to effective/upscaled approximations. Hence, we demonstrated all the essential and necessary mathematical background and the ability to approach more applied problems of direct practical interest, in science and engineering.

Therefore, as a possible future direction, one could investigate the mathematical background behind the modelling of batteries [250–252, 347, 348] and generally efficient and reliable energy storage systems, a still open and challenging research area. To this end, our considerations are not restricted to only porous media with periodic perforated structure, but we shall consider a broader range of composite media, including materials with random geometry of perforations, a more natural assumption that provides the need to sufficiently examine the related principles of stochastic homogenization [256–259, 349].

We shall establish some introductory considerations on the mathematical modelling of energy storage systems such as Lithium-Ion batteries or fuel cells, starting from a rather fundamental model, the Poisson-Nernst-Planck system (PNP). This model and some variant formulations, have been already examined in the context of existence of unique weak solutions by many authors such as for example, [47, 350–352] and due to the fact that the PNP system coupled to fluid flow (Navier-Stokes) is extensively used to model the transport of charged particles in periodic composite perforated media and homogenization [353–355], it appears in many physical and biological applications, such as fuel cells [55, 58, 59], ion particles in electrokinetic fluids [356, 357] and other advanced



concepts. In the following paragraph, we provide an overview of the general derivation of the PNP system coupled to Navier-Stokes equations by adapting the already discussed methodology on energetic variations, due to the second law of thermodynamics.

Following the same procedure as in subsection 4.1.1, the Poisson-Nerst-Planck/Navier-Stokes system can be derived by an Energetic Variational Approach consisted of the Least Action and Maximum Dissipation Principles, simultaneously with the classical idea of gradient flows, as a consequence of the Second Law of Thermodynamics for minimizing the free energy/maximizing the entropy (see [47]). It is composed of two convective Cahn-Hilliard type evolution equations for the charge distribution of particles coupled with a Navier-Stokes momentum balance and a Poisson equation for the electric potential. The derivation can be summarised in the following theorem.

**Theorem 4.2.1 (Derivation of the PNP/Navier-Stokes system).** *We consider the least action principle together with an incompressibility assumption  $J = \det(Q) = 1$ , to be formally applied to the following action functional in the Lagrangian setting:*

$$\begin{aligned} \mathcal{A}_{PNP}(\mathbf{r}) := & \int_{(D_0)_T} \left( \frac{1}{2J} \rho_0(\mathbf{R}) |\partial_t \mathbf{r}|^2 - f_L(J^{-1} \rho_0(\mathbf{R})) - \frac{\lambda^2}{2} |Q^{-T} \nabla_{\mathbf{R}} J^{-1} \phi_0|^2 \right) J d\mathbf{R} dt \\ & - \int_{(D_0)_T} C \left( J^{-1} c_-^0(\mathbf{R}) \ln((c_-^\infty J)^{-1} c_-^0(\mathbf{R})) + c_+^0(\mathbf{R}) \ln((c_+^\infty J)^{-1} c_+^0(\mathbf{R})) \right) J d\mathbf{R} dt, \end{aligned} \quad (4.2.1)$$

where  $g_0(\mathbf{R}) = g(\mathbf{R}, t)|_{t=0}$ ,  $g := \{\rho, c_-, c_+, \phi\}$ , and the parameters are interpreted as follows:  $\rho(\mathbf{r}, t)$  is the mass density as usual,  $c_+ := c_+(\mathbf{r}, t)$  and  $c_- := c_-(\mathbf{r}, t)$  are the positive and negative charge distributions, respectively and  $\phi(\mathbf{r}, t)$  stands for the electric potential, (note that  $\mathbf{r} := \mathbf{r}(\mathbf{R}, t)$ ). Finally  $C := C(\Theta)$  is a constant depending on the absolute system's temperature  $\Theta$ ,  $c_\pm^\infty$  are the characteristic charge distributions and the constant  $\lambda^2$  is interpreted in this particular problem, as the dielectrics of the solutions. In addition, we apply the maximum dissipation principle to the related dissipation functional, which can be expressed in the following form

$$\mathcal{D}(\mathbf{v}, c_\pm) := \int_D \left( \frac{C}{\mathbb{D}_-} c_- |\mathbf{v}_- - \mathbf{v}|^2 + \frac{C}{\mathbb{D}_+} c_+ |\mathbf{v}_+ - \mathbf{v}|^2 + \eta |\nabla \mathbf{v}|^2 \right) d\mathbf{x}, \quad (4.2.2)$$

where  $\mathbf{v}_\pm$  denote effective velocities of negative and positive charges and  $\mathbb{D}_\pm$  are diffusion constant coefficients of negative or positive ions, respectively. The resulting system in the Eulerian description, is the following Poisson-Nerst-Planck/Navier-Stokes coupling in  $D_T$ , (where we skipped the arguments  $(\mathbf{r}, t)$  of the functions for simplicity):

$$\begin{cases} \partial_t c_\pm + \operatorname{div}(\mathbf{v} c_\pm) = \operatorname{div}(\mathbb{D}_\pm \nabla c_\pm - C_e \mathbb{D}_\pm c_\pm \nabla \phi) =: -\operatorname{div}(\mathbf{J}_\pm(c_\pm, \phi)), \\ \rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) - \eta \Delta \mathbf{v} + \nabla p = (c_- - c_+) C_e \nabla \phi, \\ -\lambda^2 \Delta \phi = C_e (c_+ - c_-) \text{ with } \operatorname{div}(\mathbf{v}) = 0. \end{cases} \quad (4.2.3)$$

Note that in the system above we consider two equations of exactly the same type for the charge transport, one for the negative and one other for the positive (and the related diffusion constants), but we wrote it down like this for simplicity.

Furthermore in the above model, we admit the same notation as earlier for the pressure, i.e.,  $p$  and the constant term  $C_e := ze$  stands for the product of the valence  $z$  of ion and the

charge  $e$  of one electron. In addition, we assume that the related fluxes  $\mathbf{J}_+(c_+, \phi_+), \mathbf{J}_-(c_-, \phi_-)$  satisfy non-flux boundary conditions and the velocity a non-slip boundary condition, i.e.,  $\mathbf{v} = 0$  on  $\partial D$ . Finally we consider a double-well electric potential of the form:

$$\phi(\mathbf{r}) := ze\lambda^{-2} \int_D G(\mathbf{r}, \mathbf{x})(c_- - c_+)(\mathbf{x}) d\mathbf{x}, \quad (4.2.4)$$

where  $G(\mathbf{r}, \mathbf{x})$  stands for the Green's kernel.

*Proof.* The combination of the velocity transport terms in the momentum balance, i.e.,

$$\int_{D_T} \rho (\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) \cdot \tilde{\mathbf{y}} d\mathbf{r} dt, \quad (4.2.5)$$

results immediately after applying the least action principle to following part of the action functional for  $J = \det(Q) = 1$ ,

$$\int_{(D_0)_T} \frac{1}{2J} \rho_0(\mathbf{R}) |\partial_t \mathbf{r}|^2 J d\mathbf{R} dt. \quad (4.2.6)$$

Hence we obtain,

$$\begin{aligned} \frac{d}{dk} \Big|_{k=0} \int_{(D_0)_T} \left( \frac{1}{2} \rho_0(\mathbf{R}) |\partial_t \mathbf{r}|^2 \right) d\mathbf{R} dt &= - \int_{(D_0)_T} \left( \rho_0(\mathbf{R}) \frac{d}{dt} (\partial_t \mathbf{r}) \right) \cdot \mathbf{y} d\mathbf{R} dt \\ &= - \int_{D_T} \rho(\mathbf{r}, t) (\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{r} \mathbf{v}) \cdot \mathbf{y} d\mathbf{r} dt. \end{aligned} \quad (4.2.7)$$

A more detailed proof is provided also in lemma 3.3 including the related internal energy terms. Therefore, Helmholtz-Weyl's decomposition as explained in Remark 3.19 implies the existence of a pressure  $p_1 \in H^1(D)$  such that,

$$-\rho (\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = \nabla p_1. \quad (4.2.8)$$

The remaining terms in the momentum balance, can be derived formally by the maximum dissipation principle applied to the functional (4.2.18), or in other words the Gâteaux differential with respect to the velocity  $\mathbf{v}$  for all vector valued divergence free test functions, i.e.,  $\mathbf{y} \in L^2(0, T; H_{div}^1(D))_d$ ,  $\mathbf{y} \cdot \mathbf{n} = 0$  on  $\partial D$ , as follows:

$$\begin{aligned} \delta_{\mathbf{v}}^2 \mathcal{D}(\mathbf{v}, c_{\pm}) &:= \lim_{k \rightarrow 0} k^{-1} \int_D \left( \frac{C}{\mathbb{D}_-} c_- |\mathbf{v}_- - (\mathbf{v} + k\mathbf{y})|^2 + \frac{C}{\mathbb{D}_+} c_+ |\mathbf{v}_+ - (\mathbf{v} + k\mathbf{y})|^2 + \eta |\nabla \mathbf{v} + k \nabla \mathbf{y}|^2 \right) d\mathbf{r} \\ &\quad - \lim_{k \rightarrow 0} k^{-1} \int_D \left( \frac{C}{\mathbb{D}_-} c_- |\mathbf{v}_- - \mathbf{v}|^2 + \frac{C}{\mathbb{D}_+} c_+ |\mathbf{v}_+ - \mathbf{v}|^2 + \eta |\nabla \mathbf{v}|^2 \right) d\mathbf{r} \\ &= \lim_{k \rightarrow 0} k^{-1} \int_D \left( \frac{C}{\mathbb{D}_-} c_- (-2k(\mathbf{v}_- - \mathbf{v}) \cdot \mathbf{y} + k^2 \mathbf{y}^2) + \frac{C}{\mathbb{D}_+} c_+ (-2k(\mathbf{v}_+ - \mathbf{v}) \cdot \mathbf{y} + k^2 \mathbf{y}^2) \right) d\mathbf{r} \\ &\quad + \lim_{k \rightarrow 0} k^{-1} \int_D (2\eta k \nabla \mathbf{v} : \nabla \mathbf{y}) d\mathbf{r} + \lim_{k \rightarrow 0} k^{-1} \int_D \eta k^2 |\nabla \mathbf{y}|^2 d\mathbf{r} \\ &= \int_D (2\eta \nabla \mathbf{v} : \nabla \mathbf{y}) d\mathbf{r} - 2 \int_D \left( \frac{C}{\mathbb{D}_-} c_- (\mathbf{v}_- - \mathbf{v}) + \frac{C}{\mathbb{D}_+} c_+ (\mathbf{v}_+ - \mathbf{v}) \right) \cdot \mathbf{y} d\mathbf{r} \\ &= - \int_D 2\eta \Delta \mathbf{v} \cdot \mathbf{y} d\mathbf{r} - 2 \int_D \left( \frac{C}{\mathbb{D}_-} c_- (\mathbf{v}_- - \mathbf{v}) + \frac{C}{\mathbb{D}_+} c_+ (\mathbf{v}_+ - \mathbf{v}) \right) \cdot \mathbf{y} d\mathbf{r}. \end{aligned} \quad (4.2.9)$$

This provides the remaining dissipative terms in the momentum balance,

$$-\eta \Delta \mathbf{v} + \frac{C}{\mathbb{D}_-} c_- (\mathbf{v}_- - \mathbf{v}_-) + \frac{C}{\mathbb{D}_+} c_+ (\mathbf{v}_+ - \mathbf{v}_+) = \nabla p_2, \quad (4.2.10)$$

where  $p_2$  is considered as a Lagrange multiplier for  $\operatorname{div}(\mathbf{v}) = 0$  and is going to be adsorbed in the total pressure. We will next proceed with the gradient flow derivation of the evolution

equations for the distributions of the charged particles, summarised in the following lemma.

**Lemma 4.2.** *The following dynamic descriptions (4.2.11) for the charge particle distributions:*

$$\partial_t c_{\pm} = \operatorname{div}(\mathbb{D}_{\pm} \nabla c_{\pm} - C_e \mathbb{D}_{\pm} c_{\pm} \nabla \phi), \quad (4.2.11)$$

can be formally derived by the classical idea of gradient flows, that is

$$\langle \partial_t c_{\pm}, v \rangle_{L^2(D)} = -\langle \nabla_{c_{\pm}}^{L^2} \mathcal{F}_{PNP}(c_{\pm}), v \rangle_{\mathcal{Z}(D)}, \quad (4.2.12)$$

for all  $v \in L^2(D) \subseteq \mathcal{Z}(D)$ , applied in order to minimize the system's free energy functional,

$$\mathcal{F}_{PNP}(c_{\pm}) := \int_D C \left( c_+ \ln((c_+^{\infty})^{-1} c_+) + c_- \ln((c_-^{\infty})^{-1} c_-) \right) + \lambda^2 |\nabla \phi|^2 \, d\mathbf{r}, \quad (4.2.13)$$

subject to the following semi-inner product [20, 84]:

$$\langle u, v \rangle_{H^1(D)} := \langle \nabla u, \nabla v \rangle_{\mathbb{M}} := \langle \mathbb{M} \nabla u, \nabla v \rangle_{L^2(D)}, \quad \forall u, v \in H^1(D), \quad (4.2.14)$$

where in this case we make the following assumption for the mobility coefficient:  $\mathbb{M} := C^{-1} \mathbb{D}_{\pm} c_{\pm}$  in which  $C := C(\Theta)$  the absolute temperature dependent constant introduced in the assumption and  $\mathbb{D}_{\pm}$  the diffusion constants.

*Proof.* We consider the first variation ( $L^2$ -gradient) of the free energy  $\mathcal{F}_{PNP}$  at  $c_+$  and separately at  $c_-$ , with the help of the Poisson relation  $-\lambda^2 \Delta \phi = C_e (c_+ - c_-)$ , which directly implies by simple differentiation with respect to  $c_+$ :

$$\begin{aligned} \delta_{c_+}^{L^2} \mathcal{F}_{PNP}(c_+) &:= \frac{d}{dk} \Big|_{k=0} \left( \mathcal{F}_{PNP}(c_+^k) \right) = C + C \ln((c_+^{\infty})^{-1}) + C \ln(c_+) + C_e \phi \\ &= C(1 + \ln(c_+)) - C \ln(c_+^{\infty}) + C_e \phi, \end{aligned} \quad (4.2.15)$$

where we remind the identification  $C_e = z_e$ . As a result for all  $v \in L^2(D) \subseteq \mathcal{Z}(D)$ , we deduce from (4.2.14) that

$$\begin{aligned} \langle \nabla_{c_+}^{L^2} \mathcal{F}_{PNP}(c_+), v \rangle_{H^1(D)} &:= \langle C^{-1} \mathbb{D}_+ c_+ \nabla (C(1 + \ln(c_+)) - C \ln(c_+^{\infty}) + C_e \phi), \nabla v \rangle_{L^2(D)} \\ &= \langle -\operatorname{div} [\mathbb{D}_+ c_+ \nabla \ln(c_+) + C_e \mathbb{D}_+ c_+ \nabla \phi], v \rangle_{L^2(D)} \\ &= \langle -\operatorname{div} [\mathbb{D}_+ \nabla c_+ + C_e \mathbb{D}_+ \nabla \phi], v \rangle_{L^2(D)}, \end{aligned} \quad (4.2.16)$$

after integration by parts and consequently with the help of the gradient flow formulation (4.2.12), this is equivalent to (4.2.11) for  $c_+$ . Exactly the same derivation is valid for the negative charge distribution  $c_-$  with  $\mathbb{D}_-$ , (one equation for the (-) and one for the (+)).  $\square$

As a result the system of the charge transport evolution equations (4.2.11), coupled to fluid flow for the macroscopic velocity  $\mathbf{v}$ , implies the following balance equations,

$$\partial_t c_{\pm} + \operatorname{div}(\mathbf{v} c_{\pm}) = \operatorname{div}(\mathbb{D}_{\pm} \nabla c_{\pm} \pm C_e \mathbb{D}_{\pm} c_{\pm} \nabla \phi). \quad (4.2.17)$$

The convective terms  $\operatorname{div}(\mathbf{v} c_{\pm})$  can also enter the system, as a result of the maximum dissipation principle and the force balance by considering the following arguments. We calculate the first variation (with respect to the effective velocities  $\mathbf{v}_{\pm}$ ) of the dissipation

functional (4.2.18)  $\delta_{\mathbf{v}_{\pm}}^{L^2} \frac{1}{2} \mathcal{D}(\mathbf{v}_{\pm}, c_{\pm})$ , using a test function  $\mathbf{y} \in C_c^\infty(D)_d$ , separately for each of the  $\mathbf{v}_{\pm}$ . Therefore the variation with respect to  $\mathbf{v}_+$  implies

$$\begin{aligned} \delta_{\mathbf{v}_+}^{L^2} \frac{1}{2} \mathcal{D}(\mathbf{v}_{\pm}, c_{\pm}) &:= \frac{1}{2} \lim_{k \rightarrow 0} k^{-1} \int_D \left( \frac{C}{\mathbb{D}_-} c_- |\mathbf{v}_- - \mathbf{v}|^2 + \frac{C}{\mathbb{D}_+} c_+ |(\mathbf{v}_+ + k\mathbf{y}) - \mathbf{v}|^2 + \eta |\nabla \mathbf{v}|^2 \right) d\mathbf{r} \\ &\quad - \frac{1}{2} \lim_{k \rightarrow 0} k^{-1} \int_D \left( \frac{C}{\mathbb{D}_-} c_- |\mathbf{v}_- - \mathbf{v}|^2 + \frac{C}{\mathbb{D}_+} c_+ |\mathbf{v}_+ - \mathbf{v}|^2 + \eta |\nabla \mathbf{v}|^2 \right) d\mathbf{r} \\ &= \frac{1}{2} \lim_{k \rightarrow 0} k^{-1} \int_D \frac{C}{\mathbb{D}_+} c_+ (|(\mathbf{v}_+ + k\mathbf{y}) - \mathbf{v}|^2 - |\mathbf{v}_+ - \mathbf{v}|^2) d\mathbf{r} \\ &= \lim_{k \rightarrow 0} k^{-1} \int_D \frac{C}{\mathbb{D}_+} c_+ k (\mathbf{v}_+ - \mathbf{v}) \cdot \mathbf{y} d\mathbf{r} \\ &= \langle C(\mathbb{D}_+)^{-1} c_+ (\mathbf{v}_+ - \mathbf{v}), \mathbf{y} \rangle_{L^2(D)}. \end{aligned} \quad (4.2.18)$$

Analogously can be obtained the corresponding result for the variation with respect to the velocity  $\mathbf{v}_-$ , i.e.,

$$\delta_{\mathbf{v}_-}^{L^2} \frac{1}{2} \mathcal{D}(\mathbf{v}_{\pm}, c_{\pm}) = \langle C(\mathbb{D}_-)^{-1} c_- (\mathbf{v}_- - \mathbf{v}), \mathbf{y} \rangle_{L^2(D)}. \quad (4.2.19)$$

As a result the total force balance for charge distributions yields

$$c_{\pm} \mathbf{v}_{\pm} = c_{\pm} \mathbf{v} - C^{-1} (\mathbb{D}_{\pm} \nabla c_{\pm} - C_e \mathbb{D}_{\pm} c_{\pm} \nabla \phi) \quad (4.2.20)$$

and if we assume the following kinematic conservation of charge distributions, i.e,  $\partial_t c_{\pm} = -\operatorname{div}(c_{\pm} \mathbf{v}_{\pm})$ , we immediately deduce the convective dynamic descriptions (4.2.17). Finally the last term  $(c_- - c_+) = C_e \nabla \phi$  in the momentum balance appears by substituting the equations (4.2.20) to (4.2.8) and the balance

$$-\eta \Delta \mathbf{v} + \frac{C}{\mathbb{D}_-} c_- (\mathbf{v} - \mathbf{v}_-) + \frac{C}{\mathbb{D}_+} c_+ (\mathbf{v} - \mathbf{v}_+) = \nabla p_2, \quad (4.2.21)$$

which were obtained earlier by the least action/maximum dissipation principles and Weyl's decomposition. Therefore if we identify a new pressure term  $\tilde{p}_2 := p_2 - C \nabla c_- - C \nabla c_+$  therefore its gradient can be expressed in the form  $\nabla \tilde{p}_2 = -\eta \Delta \mathbf{v} - (c_- - c_+) C_e \nabla \phi$  and as a result combining the above relationships we arrive to the total balance of momentum:

$$\rho (\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) - \eta \Delta \mathbf{v} + \nabla p = (c_- - c_+) C_e \nabla \phi, \quad (4.2.22)$$

where  $p := p_1 - \tilde{p}_2$  and the proof of theorem 4.2.1 has been completed (see also [47] for more details).  $\square$

Finally, it is worth mentioning that in the same context, various boundary conditions have been considered so far. Hence, apart from homogeneous Neumann for the charge density, the no flux and no slip condition for the velocity, one of the most important constraints in the context of electrokinetics is the boundary effects related to the potential  $\phi$ , which are usually considered to be of Dirichlet or Neumann type. Further investigation on the mathematical modelling of composite batteries, the relation to the Poisson-Nerst-Planck system and Cahn-Hilliard coupled with Navier-Stokes dynamics, would be left as a possible future direction.

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