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Abstract. A recently introduced method for the derivation of thermodynamically consistent boundary conditions will be used in order to study the interaction of two fluids at the common interface and the contact line to a solid body. The calculations allow for temperature dependent surface energy/ surface tension and yield thermodynamical conditions on dynamic contact angles. Furthermore, we will show how Mean Curvature Flow and Mullins-Sekerka models fit into this general framework and give a possible explanation for the Dussan and Davis experiment [10] compared to the Huh and Scriven Paradox [17] within the presented theory.

1. Introduction

Moving interfaces and the interaction of moving interfaces with solids and liquids is an important issue in many fields of the applied physics such as engineering or biology. Some of the currently investigated problems include cell membranes in biology [21, 22] or microfluidics [33]. Other examples might be found in [6].

There is a huge literature on the subject of fluid-fluid interactions, among the most remarkable seems to us the recent paper by Buscaglia and Ausas [7], which up to now, to the author's opinion, is the most complete approach from the thermodynamical point of view. Reference to former results can be found therein.

Further interesting summaries on existing models can be found in the book by de Gennes, Brochard-Wyart and Quéré [9] and recent reviews by Bonn et. al. [6]. Further classical books on the topic of surface processes and surface energy are by Adam [5] and Oudar [26] (the latter only for solid surfaces).

Bonn et. al. [6] emphasize the different scales we face when dealing with the contact line: The molecular level, the smooth interface level and the sharp interface level. Depending on the scale, the notion of contact angle has different meaning and we note that the mathematically rigorous transition between these three scales is a challenging topic for future investigations, although this has been studied by simulations (refer to [6] and reference therein). In the present approach, we will not focus on the molecular level, but shortly discuss the smooth interface level in the context of moving contact lines. Thus, we assume the choice of the contact angle to be uniquely given by the sharp interface. However, note that we will discover that some macroscopic effects can be described within sharp interface models if we account for macroscopic effects that have their roots on the micro scale.

To the author's knowledge, there is no satisfactory approach to a complete thermodynamical description of moving fluid interfaces within modern thermodynamical approaches, and the closest approach seems to be the aforementioned approach by Buscaglia and Ausas [7]. However, they did not include several issues such as temperature dependent surface tension, fluids slipping on top of another, mean curvature flow, Mullins-Sekerka flow and moving contact lines with no slip condition for the bulk. To include all these effects into a unified framework is the main result of this study.

Of course, the major issue in this context are the derivation of boundary conditions for tangential and normal stress on the interface, derivation of thermodynamically consistent formulas for the (dynamic) contact angle and the moving contact line. A particular issue involved with the derivation of contact angles was already outlined by Buscaglia and Ausas [7]: The dynamically varying contact angles as soon as the fluid interface moves along the wall, see Bonn et. al. [6] or de Gennes et. al. [9]. While diffuse interface models come up with this feature automatically (see Heida [12], Qian, Wang and Sheng [28, 29]) in sharp interface models one might be tempted to introducing a contact line energy or entropy depending on the local contact angle. De Gennes et. al. [9] in their book show that effects of such an energy are negligible, and the calculations below will show that indeed such an assumption would lead to strange effects. However, we cannot circumvent the assumption of a contact line *dissipation*.

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Note in this context that the relation between sharp interface models and diffuse interface models has been subject to intensive studies by formal calculations and rigorous asymptotic analysis, refer to [3, 1, 6, 18, 27, 29] and references therein. However, to the authors knowledge, there is no result taking sufficient care of the limit behavior at the contact line.

Another important issue is the correct choice of the slip condition on the solid surface: While Dussan and Davis [10] observed that the moving of the contact line is due to a rolling movement with no-slip condition on the velocity field, Huh and Scriven [17] showed that coupling no-slip Stokes equation with a moving contact line should lead to tremendous thermodynamical problems, as dissipation becomes infinite. In this paper, we show that there is indeed a thermodynamically consistent way to couple a moving contact line with no-slip condition on the bulk (refer to subsection 2.10), by including microscopic effects. This approach will be based on effects at the surface that are sharp interface equivalents of diffusive processes in phase field models.

The modeling technique we use is rather simple and can be considered as a simplified version of a recently developed one by Heida [12] and Heida, Málek and Rajagopal [14] in order to study the interactions of immiscible liquids at a moving interface within a diffuse interface approach. The derivations are based on functionals for the total energy $\mathcal{E}$ and the total entropy $\mathcal{S}$. From conservation of global energy and nonnegativity of the rate of entropy production (the second law of thermodynamics) we get restrictions on the form of thermodynamically consistent boundary conditions. Note that the calculations can be performed also in the framework of the so called "assumption of maximum rate of entropy production" (Rajagopal and Srinivasa [30], Heida [12] and Heida, Málek and Rajagopal [14]) or within an Onsager framework such as usually used by Mielke and coworkers [11, 24, 23]. However, we do not focus on theory but on the constitutive equations and their physical implications.

The advantage of our approach is threefold: First, it can be combined with models derived in the context of the maximum rate of entropy production or other thermodynamical methods, second, the derivation is quite easy to understand and does not need mathematical tools beyond calculus on manifolds. This will enable the reader to easily generalize the models to a broad class of applications, deriving suitable models for his own needs. Third, our approach is formulated in an integral / variational formalism that is well suited for numerical simulations as it also provides automatically some apriori estimates.

For the calculations presented below, we focus on the interaction of immiscible Newtonian fluids with a solid boundary. Note that the constitutive equations for the interface and contact line movements are not limited to Newtonian fluids, but may also be generalized to a huge class of non-Newtonian fluids, which are considered in [19, 20] (see also references therein).

The structure of the article is as follows: The next section will provide the geometric setting, basic notations, the most important results and the discussion. In section 3 we introduce some basic concepts from continuum mechanics and some mathematical notations and results which will be used throughout the paper. In section 4, we derive a model for fluid-fluid interactions based on the assumption that surface tension is independent on temperature. These considerations are useful as they help to better understand the fully thermodynamic calculations in section 5. Finally, in section 6, we demonstrate that the inclusion of mean curvature flow or Mullins-Sekerka flow sometimes is reasonable if diffusive surface processes or phase transitions are of macroscopic importance, while in section 7, we show that these models may indeed explain the Dussan-Davis experiment [10] and provide a new view on the Huh and Scriven paradox [17].

2. Physical Setting, Summary of Results and Discussion

This section will summarize all models we derive below and discuss their physical implications as well as their range of applicability. However, it is of course not complete with regard to the class of all models we can obtain. We will mostly skip any details on how these models are derived but postpone most of such discussions to the other sections.

2.1. **Basic assumptions.**

We assume that the system is limited to a bounded domain Ω in dimension $d = 3$ with boundary $\partial\Omega$. In applications, Ω may vary with time t, but although the method we use could easily cope with such situation, we restrict to time independent Ω, for simplicity. The domain Ω is divided into two subdomains, $\Omega_1(t)$ and $\Omega_2(t)$, (now depending on time t) occupied by the respective fluids (See figure 2.1). The Interface between Ω_1 and Ω_2 is denoted Γ with $\boldsymbol{n}_\Gamma$ the outer normal vector of Ω_1 on Γ and κ its curvature. The velocity of Γ will always be denoted by $\boldsymbol{v}$, i.e. $\partial_t\Gamma = \boldsymbol{v}$.

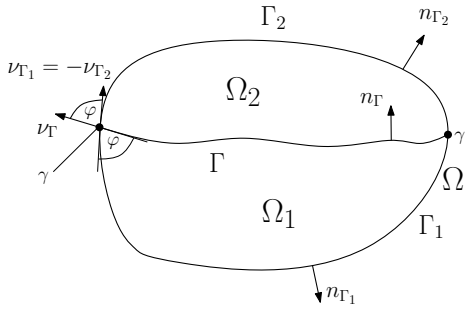

FIGURE 2.1. The domain Ω with its subdomains Ω_1, Ω_2 and the interface Γ.

We call $\Gamma_1 = \partial\Omega_1 \backslash \Gamma = \partial\Omega \cap \partial\Omega_1$ the part of the boundary of Ω_1 which is not part of the boundary of Ω_2 and $\Gamma_2 := \partial\Omega_2 \backslash \Gamma$ respectively. Furthermore, for $\gamma = \partial\Gamma$ the contact line of Γ with $\partial\Omega$, κ_γ the curvature of γ, ν_Γ is the unique normal vector of γ being tangential to Γ and pointing outwards of Γ. Similarly, we define ν_{Γ_1} the unique normal to γ being tangential to Γ_1 and pointing outwards of Γ_1 and $\nu_{\Gamma_2} := -\nu_{\Gamma_1}$. We finally denote by $\boldsymbol{a}_n$ and $\boldsymbol{a}_\tau$ the normal and tangential parts of any vector $\boldsymbol{a}$, and use ∇_τ for the tangential gradient on Γ, Γ_1 and Γ_2.

On Ω_1 and Ω_2 we introduce the densities ϱ_i, the velocity fields $\boldsymbol{v}_i$ and energy fields E_i with $i \in \{1,2\}$ respectively and material derivatives

$$\dot{a} := \partial_t a + \boldsymbol{v}_i \cdot \nabla a\,, \qquad \dot{\boldsymbol{a}} := \partial_t \boldsymbol{a} + (\nabla \boldsymbol{a})\,\boldsymbol{v}_i\,, \qquad \text{on } \Omega_i\,.$$

We then impose the following abstract balance equations of mass, momentum and energy (also refer to section 3):

$$\begin{aligned} \partial_t \varrho_i + \operatorname{div}(\boldsymbol{v}_i \varrho_i) &= 0 \\ \varrho_i \dot{\boldsymbol{v}}_i - \operatorname{div} \mathbb{T}_i &= \boldsymbol{g}_i \qquad \text{on } \Omega_i \\ \varrho_i \dot{E}_i - \operatorname{div}\,(\boldsymbol{q}_i + \mathbb{T}_i \boldsymbol{v}_i) &= \overset{+}{E}_i \end{aligned}$$

where $i \in \{1,2\}$ is the index in the respective domain. For convenience, we will usually write

$$\boldsymbol{h}_i := \boldsymbol{q}_i + \mathbb{T}_i \boldsymbol{v}_i\,. \tag{2.1}$$

If we require that external energy supply is only due to body forces, we get $\overset{+}{E}_i = \boldsymbol{g}_i \cdot \boldsymbol{v}_i$. Further, we write ϑ for the temperature of the system without providing its precise definition at this point (refer to sections 4 and 5).

For simplicity, we assume that ϑ is continuous across the interface Γ. For non-continuous ϑ, refer to Heida [12] to get an idea on how the constitutive equations change. In fact, non-continuity of ϑ basically results in some additional conditions on the temperature jumps or, equivalently, on some additional boundary conditions on the energy fluxes.

For any vector $\boldsymbol{f}$, we denote on any surface with the respective normal vectors by $\boldsymbol{f}_n$ the normal part and by $\boldsymbol{f}_\tau$ the tangential part of $\boldsymbol{f}$.

Denoting $\boldsymbol{T}_2^{\boldsymbol{\Gamma}} := \mathbb{T}_2 \boldsymbol{n}_\Gamma$, $\boldsymbol{T}_1^{\boldsymbol{\Gamma}} := \mathbb{T}_1 \boldsymbol{n}_\Gamma$ on Γ, resp. $\boldsymbol{T}_1^{\boldsymbol{\Gamma}} := \mathbb{T}_1 \boldsymbol{n}_{\Gamma_1}$, $\boldsymbol{T}_2^{\boldsymbol{\Gamma}} := \mathbb{T}_2 \boldsymbol{n}_{\Gamma_2}$ on Γ_1 and Γ_2, we note on one hand, that Newton's third law implies

$$\boldsymbol{T}_1^{\boldsymbol{\Gamma}} = \boldsymbol{T}_2^{\boldsymbol{\Gamma}} =: \boldsymbol{T}^{\boldsymbol{\Gamma}} \quad \text{on } \Gamma \quad \text{if no other forces act on } \Gamma\,. \tag{2.2}$$

while on the other hand, one would suspect$\boldsymbol{v}_1 \cdot \boldsymbol{n}_\Gamma = \boldsymbol{v}_2 \cdot \boldsymbol{n}_\Gamma$ on Γ. However, we cannot rely on (2.2) as we clearly have to expect normal and eventually tangential forces acting on Γ due to surface energy. This discussion is topic of subsection 3.5. Also note that apriori, we cannot say anything about the continuity of the tangential part of $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ on Γ, also we do not know for sure if and how the tangential part of $\boldsymbol{v}$ should be related to $\boldsymbol{v}_{1,\tau}$ and $\boldsymbol{v}_{2,\tau}$. Also note that $\boldsymbol{T}_2^{\boldsymbol{\Gamma}}$ changes orientation between Γ and Γ_2, as $\boldsymbol{n}_\Gamma = -\boldsymbol{n}_{\Gamma_2}$ on Γ.

We study the dynamics of the interface in three steps: In terms of surface energy with thermodynamical supplements, within pure thermodynamics, including temperature dependent surface energies, and finally with a focus on the global balance of mass yielding Mullins-Sekerka-type models.

2.2. **A note on velocity fields and clarifying of notation.** The most interesting quantities for the present study are the velocities of Γ and γ, which should be denoted $\boldsymbol{v}_\Gamma$ and $\boldsymbol{v}_\gamma$. However, we denote consistently the velocity fields in Ω_i by $\boldsymbol{v}_i$ and on Γ_i by $\boldsymbol{v}_{\Gamma,i}$ while we call the velocity of Γ and γ usually by $\boldsymbol{v}$, for the simple reason that the velocity $\boldsymbol{v}_\gamma$ needs to be the continuous continuation of $\boldsymbol{v}_\Gamma$. Throughout the first part of calculations below we will assume that the velocity fields are continuously matched in a sense that

$$\begin{aligned} \boldsymbol{v}_{1,n} = \boldsymbol{v}_{2,n} = \boldsymbol{v}_{\Gamma,n} = \boldsymbol{v}_n \quad &\text{on } \Gamma \text{ and } \gamma\,, \\ \boldsymbol{v}_i = \boldsymbol{v}_{\Gamma,i} \quad &\text{on } \Gamma_i \text{ and } \gamma\,, \end{aligned} \tag{2.3}$$

where $\boldsymbol{v}_n$ is the normal velocity of Γ. For the tangential part, we are left with more degrees of freedom, and we will discuss the several possible models separately.

In section 6 we will give some reasons from asymptotic analysis of phase field models that the velocity field of the interface Γ needs not to coincide with the bulk velocities. Thus, in this case we find

$$\boldsymbol{v} = \boldsymbol{v}_1 + \delta\boldsymbol{v}_1 = \boldsymbol{v}_2 + \delta\boldsymbol{v}_2\,, \tag{2.4}$$

where $\delta\boldsymbol{v}_i$ are perturbations of $\boldsymbol{v}_i$ that are normal to Γ.

2.3. **Resulting equations.** The resulting set of equations under the assumption of (2.3) reads

$$\begin{aligned} \partial_t \varrho_i + \operatorname{div}(\boldsymbol{v}_i \varrho_i) &= 0 & \mathbb{T}_i &= \mu_i \mathbb{D}\boldsymbol{v}_i + (\lambda \operatorname{div} \boldsymbol{v}_i - p_i)\,\mathbb{I} & \\ \varrho_i \dot{\boldsymbol{v}}_i - \operatorname{div} \mathbb{T}_i &= \boldsymbol{g}_i & \boldsymbol{q}_i &= \beta_i \vartheta^{-1} \nabla\vartheta & \text{on } \Omega_i \\ \varrho_i \dot{E}_i - \operatorname{div}(\boldsymbol{q}_i + \mathbb{T}_i \boldsymbol{v}_i) &= \overset{+}{E}_i & & & \end{aligned}$$

and

$$\begin{aligned} \boldsymbol{v}_{i,\tau} = -\alpha_i \boldsymbol{T}^{\boldsymbol{\Gamma}}_{i,\tau} \quad \text{or} \quad \boldsymbol{T}^{\boldsymbol{\Gamma}}_{i,\tau} = \boldsymbol{0} \quad \text{or} \quad \boldsymbol{v}_{i,\tau} = \boldsymbol{0} \quad &\text{on } \Gamma_i\,, \\ \text{and} \quad 0 = \left(\left[\left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1 \right) \cdot \boldsymbol{n}_\Gamma \right] - \kappa\sigma_\Gamma \right)\,, \quad &\text{on } \Gamma\,, \end{aligned}$$

together with

$$\boldsymbol{v}_\tau = -\alpha_\gamma \left(\sigma_\Gamma \nu_\Gamma + \sigma_1 \nu_{\Gamma_1} + \sigma_2 \nu_{\Gamma_2} + \sigma_\gamma \boldsymbol{\kappa}_\gamma \right)_\tau \qquad \text{on } \gamma\,.$$

The last equality can be considered as a generalization of the dynamical contact angle condition

$$v = \alpha\sigma_\Gamma \left(\cos\varphi_{eq} - \cos\varphi \right)\,,$$

with $v = \boldsymbol{v} \cdot \nu_{\Gamma_1}$, which we will also derive below under certain conditions.

Additionally, we find for the tangential part of the constitutive equations on Γ either in case $\boldsymbol{v}_{1,\tau} \neq \boldsymbol{v}_{2,\tau} \neq \boldsymbol{v}_\tau$ on Γ Newtons third law $\boldsymbol{T}^{\boldsymbol{\Gamma}}_1 = \boldsymbol{T}^{\boldsymbol{\Gamma}}_2$ together with

$$\boldsymbol{v}_\tau = \boldsymbol{0}\,, \qquad \boldsymbol{T}^{\boldsymbol{\Gamma}}_{1,\tau} = \beta_2 \left(\boldsymbol{v}_2 - \boldsymbol{v}_1 \right)_\tau\,.$$

Alternatively, we can find in case $\boldsymbol{v}_\tau = \boldsymbol{v}_{1,\tau} \neq \boldsymbol{v}_{2,\tau}$ on Γ that

$$\begin{aligned} \left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1 \right)_\tau = \boldsymbol{0} \quad &\text{on } \Gamma\,, \\ \text{resp.} \quad \left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1 \right)_\tau = \alpha_1 \boldsymbol{v}_\tau \quad &\text{on } \Gamma\,, \\ \text{and} \quad \boldsymbol{T}^{\boldsymbol{\Gamma}}_2 = \alpha_2 \left(\boldsymbol{v}_2 - \boldsymbol{v}_1 \right)_\tau\,. & \end{aligned}$$

Under the assumption of 2.4, we get additional conditions on $\delta\boldsymbol{v}$ which read

$$\delta\boldsymbol{v}_1 = \alpha_\Gamma \left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_{2,n} \left(1 - \tfrac{\tilde{m}_1(\varrho_1,\varrho_2)}{\tilde{m}_2(\varrho_1,\varrho_2)} \right) - \kappa\sigma_\Gamma \boldsymbol{n}_\Gamma \right)$$

for reactive flows, which is a generalization of the mean-curvature flow, see subsections 2.9 and 7.2. Under the constraint $\boldsymbol{v}_1 = \boldsymbol{v}_2$ on Γ, we find

$$\delta\boldsymbol{v}_{1,n} = -\alpha_\Gamma \kappa\sigma_\Gamma \boldsymbol{n}_\Gamma\,.$$

In case of non-reactive flows, i.e. the class of Mullins-Sekerka models, we find under the assumption that $\boldsymbol{v}_1 = \boldsymbol{v}_2$ on Γ that

$$\delta\boldsymbol{v} = \frac{1}{m_{1,0}(\varrho_1,\varrho_2)} \Delta_\Gamma \left(\frac{\kappa\sigma_\Gamma}{m_{1,0}(\varrho_1,\varrho_2)} \right) \boldsymbol{n}_\Gamma\,.$$

2.4. **A first approach to static contact angles.** We start with a very simple model in section 4.1 assuming that the energy $\mathcal{E}$ and entropy $\mathcal{S}$ of the system are given through

$$\mathcal{E} = \int_{\Omega_1} \varrho_1 E_1 + \int_{\Omega_2} \varrho_2 E_2 + \int_\Gamma \sigma_\Gamma + \int_{\Gamma_1} \sigma_1 + \int_{\Gamma_2} \sigma_2 \,, \tag{2.5}$$

$$\mathcal{S} = \int_{\Omega_1} \varrho_1 \eta_1 + \int_{\Omega_2} \varrho_2 \eta_2 \,, \tag{2.6}$$

where η_1 and η_2 measure entropy per energy in the respective domain and σ_Γ, σ_1 and σ_2 are energy per surface area. We assume that $E_i = u_i(\varrho_i, \eta_i) + \frac{1}{2}|\boldsymbol{v}_i|^2$ with u_i the internal energy per mass, or, equivalently, $\eta_i = \eta_i(\varrho_i, E_i, \boldsymbol{v}_i)$ since we know from thermodynamics that $\frac{\partial u_i}{\partial \eta_i} > 0$. This approach corresponds to low surface entropy, i.e. to negligible surface entropy effects. In particular, the surface energy is assumed not to depend on temperature. For simplicity, we further assume $\delta \boldsymbol{v}_i = \boldsymbol{0}$.

Remember that we assume only the normal part of the velocity to be continuous across the interface while the tangential parts may not be continuous. Furthermore, we assume (2.2) to hold for the tangential parts, i.e.

$$\boldsymbol{T}^{\boldsymbol{\Gamma}}_{1,\tau} = \boldsymbol{T}^{\boldsymbol{\Gamma}}_{2,\tau} =: \boldsymbol{T}^{\boldsymbol{\Gamma}}_{\tau} \,, \qquad \text{while} \qquad \boldsymbol{T}^{\boldsymbol{\Gamma}}_{1,n} \not\equiv \boldsymbol{T}^{\boldsymbol{\Gamma}}_{2,n} \,.$$

Denoting φ the angle between ν_1 and ν_Γ, i.e. through $\cos\varphi = \nu_1 \cdot \nu_\Gamma$, global energy balance yields the following condition at the contact line γ:

$$\sigma_\Gamma \cos\varphi + \sigma_1 - \sigma_2 = 0 \,.$$

This is the classical law for the contact angle and is thus not surprising. However, its derivation in section 4 yields some insight into the more complicated calculations afterwards and is thus interesting in itself.

The constitutive equations we derive for the Cauchy stress tensors and the energy fluxes are

$$\begin{aligned} \mathbb{T}_i &= \mu_i \mathbb{D}\boldsymbol{v}_i + (\lambda \operatorname{div} \boldsymbol{v}_i - p_i)\,\mathbb{I} \,, \\ \boldsymbol{q}_i &= \beta_i \vartheta^{-1} \nabla \vartheta \,, \end{aligned} \tag{2.7}$$

where $\mathbb{D}\boldsymbol{v} = \frac{1}{2}\left(\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T\right)$ and $p_i := \varrho_i^2 \frac{\partial E_i}{\partial \varrho_i}$, and we get Newton's third law in presence of surface tension as well as the slip between the fluids at Γ

$$\begin{aligned} 0 &= \left(\left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1\right) \cdot \boldsymbol{n}_\Gamma - \kappa \sigma_\Gamma\right) \,, \\ \boldsymbol{T}^{\boldsymbol{\Gamma}}_{\tau} &= \alpha_\Gamma \left[(\boldsymbol{v}_2)_\tau - (\boldsymbol{v}_1)_\tau\right] \,. \end{aligned} \tag{2.8}$$

The second equation may be replaced by the no-slip condition $(\boldsymbol{v}_2)_\tau - (\boldsymbol{v}_1)_\tau = \boldsymbol{0}$ or the perfect slip $\boldsymbol{T}^{\boldsymbol{\Gamma}}_{\tau} = \boldsymbol{0}$.

Remark 2.1. Under the above assumptions, the contact angle is determined by global energy conservation, while the shape of the interface, its curvature and its evolution are determined by the second law of thermodynamics, i.e. $\frac{d}{dt}\mathcal{S} \geq 0$. This is since we assumed surface entropy to be of lower order. However, we will see that the inclusion of surface entropy leads almost automatically to dynamic contact angles.

2.5. **The complete thermodynamic approach: Definition of Surface Tension.** The entropy and energy functionals are given through

$$\mathcal{E} = \int_{\Omega_1} \varrho_1 E_1 + \int_{\Omega_2} \varrho_2 E_2 + \int_\Gamma E_\Gamma + \int_{\Gamma_1} E_{\Gamma_1} + \int_{\Gamma_2} E_{\Gamma_2} + \int_\gamma E_\gamma \,, \tag{2.9}$$

$$\mathcal{S} = \int_{\Omega_1} \varrho_1 \eta_1 + \int_{\Omega_2} \varrho_2 \eta_2 + \int_\Gamma \eta_\Gamma + \int_{\Gamma_1} \eta_{\Gamma_1} + \int_{\Gamma_2} \eta_{\Gamma_2} + \int_\gamma \eta_\gamma \,, \tag{2.10}$$

where

$$\eta_i = \tilde{\eta}_i(\varrho_i, E_i, \boldsymbol{v}_i) \,, \quad i = 1, 2 \,, \qquad \eta_j = \tilde{\eta}_j(E_j) \,, \quad j = \Gamma, \Gamma_1, \Gamma_2, \gamma \,.$$

Following Callen [8], we assume η_i as differentiable functions of the internal energy u_i, $i = 1, 2$, or E_j, $j = \Gamma, \Gamma_1, \Gamma_2, \gamma$, and other state variables $\boldsymbol{y} = (\boldsymbol{y}_1, \dots, \boldsymbol{y}_M)$. Thus, assuming $E_i = \tilde{u}_i(\eta, \boldsymbol{y}) + \frac{1}{2}|\boldsymbol{v}|^2$ with $\tilde{u}_i$ being increasing with respect to η_i, we set E_i and η_i in relation by $E = u + \frac{1}{2}|\boldsymbol{v}|^2$. Then, the inverse function theorem implies that

$$\eta_i = \tilde{\eta}_i(E_i, \boldsymbol{y}) \,, \tag{2.11}$$

where we set for simplicity of notation

$$\boldsymbol{y}_0 := \boldsymbol{v} \quad \text{and} \quad \boldsymbol{y}_1 := \varrho\,.$$

The temperature is given through $\vartheta := \dfrac{\partial \tilde{E}_i}{\partial \eta_i}, i \in \{1, 2, \Gamma, \Gamma_1, \Gamma_2, \gamma\}$ and we assume for simplicity, that this quantity indeed is continuous all across Ω. Again, we assume $\delta \boldsymbol{v}_i = \boldsymbol{0}$, for simplicity.

Our aim is to derive constitutive equations in the bulk and on the surface / contact line that satisfy the two conditions

$$\frac{d}{dt}\mathcal{E} = \int_{\Omega_1} \boldsymbol{g}_1 \cdot \boldsymbol{v}_1 + \int_{\Omega_2} \boldsymbol{g}_2 \cdot \boldsymbol{v}_2\,, \qquad \frac{d}{dt}\mathcal{S} \geq 0\,.$$

A dependence of contact line energy / entropy on the contact angle can best be reflected by a dependence of η_γ on ν_Γ. We neglect such a dependence at this point both for simplicity and for the aforementioned discussion in [9], section 3.2. However, note that we include such dependence in the calculations in section 5 in order to derive its effect on dissipation. Also note that in section 5, we derive balance equations for the surface energy which we will not discuss at this point.

The following quantities will appear in in the calculations and we will spend the rest of this subsection to discuss their physical meaning

$$\sigma_\Gamma := -\left(\vartheta \eta_\Gamma - E_\Gamma\right)\,, \quad \sigma_1 := -\left(\vartheta \eta_{\Gamma_1} - E_{\Gamma_1}\right)\,, \quad \sigma_2 := -\left(\vartheta \eta_{\Gamma_2} - E_{\Gamma_2}\right)\,, \quad \sigma_\gamma = -\left(\vartheta \eta_\gamma - E_\gamma\right)\,, \tag{2.12}$$

where ϑ is temperature. Giving σ_i a proper meaning is *the* crucial step in the interpretation of the resulting constitutive relations.

In classical thermodynamics, it is known (see Adam [5]) that the surface tension σ is the derivative of Gibbs free energy G w.r.t. area A at constant temperature T and pressure P:

$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,P}\,.$$

As $G = H - TS$ for entropy S and enthalpy H, we can get the entropy per area

$$\left(\frac{\partial \sigma}{\partial T}\right)_{A,P} = -S^A\,, \tag{2.13}$$

where S^A is the surface entropy per unit area. Rearranging the previous two equations, we get Kelvin's equation for the enthalpy per area H^A through

$$H^A = \sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_P\,. \tag{2.14}$$

This equation gives the relation between enthalpy per area, temperature and surface tension at constant pressure. If (2.13) would also hold for variable total area, the resulting relation between enthalpy per area, entropy per area, temperature and surface tension would read

$$H^A = \sigma + T\,S^A\,.$$

Thus, in order to argue that σ_Γ, σ_1 and σ_2 are the surface energies of the respective surfaces, note that E_Γ, E_{Γ_1} and E_{Γ_2} are indeed the enthalpies of the surfaces, as enthalpy is by definition nothing but the total energy of the system. As E_Γ, E_{Γ_1} and E_{Γ_2} capture the total energies per area of the surfaces, this means that we identified the surface energies by (2.12).

2.6. **Dynamic contact angles.** The resulting dynamic condition on the contact angle reads

$$-\left(\sigma_\Gamma \nu_\Gamma + \sigma_1 \nu_{\Gamma_1} + \sigma_2 \nu_{\Gamma_2} + \sigma_\gamma \boldsymbol{\kappa}_\gamma\right) \cdot \boldsymbol{v} \geq 0\,. \tag{2.15}$$

In order to give a proper interpretation of (2.15), imagine a cylindrical capillary filled with water and air, such that water rises with velocity $\boldsymbol{v}$ (Fig. 2.2). In this case, we find $\boldsymbol{\kappa}_\gamma \cdot \boldsymbol{v} = 0$. Equation (2.15) then states that the 1-component of ν_Γ is increased compared to equilibrium. Even in the general case, we can write $\boldsymbol{v} = v\nu_{\Gamma_1}$ at the boundary, as the contact line moves parallel to $\partial \boldsymbol{Q}$, and we obtain from (2.15):

$$-\left(\sigma_\Gamma \cos\varphi + \sigma_1 - \sigma_2\right) \cdot v \geq 0\,.$$

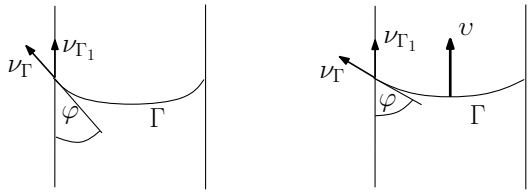

FIGURE 2.2. Two liquids in a vertical tube. In the left picture, the setting is static, while in the right picture, the level of the lower fluid is rising.

We define the equilibrium contact angle φ_{eq} as the solution to the problem $\sigma_\Gamma \cos\varphi + \sigma_1 - \sigma_2 = 0$ (if such solution exists) and note that (2.15) then reads

$$\sigma_\Gamma v\,(\cos\varphi_{eq} - \cos\varphi) \geq 0\,. \tag{2.16}$$

The dissipation at the contact line is nonnegative if we assume for example the linear dependence

$$v = \alpha\sigma_\Gamma\,(\cos\varphi_{eq} - \cos\varphi)\ , \tag{2.17}$$

which corresponds to an Onsager principle for v. Using purely mechanical calculations, de Gennes, Brochard-Wyart and Quéré [9, (6.7)] provide

$$\alpha = \frac{\varphi}{6l\mu}\,,$$

where μ is the viscosity of fluid 1 and $l = \ln(L/a)$ is a length scale parameter with macroscopic length scale L and atomic scale a. Note that they use the approximation $\cos\varphi \approx 1 - \frac{\varphi^2}{2}$ for small angles.

Of course, also different relations between φ and φ_{eq} are thinkable as long as (2.15) or (2.16) are satisfied.

2.7. **Normal and tangential stresses on Γ, Γ_1 and Γ_2 ; Slip conditions on $\partial\Omega$.** Newtons third law for the normal component as the relation between normal stress acting on Γ curvature of Γ turns out to be given through

$$0 = \left(\left[\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)\cdot\boldsymbol{n}_\Gamma\right] - \kappa\sigma_\Gamma\right)\ , \tag{2.18}$$

similar to $(2.8)_1$. Depending on the assumptions one makes, for the tangential part of the surface stress, we obtain a Navier-Slip condition

$$\boldsymbol{v}_{i,\tau} = -\alpha_i \boldsymbol{T}_{i,\tau}^{\boldsymbol{\Gamma}} \quad \text{on } \Gamma_i \tag{2.19}$$

or the perfect slip condition $\boldsymbol{T}_{i,\tau}^{\boldsymbol{\Gamma}} = \boldsymbol{0}$. As already discussed by several authors, the no-slip condition on $\partial\Omega$ in general is not compatible with the moving contact line as dissipation diverges towards infinity[1] [7, 32, 29]. We refer to the discussion in subsection 2.10 for the solution to this problem proposed in this work.

2.8. **Tangential velocity on Γ.** Concerning the tangential part of the velocities on Γ, we will discuss three different fundamental assumptions:

(1) The velocity fields of fluid 1, fluid 2 and Γ are different, i.e. $\boldsymbol{v}_{1,\tau} \neq \boldsymbol{v}_{2,\tau} \neq \boldsymbol{v}_\tau$ on Γ. This reflects a situation when one fluid slips on the other fluid and the velocity of the interface is not related to this movement.
(2) The interface velocity coincides with the velocity of fluid 1, but fluid two slips on the interface, i.e. $\boldsymbol{v}_\tau = \boldsymbol{v}_{1,\tau} \neq \boldsymbol{v}_{2,\tau}$.
(3) The velocity is continuous across the interface, i.e. $\boldsymbol{v}_\tau = \boldsymbol{v}_{1,\tau} = \boldsymbol{v}_{2,\tau}$ on Γ.

In all three cases the three velocity fields coincide at γ. Also we assume that the normal velocity is continuous across Γ, i.e. $\boldsymbol{v}_n = \boldsymbol{v}_{1,n} = \boldsymbol{v}_{2,n}$. We then get the following three different models:

2.8.1. *Model A ($\boldsymbol{v}_{1,\tau} \neq \boldsymbol{v}_{2,\tau} \neq \boldsymbol{v}_\tau$ on Γ).* Newtons third law for the stresses on Γ simply reads $\boldsymbol{T}_1^{\boldsymbol{\Gamma}} = \boldsymbol{T}_2^{\boldsymbol{\Gamma}}$ and we get the following Navier-slip condition and velocity of Γ:

$$\boldsymbol{v}_\tau = \boldsymbol{0}\,, \qquad \boldsymbol{T}_{1,\tau}^{\boldsymbol{\Gamma}} = \beta_2\left(\boldsymbol{v}_2 - \boldsymbol{v}_1\right)_\tau\ .$$

Note that a perfect slip in the sense of $\boldsymbol{T}_{1,\tau}^{\boldsymbol{\Gamma}} \equiv 0$ on Γ can make sense only in very limited cases.

[1]The contradiction to experiments by Dussan and Davis [10] is not resolved until today. However, the author refers to [12] how the results in [10] can be interpreted within diffuse interface models.

2.8.2. *Model B ($\boldsymbol{v}_\tau = \boldsymbol{v}_{1,\tau} \neq \boldsymbol{v}_{2,\tau}$ on Γ) and Model C ($\boldsymbol{v}_\tau = \boldsymbol{v}_{1,\tau} = \boldsymbol{v}_{2,\tau}$ on Γ).* The results in this case do not differ except for the fact that Newtons third law has to be modified into

$$\begin{aligned} &\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)_\tau = \mathbf{0} \qquad \text{on } \Gamma\,, \\ \text{resp.} \qquad &\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)_\tau = \alpha_1 \boldsymbol{v}_\tau \qquad \text{on } \Gamma\,, \end{aligned} \tag{2.20}$$

and

$$\boldsymbol{T}_2^{\boldsymbol{\Gamma}} = \alpha_2 \left(\boldsymbol{v}_2 - \boldsymbol{v}_1\right)_\tau\,. \tag{2.21}$$

Equations $(2.20)_2$ and (2.21) together yield a Navier-slip condition in case of friction at the interface. The no-slip corresponds to a Model C, i.e. $\boldsymbol{v}_{2,\tau} - \boldsymbol{v}_{1,\tau} = \mathbf{0}$ together with $(2.20)_1$. Interestingly, we can also identify a perfect slip condition: This corresponds to the case $(2.20)_1$ with $\boldsymbol{T}_{2,\tau}^{\boldsymbol{\Gamma}} = \mathbf{0}$, i.e. to the frictionless case.

2.9. **Discontinuous normal velocity: Mean-curvature flow and Mullins-Sekerka flow.** There is huge evidence from asymptotic analysis that $\boldsymbol{v}_n := \partial_t \Gamma \neq \boldsymbol{v}_{1,n} \neq \boldsymbol{v}_{2,n}$. In particular, this evidence stems from the asymptotics of the Allen-Cahn equation converging to mean curvature flow and from the Cahn-Hilliard equation converging to the Mullins-Sekerka equation, see section 6. As the assumption that the variation of Γ with time is different from the normal bulk velocity may sound strange to the reader, we will shortly discuss these two limit processes in section 6 without going into details and discussing the physical implications.

We will follow two different approaches: In both approaches, we will assume continuity of the bulk velocity, i.e. $\boldsymbol{v}_1|_\Gamma = \boldsymbol{v}_2|_\Gamma$. Additionally, for simplicity we assume $\boldsymbol{v}_\tau = \boldsymbol{v}_{1,\tau} = \boldsymbol{v}_{2,\tau}$.

Then, we investigate two cases: In the case that the masses $\int_{\Omega_1} \varrho_1$ and $\int_{\Omega_2} \varrho_2$ are conserved, we get for $\delta\boldsymbol{v}_1 = \boldsymbol{v} - \boldsymbol{v}_1$ on Γ

$$\delta\boldsymbol{v}_1 = m_{1,0}^{-1} \Delta_\Gamma \left(\frac{\kappa\sigma_\Gamma}{m_{1,0}}\right) \boldsymbol{n}_\Gamma$$

with $m_{1,0}$ depending on ϱ_1 and ϱ_2. If mass conservation of fluids 1 and 2 are violated but the total mass of the system is conserved, we find

$$\delta\boldsymbol{v} = -\alpha_\Gamma \kappa\sigma_\Gamma \boldsymbol{n}_\Gamma\,.$$

Furthermore, under the assumption $\delta\boldsymbol{v}_1 \neq \delta\boldsymbol{v}_2$, we obtain

$$\delta\boldsymbol{v}_1 = \alpha_\Gamma \left(\boldsymbol{T}_{2,n}^{\boldsymbol{\Gamma}} \left(1 - \tfrac{\tilde{m}_1(\varrho_1,\varrho_2)}{\tilde{m}_2(\varrho_1,\varrho_2)}\right) - \kappa\sigma_\Gamma \boldsymbol{n}_\Gamma\right)\,,$$

where the coefficients $\tilde{m}_i$ have to be measured through experiments and relate $\delta\boldsymbol{v}_i$ with the local mass exchange at Γ. Of course, we can also think of models including both, conservative and non-conservative normal flows through Γ. It can be seen from the calculations, that such models can be obtained using this method.

2.10. **Huh and Scriven's Paradox.** Dussan and Davis [10] studied the decoupling of the movement of the contact line from the bulks movement: More precisely, they showed in a series of experiments that under some circumstances, the contact line (where the fluid-fluid interface touches the solid's surface) is moving due to a rolling effect, which means "that the fluid-fluid interface rolls on or unrolls off the solid" [10] which is: the contact line moves while the fluids follow a no-slip boundary condition. For example, they investigated the movement of a honey drop on a tilted Plexiglas plate: Using food dye, they marked a small spot on the honey-drop's surface. Following the movement of the dye spot relatively to the movement of the honey-drop, they came to the conclusion that the honey is rolling over the Plexiglas instead of sliding. However, as already mentioned by the author in [12], with the experiments carried out for small velocities, there is no reason to assume that for high bulk velocities the no slip condition would sill hold.

Nevertheless, their results are of great importance, and we think that any general theory of moving interfaces should be able to give an explanation of these experiments. However, prior to Dussan and Davis, Huh and Scriven [17] had already discovered that a moving contact line contradicts with any solution to Stokes equation with no-slip boundary conditions, as such a model would imply infinite dissipation. The problem that arises in these calculations stems from the assumption that the interface moves with the bulks averaged macroscopic velocity field. As we have seen in the previous subsection, this needs not to be the case, and in what follows we will give reason why the Mullins-Sekerka model is an appropirate approach to resolve the Huh and Scriven paradox and to explain the experiments by Dussan and Davis.

From a purely mathematical point of view, the Mullins-Sekerka model is the sharp interface limit of the Cahn-Hilliard equation (see section 6 below). This means that it is the sharp interface description of diffusion effects that act on a scale comparable to the thickness of the diffuse interface. From molecular dynamics simulations, we know that the movement of the contact line is basically non-convective but due to sometimes complex interactions of the liquid molecules with the solid surface and due to diffusive movements of these molecules (refer to Bonn et. al. [6] and references therein). Such effects can be captured within diffuse interface models with dynamic boundary conditions (see [12]) and due to our mathematical knowledge on sharp interface limits of such phase field models, it is natural to assume that these diffusive interactions should be captured within the interaction of a Mullins-Sekerka type movement with the solid wall.

Thus, we assume no-slip condition for the bulks velocity field, i.e. $\boldsymbol{v}_1|_{\partial\Omega} \equiv \mathbf{0}$, $\boldsymbol{v}_2|_{\partial\Omega} \equiv \mathbf{0}$ and find that the entropy production on the contact line γ is given through

$$\xi_\gamma := -\left(\sigma_\Gamma \nu_\Gamma + \sigma_1 \nu_{\Gamma_1} + \sigma_2 \nu_{\Gamma_2} + \sigma_\gamma \boldsymbol{\kappa}_\gamma\right) \cdot \delta \boldsymbol{v}_\tau \,,$$

where once more $\boldsymbol{v} = \boldsymbol{v}_1 + \delta\boldsymbol{v}$ on Γ. As we assume $\delta\boldsymbol{v} = m_{1,0}^{-1} \Delta_\Gamma m_1 \boldsymbol{n}_\Gamma$ for some m_1, note that automatically $\delta\boldsymbol{v}_n \equiv \mathbf{0}$ on $\partial\Omega$.

In case of the situation in Figure 2.2 and discussed in subsection 2.6, the tangential part of $\delta\boldsymbol{v}$ has to comply with (2.16), in particular, we find

$$\delta v = \alpha \sigma_\Gamma \left(\cos\varphi_{eq} - \cos\varphi\right) , \qquad \alpha = \frac{\varphi}{6l\mu} \,.$$

As the velocity of Γ is given through $\boldsymbol{v} = \boldsymbol{v}_1 + \delta\boldsymbol{v}$, we found a model for the moving contact line with no-slip boundary condition.

3. Preliminaries

3.1. **Balance Equations.** As mentioned, we assume that for both fluids the standard balance laws hold in a way they are introduced in most books on continuum thermodynamics (e.g. Truesdell [34]). In particular, we assume conservation of mass, momentum and energy. To make ourselves more clear, we denote ϱ the density, $\boldsymbol{v}$ the velocity field and E the total energy density.

Thus, we assume existence of an internal energy per mass u of the mixture with total energy per mass E through

$$E = u + \frac{1}{2}\left|\boldsymbol{v}\right|^2 \tag{3.1}$$

and claim local conservation of mass, momentum and energy through

$$\partial_t \varrho + \operatorname{div}\left(\boldsymbol{v}\varrho\right) = 0 \tag{3.2}$$

$$\partial_t(\varrho\boldsymbol{v}) + \operatorname{div}\left(\varrho\boldsymbol{v}\otimes\boldsymbol{v}\right) - \operatorname{div}\mathbb{T} = \boldsymbol{g} \tag{3.3}$$

$$\varrho\dot{E} - \operatorname{div}\boldsymbol{h} = \overset{+}{E} \tag{3.4}$$

where $\mathbb{T}$ is the Cauchy-stress tensor, $\boldsymbol{g}$ the external body force and $\boldsymbol{h}$ is some energy flux. We note that classically, $\boldsymbol{h}$ is split up into

$$\boldsymbol{h} = \mathbb{T}\boldsymbol{v} + \boldsymbol{k} \tag{3.5}$$

with an energy flux $\boldsymbol{k}$ which is often referred to as heat flux. Also, for simplicity, we assume throughout this article that

$$\overset{+}{E} - \boldsymbol{g}\cdot\boldsymbol{v} = 0 \,, \tag{3.6}$$

which reflects the physical assumption that the only external energy supply is due to the work done by external body forces. Finally, angular momentum conservation is guarantied if we assume that

$$\mathbb{T} = \mathbb{T}^T \,.$$

Indexing each of the above equations by i, $i \in \{1,2\}$ we get the equations from 2.1.

3.2. **Surfaces.** For calculations below, we will need the following notations and results which can be found in the paper by Buscaglia and Ausas [7]. Let Υ be any bounded two-dimensional C^2-manifold in $\mathbb{R}^3$. On Υ, let $\boldsymbol{n}_\Upsilon$ be the normal vector field and for each arbitrary vector field $\boldsymbol{a} : \mathbb{R}^3 \to \mathbb{R}^3$, we define the normal part a_n and the tangential part $\boldsymbol{a}_\tau$ on Υ via

$$a_n := \boldsymbol{a} \cdot \boldsymbol{n}_\Upsilon, \qquad \boldsymbol{a}_n := a_n \cdot \boldsymbol{n}_\Upsilon, \qquad \boldsymbol{a}_\tau := \boldsymbol{a} - a_n \boldsymbol{n}_\Upsilon \,.$$

We define the normal derivative on Υ through

$$\partial_n a := \nabla a \cdot \boldsymbol{n}_\Upsilon$$

and the tangential gradient ∇_τ for any smooth scalar function $a : \mathbb{R}^3 \to \mathbb{R}$ through

$$\nabla_\tau a := (\nabla a)_\tau = \nabla a - \partial_n a \, \boldsymbol{n}_\Upsilon \,.$$

For any vector field $\boldsymbol{f} : \mathbb{R}^3 \to \mathbb{R}^3$ we define the tangential divergence

$$\mathrm{div}_\tau \boldsymbol{f} := \mathrm{tr} \nabla_\tau \boldsymbol{f} \,.$$

Buscaglia and Ausas [7] present a very nice way to introduce all these quantities for functions being only defined on Υ without the need of differential geometry. Note that their approach holds if Υ is regular enough, which we will assume for the surfaces considered in the present paper.

The mean curvature of Υ is defined through

$$\kappa_\Upsilon := \mathrm{tr} \left(\nabla_\tau \boldsymbol{n}_\Upsilon \right)$$

and we find the following important result:

Lemma 3.1. [7] *For any $f \in C^1(\Upsilon)$ holds*

$$\int_\Upsilon \nabla_\tau f = \int_\Upsilon f \kappa_\Upsilon \boldsymbol{n}_\Upsilon + \int_{\partial\Upsilon} f \boldsymbol{\nu}$$

where $\boldsymbol{\nu}$ is the unit vector tangent to Υ and normal to $\partial\Upsilon$. Furthermore, for any tangentially differentiable field $\boldsymbol{q}$ holds

$$\int_\Upsilon div_\tau \boldsymbol{q} = \int_\Upsilon \kappa_\Upsilon \boldsymbol{q} \cdot \boldsymbol{n}_\Upsilon + \int_{\partial\Upsilon} \boldsymbol{q} \cdot \boldsymbol{\nu} \,.$$

This result is used to proof the following important theorem:

Theorem 3.2. [7, Prop. 3.5] *Let $\Upsilon(t)$ be a smooth surface in $\mathbb{R}^3$ which moves with velocity $\boldsymbol{v}$ and let*

$$\mathcal{E}(\Upsilon(t)) := \int_{\Upsilon(t)} E_\Upsilon d\Upsilon \,.$$

Then, the following variational formula holds:

$$\frac{d}{dt}\mathcal{E}(\Upsilon(t)) = \int_{\Upsilon(t)} E_\Upsilon \kappa \boldsymbol{n}_\Gamma \cdot \boldsymbol{v} d\Upsilon + \int_{\partial\Upsilon(t)} E_\Upsilon \boldsymbol{\nu} \cdot \boldsymbol{v} \, d\partial\Upsilon \,, \tag{3.7}$$

where κ is the curvature and $\boldsymbol{\nu}$ is the unit vector normal to $\partial\Upsilon$ and $\boldsymbol{n}_\Gamma$.

Remark 3.3. Note that in the original statement in [7], (3.7) has the form

$$\frac{d}{dt}\mathcal{E}(\Upsilon(t)) = \int_{\Upsilon(t)} (E_\Upsilon \kappa \boldsymbol{n}_\Gamma - \nabla_\Upsilon E_\Upsilon) \cdot \boldsymbol{v} d\Upsilon + \int_{\partial\Upsilon(t)} E_\Upsilon \boldsymbol{\nu} \cdot \boldsymbol{v} \, d\partial\Upsilon \,,$$

which is due to an unfortunate error in the ansatz. Denote

$$F_{\delta t} : \ \Upsilon(t) \to \Upsilon(t + \delta t) \,, \quad x \mapsto \tilde{x}(x, \delta t)$$

where $\tilde{x}(x, t + s)$ solves the ODE

$$\partial_s \tilde{x} = \boldsymbol{v}(t + s) \,, \quad \tilde{x}(x, t) = x$$

the evolution operator for $\Upsilon(t)$ and $JF_{\delta t}$ its Jacobian. Buscaglia and Ausas use the ansatz

$$\frac{d}{dt}\mathcal{E}(\Upsilon(t)) = \lim_{\delta t \to 0} \frac{1}{\delta t} \int_{\Upsilon(t)} E_\Upsilon(x) JF_{\delta t} - E_\Upsilon(x, t) \,,$$

while indeed, in accordance with the derivation of Reynold's transport theorem, we would find

$$\frac{d}{dt}\mathcal{E}(\Upsilon(t)) = \lim_{\delta t \to 0} \frac{1}{\delta t} \int_{\Upsilon(t)} E_\Upsilon(\tilde{x}(x, t + \delta t)) JF_{\delta t} - E_\Upsilon(x, t) \,.$$

Using this ansatz yields Theorem 3.2.

We can easily generalize the above theorem to the following more general situation:

Proposition 3.4. *Like in the previous theorem, let* $\mathcal{E}(t,\Upsilon(t)) := \int_{\Upsilon(t)} E_\Upsilon(t) d\Upsilon(t)$. *Then, the following variational formula holds:*

$$\frac{d}{dt}\mathcal{E}(\Upsilon(t)) = \int_{\Upsilon(t)} \left[\partial_t E_\Upsilon + E_\Upsilon \kappa \boldsymbol{n}_\Gamma \cdot \boldsymbol{v}\right] d\Upsilon + \int_{\partial\Upsilon(t)} E_\Upsilon \boldsymbol{\nu}\cdot\boldsymbol{v}\, d\partial\Upsilon\,.$$

3.3. **Curves.** Now, for each $t \in [0,T]$ let $\gamma(t)$ be a closed curve in $\mathbb{R}^3$ moving with velocity $\boldsymbol{v}$. For any t, let $\widetilde{\gamma}_t : [a_t, b_t] \to \mathbb{R}^3$ be an arc-length parametrization of $\gamma(t)$. We denote $\boldsymbol{\tau}$ the unique tangential vector such that γ is an oriented curve, i.e. $\boldsymbol{\tau} = \widetilde{\gamma}_t{}'$. Then, the curvature κ of $\gamma(t)$ is given by $\kappa = \|\widetilde{\gamma}_t{}''\|$ and the curvature vector $\boldsymbol{\kappa} := \widetilde{\gamma}_t''$ satisfies $\boldsymbol{\kappa}\cdot\boldsymbol{\tau} = 0$. In particular, comparing with theorem 3.4, we find the following result:

Proposition 3.5. *For each* t *let* f_t *be a continuously differentiable function* $f_t : \gamma(t) \to \mathbb{R}$. *Then, for*

$$\mathcal{E}(\gamma(t)) := \int_{\gamma(t)} f_t(\cdot)\, d\gamma(t)$$

the following variational formula holds:

$$\frac{d}{dt}\mathcal{E}(\gamma(t)) = \int_{\gamma(t)} \left[\partial_t f_t + f_t \boldsymbol{\kappa}\cdot\boldsymbol{v}\right] d\gamma\,.$$

We will proof this proposition in the appendix. The proof will show that we might understand proposition 3.5 as a kind of Reynolds theorem for closed curves.

3.4. **The distributional Laplacian on** Γ**.** On Γ, we will need a particular operator in order to formulate the Mullins-Sekerka model. To this aim, let be given any scalar function f on Γ. We then solve the problem

$$\begin{aligned} w &= f \quad \text{on}\Gamma\,, \qquad \frac{\partial w}{\partial n} = 0 \quad \text{on}\partial\Omega\,, \\ -\Delta w &= 0 \quad \text{in}\Omega\backslash\Gamma\,. \end{aligned} \tag{3.8}$$

Let $\partial_n^+ w$ denote the normal derivative of $w|_{\Omega_1}$ on Γ with respect to $\boldsymbol{n}_\Gamma$ and $\partial_n^- w$ the normal derivative of $w|_{\Omega_2}$ on Γ with respect to $-\boldsymbol{n}_\Gamma$, as well as $[\partial_n w] := \partial_n^+ w - \partial_n^- w$. Then, we get for any φ with $\frac{\partial\varphi}{\partial n} = 0$ on $\partial\Omega$:

$$-\int_\Omega w\Delta\varphi = -\int_\Gamma w\,[\partial_n\varphi] + \int_\Gamma \varphi\,[\partial_n w]\,.$$

In particular, in case φ is continuously differentiable on Ω, we get

$$-\int_\Omega w\Delta\varphi = \int_\Gamma \varphi\,[\partial_n w]\,.$$

Thus, with $\mathcal{H}^{n-1}_\Gamma(\cdot)$ being the Hausdorff measure on Γ, $-[\partial_n w]\,\mathcal{H}^{n-1}_\Gamma(\cdot)$ is the distributional Laplacian of f and we write $-\Delta_\Gamma f := [\partial_n w]$. Note that Δ_Γ is different from the so called Laplace-Beltrami operator. Interestingly, the former calculations yield for any two functions f, g on Γ the simple relation

$$\int_\Gamma f\,\Delta_\Gamma g = \int_\Gamma g\,\Delta_\Gamma f\,. \tag{3.9}$$

Furthermore, denote by w_f and w_g the solutions to (3.8) for f resp. g. Then, we find

$$0 = -\int_\Omega w_f \Delta w_g = \int_\Omega \nabla w_f\cdot\nabla w_g + \int_\Gamma f\Delta_\Gamma g\,,$$

implying

$$-\int_\Gamma f\Delta_\Gamma f = \int_\Omega |\nabla w_f|^2\,.$$

Remark 3.6. Note that (3.9) at least formally implies that $\Delta_\Gamma g = f$ is solvable for arbitrary f iff $\int_\Gamma f = 0$. This can be easily proved if for example $f \in L^2(\Gamma)$.

3.5. **Friction: Global balance of energy, momentum and angular momentum.** If we want to understand the complex interactions between bulk and interface, we have to take into account not only the global balance of entropy (i.e. global dissipation, the 2nd law) but also global balance of energy, momentum and angular momentum. For simplicity, in this subsection, we will only focus on energy and momentum and do not dig into the details of the angular momentum balance, though the argumentation concerning the exchange of angular momentum with the surrounding is similar to the discussion for momentum. Note in this context that in presence of friction we will always face a loss of angular momentum if no energy is supplied to the system, as the velocity field will tend to zero.

First note that the energy stored on the interface Γ may change with deformation and it surely will change in case of interface generation (phase transition, crystal growth, *nucleation*) or annihilation. These effects are taken into account by setting up a global energy functional $\mathcal{E}$ that contain the integrated energy of bulk and interfaces, in a way we set them up in section 2, i.e. formulas (2.5), (**??**), (2.9).

Global energy conservation then requires

$$\frac{d}{dt}\mathcal{E} = 0\,,$$

or modified versions in case of controlled energy supply, and below we will derive several consequences of this physical condition, depending on the situation we focus on. Note that energy conservation is a critical assumption in the derivations below. Once we supply an arbitrary amount of energy to the system, we basically have no control over the processes that happen inside.

For momentum conservation, things become more complicated. Note that momentum and angular momentum are carried only by the bulk, i.e. the surfaces and interfaces in general are lower dimensional and massless and should thus not carry any momentum. This means, denoting $\mathcal{T}$ the total momentum of the system, we find

$$\mathcal{T} = \int_\Omega \varrho \boldsymbol{v}\,.$$

It is well known (e.g. [34]) that the local laws of momentum conservation in the bulk take the form (3.3) for Cauchy stress $\mathbb{T}$ and external forcing $\boldsymbol{g}$. In particular, in the absence of any external forcing, global momentum should be conserved by Newton's first law, i.e. $\mathbf{0} = \frac{d}{dt}\mathcal{T}$. However, total momentum may also increase or decrease with time, while we observe that such increase or decrease is always due to forces acting on $\partial\Omega$ or forces acting on the bulk. Thus, taking the time derivative of $\mathcal{T}$, we find

$$\int_\Omega \boldsymbol{g} + \int_{\partial\Omega} \boldsymbol{f} = \frac{d}{dt}\mathcal{T} = \int_{\Gamma_1} \boldsymbol{T}_1^{\boldsymbol{\Gamma}} + \int_{\Gamma_2} \boldsymbol{T}_2^{\boldsymbol{\Gamma}} + \int_\Gamma \left(\boldsymbol{T}_1^{\boldsymbol{\Gamma}} - \boldsymbol{T}_2^{\boldsymbol{\Gamma}}\right)\,.$$

For simplicity, we discuss the case $\boldsymbol{g} = \mathbf{0}$. In case $\boldsymbol{f} = \mathbf{0}$, the first two terms are on the right hand side are easily handled by usually claiming $\boldsymbol{T}_i^{\boldsymbol{\Gamma}} = \mathbf{0}$ locally on Γ_i. The more general ansatz of course would be

$$\mathbf{0} = \int_{\Gamma_1} \boldsymbol{T}_1^{\boldsymbol{\Gamma}} + \int_{\Gamma_2} \boldsymbol{T}_2^{\boldsymbol{\Gamma}}\,, \tag{3.10}$$

reflecting the intuitive meaning of "no net force on Ω through the boundary".

To the contrary, we observe in all applications presence of friction forces on the boundary. The most popular choice for boundary conditions in fluid mechanics is $\boldsymbol{v}_\tau = \mathbf{0}$. This may lead to a break down in global momentum conservation or angular momentum conservation (and usually does). This loss in (angular) momentum in Ω goes together with an exchange of (angular) momentum with the surrounding. Note that such an exchange is compatible with global energy conservation if we assign an infinite mass to the surrounding[2].

We now want to discuss global conservation of momentum with respect to the interface Γ. Newton's third law how it is usually understood in continuum mechanics (i.e. in the absence of any external forces) claims continuity of $\mathbb{T}$ even across the interface Γ, i.e. $\left(\boldsymbol{T}_1^{\boldsymbol{\Gamma}} - \boldsymbol{T}_2^{\boldsymbol{\Gamma}}\right) = \mathbf{0}$ locally. The problem we want to highlight here, and which is also well known in fluid surface dynamics, is that the interface might exert a stress $\boldsymbol{p}_\Gamma$ on the fluid depending on its shape and other local parameters.

Note that if we say "exert a stress", this is precisely what we mean. In particular, there is no external force exerted on Γ. Furthermore, $\boldsymbol{p}_\Gamma$ carries the unit of pressure, but pressure is a scalar while we are interested in a quantity that has a particular direction. However, the *force* that is exerted by $\boldsymbol{p}_\Gamma$ on the fluid is given

[2]An everyday example may be a bouncy ball that looses almost no energy when hitting the ground (with the experiment performed in vacuum), but significantly changes its direction.

by $\int_\Gamma \boldsymbol{p}_\Gamma$. Since this force is exerted by the system onto itself, we still find global conservation of momentum but now in the form of Once we take this into account, we find

$$\mathbf{0} = \frac{d}{dt}\mathcal{T} = \int_{\Gamma_1} \boldsymbol{T}_1^{\boldsymbol{\Gamma}} + \int_{\Gamma_2} \boldsymbol{T}_2^{\boldsymbol{\Gamma}} + \int_\Gamma \left(\boldsymbol{T}_1^{\boldsymbol{\Gamma}} - \boldsymbol{T}_2^{\boldsymbol{\Gamma}}\right) + \int_\Gamma \boldsymbol{p}_\Gamma \,,$$

yielding the generalized version of Newton's third law

$$\mathbf{0} = \left(\boldsymbol{T}_1^{\boldsymbol{\Gamma}} - \boldsymbol{T}_2^{\boldsymbol{\Gamma}}\right) + \boldsymbol{p}_\Gamma \quad \text{on } \Gamma \,.$$

We put so much emphasis on this topic because, as we will see, $\boldsymbol{p}_\Gamma$ will be one of the thermodynamical fluxes. In general, $\boldsymbol{p}_\Gamma$ may be any kind of stress, mechanical or friction. It is commonly observed that the normal component of $\boldsymbol{p}_\Gamma$ depends on curvature and surface energy, while frictive forces seem not to appear, although they would be compatible with thermodynamics.

However, to the authors knowledge, there seems no result on the tangential part of $\boldsymbol{p}_\Gamma$, which may be related to frictive forces at interfaces of slipping fluids. Note in this context that we expect friction forces on Γ to be given through a proportionality $(\boldsymbol{p}_\Gamma)_\tau \simeq \boldsymbol{v}_\tau$. To see this, consider the Navier-slip condition $\boldsymbol{T}_{i,\tau}^{\boldsymbol{\Gamma}} = \alpha_i \boldsymbol{v}_{i,\tau}$ at the outer boundaries Γ_i.

4. Fluid-Fluid Interaction: A first Study

4.1. **Equilibrium contact angles.** We will first consider the case of equilibrium contact angles and lateron focus on dynamic contact angles. A contact angle that is independent on the tangential velocity, as we will see, corresponds to the case of negligible surface entropy effects. The total energy is then given in the form (2.5). As the only external energy supply is due to the forcing $\boldsymbol{g}_i$, we find for the energy balance on one hand

$$\frac{d}{dt}\mathcal{E} - \int_{\Omega_1} \boldsymbol{g}_1 \cdot \boldsymbol{v}_1 - \int_{\Omega_2} \boldsymbol{g}_2 \cdot \boldsymbol{v}_2 = 0 \,. \tag{4.1}$$

On the other hand, the balance of total energy is with help of (2.1), Theorem 3.2 and Proposition 3.5

$$\begin{aligned} 0 \overset{!}{=} \frac{d}{dt}\mathcal{E} - \int_{\Omega_1} \boldsymbol{g}_1 \cdot \boldsymbol{v}_1 - \int_{\Omega_2} \boldsymbol{g}_2 \cdot \boldsymbol{v}_2 &= \int_{\Omega_1} \varrho_1 \dot{E}_1 + \int_{\Omega_2} \varrho_2 \dot{E}_2 + \int_\Gamma \sigma_\Gamma \kappa \boldsymbol{v}_n - \int_{\Omega_1} \boldsymbol{g}_1 \cdot \boldsymbol{v}_1 - \int_{\Omega_2} \boldsymbol{g}_2 \cdot \boldsymbol{v}_2 \\ &= \int_{\Gamma_1} \boldsymbol{h}_1 \cdot \boldsymbol{n}_{\boldsymbol{Q}} + \int_{\Gamma_2} \boldsymbol{h}_2 \cdot \boldsymbol{n}_{\boldsymbol{Q}} + \int_\Gamma (\boldsymbol{h}_1 - \boldsymbol{h}_2 + \kappa\sigma_\Gamma \boldsymbol{v}_n) \cdot \boldsymbol{n}_\Gamma + \int_{\partial\Gamma} (\sigma_\Gamma \nu_\Gamma + \sigma_1 \nu_1 + \sigma_2 \nu_2) \cdot \boldsymbol{v} \,, \end{aligned}$$

where we assume $\delta \boldsymbol{v}_i = \mathbf{0}$, for simplicity. From the last equation, we identify the following local conditions:

$$\begin{gathered} \boldsymbol{h}_1 \cdot \boldsymbol{n}_{\boldsymbol{Q}} = 0 \text{ on } \Gamma_1, \qquad \boldsymbol{h}_2 \cdot \boldsymbol{n}_{\boldsymbol{Q}} = 0 \text{ on } \Gamma_2, \qquad (\boldsymbol{h}_1 - \boldsymbol{h}_2 + \kappa \boldsymbol{v}) \cdot \boldsymbol{n}_\Gamma = 0 \text{ on } \Gamma(t) \\ (\sigma_\Gamma \nu_\Gamma + \sigma_1 \nu_1 + \sigma_2 \nu_2) \cdot \boldsymbol{v} = 0 \text{ on } \partial\Gamma \,. \end{gathered} \tag{4.2}$$

Note that the last equation is the well known equation for the contact angle. To see this, note that $\boldsymbol{v}$ is tangential to $\partial \boldsymbol{Q}$ as $\boldsymbol{v}_n = 0$. We have to allow for a tangential slip in $\partial\Gamma$ as we know from experiments that this contact line is moving which in general means $\nu_1 \cdot \boldsymbol{v} = -\nu_2 \cdot \boldsymbol{v} \neq 0$. Thus, we obtain the necessary condition

$$\sigma_\Gamma \nu_\Gamma + \sigma_1 \nu_1 + \sigma_2 \nu_2 = \mathbf{0} \,.$$

As we denoted φ the angle between ν_Γ and ν_1, multiplying the last equation by ν_1, we easily obtain

$$\sigma_\Gamma \cos\varphi + \sigma_1 - \sigma_2 = 0 \,.$$

Let the entropy of the system be given through (2.6). We introduce the constitutive assumptions

$$E_i = \tilde{E}_i(\eta_i, \varrho_i, \boldsymbol{v}_i) = u_i(\eta_i, \varrho_i) + \frac{1}{2}\left|\boldsymbol{v}_i\right|^2 \qquad i = 1, 2 \,,$$

and the notations

$$p_i := \varrho_i^2 \frac{\partial u_i}{\partial \varrho_i} \,, \qquad \vartheta_i := \frac{\partial u_i}{\partial \eta_i} \qquad \text{for } i \in \{s, f\}$$

and calculate

$$\dot{E}_i = \vartheta_i \dot{\eta}_i - p_i \operatorname{div} \boldsymbol{v}_i + \boldsymbol{v}_i \cdot \dot{\boldsymbol{v}}_i \,,$$

which yields

$$\frac{d}{dt}\mathcal{S} = \sum_{i=1,2}\int_{\Omega_i}\frac{1}{\vartheta_i}\left(\mathbb{T}_i^d\cdot\mathbb{D}^d\boldsymbol{v}_i + (m_i+p_i)\operatorname{div}\boldsymbol{v}_i + \boldsymbol{q}_i\cdot\frac{\nabla\vartheta_i}{\vartheta_i}\right)$$
$$+\int_{\Gamma(t)}\left(\frac{1}{\vartheta_2}\boldsymbol{n}_\Gamma\mathbb{T}_2\boldsymbol{v}_2 - \frac{1}{\vartheta_1}\boldsymbol{n}_\Gamma\mathbb{T}_1\boldsymbol{v}_1 + \frac{1}{\vartheta_1}\boldsymbol{h}_1\cdot\boldsymbol{n}_\Gamma - \frac{1}{\vartheta_2}\boldsymbol{h}_2\cdot\boldsymbol{n}_\Gamma\right) - \int_{\Gamma_1(t)}\frac{1}{\vartheta_1}\boldsymbol{n}_{\Gamma_1}\mathbb{T}\boldsymbol{v}_1 - \int_{\Gamma_2(t)}\frac{1}{\vartheta_2}\boldsymbol{n}_{\Gamma_2}\mathbb{T}\boldsymbol{v}_2\,.$$

For simplicity, we assume thermal equilibrium, i.e. $\vartheta_1\equiv\vartheta_2$, across the interface Γ, and simply write ϑ.

Using equations (4.2) we then get

$$\int_{\Gamma(t)}\left(\frac{1}{\vartheta_2}\boldsymbol{n}_\Gamma\mathbb{T}_2\boldsymbol{v}_2 - \frac{1}{\vartheta_1}\boldsymbol{n}_\Gamma\mathbb{T}_1\boldsymbol{v}_1 + \frac{1}{\vartheta_1}\boldsymbol{h}_1\cdot\boldsymbol{n}_\Gamma - \frac{1}{\vartheta_2}\boldsymbol{h}_2\cdot\boldsymbol{n}_\Gamma\right)$$
$$= \int_{\Gamma(t)}\frac{1}{\vartheta}\left(\boldsymbol{n}_\Gamma\mathbb{T}_2\left(\boldsymbol{v}_2-\boldsymbol{v}_1\right) + \left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}} - \kappa\sigma_\Gamma\boldsymbol{n}_\Gamma\right)\cdot\boldsymbol{v}_n + \left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)\cdot\boldsymbol{v}_{1,\tau}\right)\,.$$

Newtons third law for the tangential stresses in this case yields $\left(\mathbb{T}_1\boldsymbol{n}_\Gamma\right)_\tau = \left(\mathbb{T}_2\boldsymbol{n}_\Gamma\right)_\tau$ and for the normal part, we obtain $(2.8)_1$. In particular, we find

$$\begin{aligned}\xi_1 &:= \mathbb{T}_1^d\cdot\mathbb{D}^d\boldsymbol{v}_1 + (m_1+p_1)\operatorname{div}\boldsymbol{v}_1 + \boldsymbol{q}_1\cdot\frac{\nabla\vartheta}{\vartheta}\,,\\ \xi_2 &:= \mathbb{T}_2^d\cdot\mathbb{D}^d\boldsymbol{v}_2 + (m_2+p_2)\operatorname{div}\boldsymbol{v}_2 + \boldsymbol{q}_2\cdot\frac{\nabla\vartheta}{\vartheta}\,,\\ \xi_\Gamma &:= \boldsymbol{T}_\tau^{\boldsymbol{\Gamma}}\left(\boldsymbol{v}_2-\boldsymbol{v}_1\right)_\tau\,.,\end{aligned}\tag{4.3}$$

where $\boldsymbol{q}_i = \boldsymbol{h}_i - \mathbb{T}_i\boldsymbol{v}_i$.

We assume linear relations between the forces and thermodynamic potentials that appear in the products (4.3). Note in this context that the forces are the left hand side factors. Doing so, we obtain (2.7) and (2.8), where we note that $\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}} = \boldsymbol{p}_\Gamma$ is the normal stress exerted by the surface and we assume that there is no friction due to normal movements of Γ.

5. Fluid-Fluid interfaces: Complete thermodynamic setting

Based on the results from the last section, we see that we need more flexibility in the thermodynamic framework. We will now show that the method introduced in [12] can provide this flexibility.

We start from the energy and entropy functionals (2.9)-(2.10), where we additionally assume that $\eta_\gamma = \eta_\gamma(E_\gamma,\nu_\Gamma)$. Note that (4.1) remains valid and we once more assume $\delta\boldsymbol{v}_i = \boldsymbol{0}$. The energy balance becomes with help of Propositions 3.4 and 3.5

$$\begin{aligned}0 \overset{!}{=} \frac{d}{dt}\mathcal{E} - \int_{\Omega_1}\boldsymbol{g}_1\cdot\boldsymbol{v}_1 - \int_{\Omega_2}\boldsymbol{g}_2\cdot\boldsymbol{v}_2 &= \int_{\Omega_1}\left(\varrho_1\dot{E}_1 - \boldsymbol{g}_1\cdot\boldsymbol{v}_1\right) + \int_{\Omega_2}\left(\varrho_2\dot{E}_2 - \boldsymbol{g}_2\cdot\boldsymbol{v}_2\right)\\ &+\int_{\Gamma_1}\left[\partial_t E_{\Gamma_1} + \nabla_\tau\cdot\left(E_{\Gamma_1}\boldsymbol{v}\right)\right] + \int_{\Gamma_2}\left[\partial_t E_{\Gamma_2} + \nabla_\tau\cdot\left(E_{\Gamma_2}\boldsymbol{v}\right)\right]\\ &+\int_{\Gamma}\left[\partial_t E_{\Gamma} + \nabla_\tau\cdot\left(E_{\Gamma}\boldsymbol{v}\right)\right] + \int_{\gamma}\left[\partial_t E_{\gamma} + E_\gamma\boldsymbol{\kappa}\right]\end{aligned}\tag{5.1}$$

We further assume that E_Γ, E_{Γ_1} and E_{Γ_2} as well as E_γ satisfy the local balance laws

$$\begin{aligned}\partial_t E_\Gamma + \operatorname{div}_\tau\left(E_\Gamma\boldsymbol{v}\right) + \operatorname{div}_\tau\boldsymbol{h}_\Gamma &= \overset{\oplus}{E}_\Gamma\,, \qquad \partial_t E_{\Gamma_2} + \operatorname{div}_\tau\left(E_{\Gamma_2}\boldsymbol{v}_2\right) + \operatorname{div}_\tau\boldsymbol{h}_{\Gamma_2} = \overset{\oplus}{E}_{\Gamma_2}\,,\\ \partial_t E_{\Gamma_1} + \operatorname{div}_\tau\left(E_{\Gamma_1}\boldsymbol{v}_1\right) + \operatorname{div}_\tau\boldsymbol{h}_{\Gamma_1} &= \overset{\oplus}{E}_{\Gamma_1}\,, \qquad \partial_t E_\gamma + E_\gamma\boldsymbol{\kappa} = \overset{\oplus}{E}_\gamma\,,\end{aligned}\tag{5.2}$$

where $\overset{\oplus}{E}_\Gamma$, $\overset{\oplus}{E}_{\Gamma_1}$, $\overset{\oplus}{E}_{\Gamma_2}$and $\overset{\oplus}{E}_\gamma$ are local energy source terms and $\boldsymbol{h}_\Gamma$, $\boldsymbol{h}_{\Gamma_1}$ and $\boldsymbol{h}_{\Gamma_2}$ are energy fluxes parallel to Γ, Γ_1 and Γ_2 respectively. The terms $\operatorname{div}_\tau\left(E_\Gamma\boldsymbol{v}\right)$ reflect the idea that the moving surface carries the energy E_Γ along its velocity field $\boldsymbol{v}$. This idea is implicitly contained in Propositions 3.4 and 3.5.

Then, (5.1) with help of (3.6) and notation (2.1) can be rearranged into

$$0=\int_\Gamma\left[\overset{\oplus}{E}_\Gamma+\boldsymbol{n}_\Gamma\cdot(\boldsymbol{h}_1-\boldsymbol{h}_2)\right]+\int_{\Gamma_1}\left[\overset{\oplus}{E}_{\Gamma_1}+\boldsymbol{n}_{\Gamma_1}\cdot\boldsymbol{h}_1\right]+\int_{\Gamma_2}\left[\overset{\oplus}{E}_{\Gamma_2}+\boldsymbol{n}_{\Gamma_2}\cdot\boldsymbol{h}_2\right]$$
$$+\int_\gamma\left[\overset{\oplus}{E}_\gamma+\nu_\Gamma\cdot\boldsymbol{h}_\Gamma+\nu_1\cdot\boldsymbol{h}_{\Gamma_1}+\nu_2\cdot\boldsymbol{h}_{\Gamma_2}+\boldsymbol{v}\cdot(E_\Gamma\nu_\Gamma+E_{\Gamma_1}\nu_1+E_{\Gamma_2}\nu_2)\right].$$

It is easy to see that the last equation is satisfied by the following local equations:

$$\begin{aligned}&\overset{\oplus}{E}_\Gamma+\boldsymbol{n}_\Gamma\cdot(\boldsymbol{h}_1-\boldsymbol{h}_2)=0\,,\qquad\overset{\oplus}{E}_{\Gamma_1}+\boldsymbol{n}_{\Gamma_1}\cdot\boldsymbol{h}_1=0\,,\qquad\overset{\oplus}{E}_{\Gamma_2}+\boldsymbol{n}_{\Gamma_2}\cdot\boldsymbol{h}_2=0\\&\overset{\oplus}{E}_\gamma+\nu_\Gamma\cdot\boldsymbol{h}_\Gamma+\nu_1\cdot\boldsymbol{h}_{\Gamma_1}+\nu_2\cdot\boldsymbol{h}_{\Gamma_2}+\boldsymbol{v}\cdot(E_\Gamma\nu_\Gamma+E_{\Gamma_1}\nu_1+E_{\Gamma_2}\nu_2)=0\,,\end{aligned}\tag{5.3}$$

which state that the loss of energy in the bulk is due to energy supply to the surfaces and the loss or gain of surface energy is due to interaction with the bulk or the contact line. These processes of exchanging energy are the most natural we can think of: On the surfaces, this is evident. On γ, we find energy supply due to tangential fluxes on Γ, Γ_i and supply due to work that is exerted to Γ, Γ_i on γ if they move with speed $\boldsymbol{v}$. Once we use the constitutive equation that we find below, we will see that except for thermal heat, no energy is supplied to γ.

The time derivative of $\mathcal{S}$ can be calculated as follows:

$$\begin{aligned}\frac{d}{dt}\mathcal{S}=&\int_{\Omega_1}\frac{\xi_1}{\vartheta}+\int_{\Omega_2}\frac{\xi_2}{\vartheta}+\int_{\Gamma(t)}\left[\frac{d}{dt}\eta_\Gamma+\eta_\Gamma\kappa\boldsymbol{v}\cdot\boldsymbol{n}_\Gamma+\vartheta^{-1}\left(\boldsymbol{n}_\Gamma\mathbb{T}_2\boldsymbol{v}_2-\boldsymbol{n}_\Gamma\mathbb{T}_1\boldsymbol{v}_1+(\boldsymbol{h}_1-\boldsymbol{h}_2)\cdot\boldsymbol{n}_\Gamma\right)\right]\\&+\int_{\Gamma_1}\left(\frac{d}{dt}\eta_{\Gamma_1}+\eta_{\Gamma_1}\kappa\boldsymbol{v}\cdot\boldsymbol{n}_{\Gamma_1}+\frac{1}{\vartheta}\left(\boldsymbol{h}_{\Gamma_1}\cdot\boldsymbol{n}_{\Gamma_1}-\boldsymbol{n}_{\Gamma_1}\mathbb{T}_1\boldsymbol{v}_1\right)\right)\\&+\int_{\Gamma_2}\left(\frac{d}{dt}\eta_{\Gamma_2}+\eta_{\Gamma_2}\kappa\boldsymbol{v}\cdot\boldsymbol{n}_{\Gamma_2}+\frac{1}{\vartheta}\left(\boldsymbol{h}_{\Gamma_2}\cdot\boldsymbol{n}_{\Gamma_2}-\boldsymbol{n}_{\Gamma_2}\mathbb{T}_2\boldsymbol{v}_2\right)\right)\\&+\int_\gamma\left[\frac{d}{dt}\eta_\gamma+\eta_\gamma\boldsymbol{\kappa}\cdot\boldsymbol{v}+\eta_\Gamma\boldsymbol{v}\cdot\nu_\Gamma+\eta_{\Gamma_1}\boldsymbol{v}\cdot\nu_{\Gamma_1}+\eta_{\Gamma_2}\boldsymbol{v}\cdot\nu_{\Gamma_2}\right].\end{aligned}$$

We use $\frac{d}{dt}\eta_a=\frac{\partial\eta_a}{\partial E_a}\partial_t E_a$ for any index $a\in\{\Gamma,\Gamma_1,\Gamma_2\}$ with the assumption of continuity of temperatures, i.e. $\frac{\partial\eta_a}{\partial E_a}=\vartheta$, as well as (5.2), $\frac{d}{dt}\eta_\gamma=\frac{\partial\eta_\gamma}{\partial E_\gamma}\partial_t E_\gamma+\frac{\partial\eta_\gamma}{\partial\nu_\Gamma}\cdot\partial_t\nu_\Gamma$ and the notations (2.12)

$$\begin{aligned}\frac{d}{dt}\mathcal{S}=&\int_{\Omega_1}\frac{\xi_1}{\vartheta}+\int_{\Omega_2}\frac{\xi_2}{\vartheta}+\int_{\Gamma(t)}\vartheta^{-1}\left[\sigma_\Gamma\kappa\boldsymbol{v}\cdot\boldsymbol{n}_\Gamma+\left(\boldsymbol{n}_\Gamma\left(\mathbb{T}_2-\mathbb{T}_1\right)\right)\cdot\boldsymbol{v}_1+\frac{\nabla_\tau\vartheta}{\vartheta}E_\Gamma\cdot\boldsymbol{v}+\boldsymbol{n}_\Gamma\mathbb{T}_2\left(\boldsymbol{v}_2-\boldsymbol{v}_1\right)-\boldsymbol{h}_\Gamma\cdot\frac{\nabla_\tau\vartheta}{\vartheta}\right]\\&+\int_{\Gamma_1}\frac{1}{\vartheta}\left(\sigma_1\kappa\boldsymbol{v}\cdot\boldsymbol{n}_{\Gamma_1}-\left(\boldsymbol{n}_{\Gamma_1}\mathbb{T}_1\right)\cdot\boldsymbol{v}_1-\left(\boldsymbol{h}_{\Gamma_1}+\boldsymbol{v}_1E_{\Gamma_1}\right)\cdot\frac{\nabla_\tau\vartheta}{\vartheta}\right)\\&+\int_{\Gamma_2}\frac{1}{\vartheta}\left(\sigma_2\kappa\boldsymbol{v}\cdot\boldsymbol{n}_{\Gamma_2}-\left(\boldsymbol{n}_{\Gamma_2}\mathbb{T}_2\right)\cdot\boldsymbol{v}_2-\left(\boldsymbol{h}_{\Gamma_2}+\boldsymbol{v}_2E_{\Gamma_2}\right)\cdot\frac{\nabla_\tau\vartheta}{\vartheta}\right)\\&+\int_\gamma\frac{1}{\vartheta}\left[\vartheta\frac{\partial\eta_\gamma}{\partial\nu_\Gamma}\cdot\partial_t\nu_\Gamma+\sigma_\gamma\boldsymbol{\kappa}\cdot\boldsymbol{v}+\sigma_\Gamma\boldsymbol{v}\cdot\nu_\Gamma+\sigma_1\boldsymbol{v}\cdot\nu_{\Gamma_1}+\sigma_2\boldsymbol{v}\cdot\nu_{\Gamma_2}\right].\end{aligned}\tag{5.4}$$

We rewrite (5.4) as

$$\frac{d}{dt}\mathcal{S}=\int_{\Omega_1}\frac{\xi_1}{\vartheta}+\int_{\Omega_2}\frac{\xi_2}{\vartheta}+\int_\Gamma\frac{\xi_\Gamma}{\vartheta}+\int_{\Gamma_1}\frac{\xi_{\Gamma_1}}{\vartheta}+\int_{\Gamma_2}\frac{\xi_{\Gamma_2}}{\vartheta}+\int_\gamma\frac{\xi_\gamma}{\vartheta}\,,\tag{5.5}$$

where ξ_1, ξ_2 are given through (4.3),

$$\xi_{\Gamma_1}:=-\boldsymbol{T}_1^{\boldsymbol{\Gamma}}\cdot\boldsymbol{v}_{1,\tau}-\left(\boldsymbol{h}_{\Gamma_1}+\boldsymbol{v}_1E_{\Gamma_1}\right)\cdot\frac{\nabla_\tau\vartheta}{\vartheta}\qquad\xi_{\Gamma_2}:=-\boldsymbol{T}_2^{\boldsymbol{\Gamma}}\cdot\boldsymbol{v}_{2,\tau}-\left(\boldsymbol{h}_{\Gamma_2}+\boldsymbol{v}_2E_{\Gamma_2}\right)\cdot\frac{\nabla_\tau\vartheta}{\vartheta}\tag{5.6}$$

and

$$\begin{aligned}\xi_\Gamma&:=\left(-\kappa\sigma_\Gamma\boldsymbol{n}_\Gamma\right)\boldsymbol{v}_n+\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}}-\boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)\cdot\boldsymbol{v}_{1,\tau}+\boldsymbol{T}_2^{\boldsymbol{\Gamma}}\left(\boldsymbol{v}_2-\boldsymbol{v}_1\right)_\tau-\left(\boldsymbol{h}_\Gamma+E_\Gamma\cdot\boldsymbol{v}_\tau\right)\cdot\frac{\nabla_\tau\vartheta}{\vartheta}\,,\\\xi_\gamma&:=-\left(\sigma_\Gamma\nu_\Gamma+\sigma_1\nu_{\Gamma_1}+\sigma_2\nu_{\Gamma_2}+\sigma_\gamma\boldsymbol{\kappa}_\gamma\right)\cdot\boldsymbol{v}+\vartheta\frac{\partial\eta_\gamma}{\partial\nu_\Gamma}\cdot\partial_t\nu_\Gamma\end{aligned}\tag{5.7}$$

We assume proportionalities between the factors in (5.6) such that we find

$$\tilde{\xi}_{\Gamma_i}\left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_{i,\tau}\right) = \alpha_i \left|\boldsymbol{T}^{\boldsymbol{\Gamma}}_{i,\tau}\right|^2 + \kappa_\Gamma \left|\boldsymbol{h}_\Gamma + \boldsymbol{v}_i E_{\Gamma_i}\right|^2 ,$$

and together with (5.6) this leads to (2.19).

The implications of $(5.7)_2$ have been discussed in detail in 2.6 once we assume $\frac{\partial \eta_\gamma}{\partial \nu_\Gamma} \equiv \mathbf{0}$ to get the local condition (2.15). In the case $\frac{\partial \eta_\gamma}{\partial \nu_\Gamma} \not\equiv \mathbf{0}$, refer to subsection **??**.

With respect to $(5.7)_1$, note that the first term, including normal velocity, will always lead to a relation of the form (2.18). We will split the discussion of $(5.7)_1$ into three parts.

Note that interestingly, as a consequence of the constitutive equations for $\boldsymbol{h}_{\Gamma_i}$, the convective terms in (5.2) cancel out. This phenomenon has already been observed in [12].

5.1. **Completely discontinuous velocity field (Model A).** We first study the case that $\boldsymbol{v}_1 \neq \boldsymbol{v}_2 \neq \boldsymbol{v}$ on Γ. Thus, we make use of $(5.7)_1$ and Newtons third law in the form $\left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1\right)_\tau = \mathbf{0}$ as well as $\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 \cdot \boldsymbol{n}_\Gamma - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1 \cdot \boldsymbol{n}_\Gamma - \kappa\sigma_\Gamma = 0$ on Γ and assume that dissipation is given through

$$\tilde{\xi}_\Gamma := \beta_1^{-1} \left|\boldsymbol{v}_\tau\right|^2 + \beta_2 \left|\boldsymbol{T}^{\boldsymbol{\Gamma}}_{1,\tau}\right|^2 + \beta_3 \left|\boldsymbol{h}_\Gamma\right|^2 .$$

We then end up with model A in 2.8.1.

5.2. **Slipping fluids (Model B).** In case $\boldsymbol{v} = \boldsymbol{v}_1 \neq \boldsymbol{v}_2$, we can reformulate $(5.7)_1$ in the form

$$\xi_\Gamma := \left(\left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1\right)_n - \kappa\sigma_\Gamma \boldsymbol{n}_\Gamma\right)\boldsymbol{v}_n + \left(\left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1\right)_\tau\right) \cdot \boldsymbol{v}_{1,\tau} + \boldsymbol{T}^{\boldsymbol{\Gamma}}_2 \cdot (\boldsymbol{v}_2 - \boldsymbol{v}_1)_\tau - (\boldsymbol{h}_\Gamma + E_\Gamma \cdot \boldsymbol{v}_\tau) \cdot \frac{\nabla_\tau \vartheta}{\vartheta} . \tag{5.8}$$

As we assume that the normal movement of Γ does not come up with any friction processes, we find Newton's third law in normal direction through $\left(\left(\boldsymbol{T}^{\boldsymbol{\Gamma}}_2 - \boldsymbol{T}^{\boldsymbol{\Gamma}}_1\right) \cdot \boldsymbol{n}_\Gamma - \kappa\sigma_\Gamma\right) = 0$. In the second product on the right hand side, the term $\frac{\nabla_\tau \vartheta}{\vartheta} E_\Gamma$ appears as a stress and should thus, as $\kappa\sigma_\Gamma \boldsymbol{n}_\Gamma$ in the first term, also appear in the final set of constitutive equations. Indeed, it suggests that Newtons third law has to be modified into either one of the equations (2.20).

5.3. **Model C.** The term proportional to $(\boldsymbol{v}_1 - \boldsymbol{v}_2)_\tau$ vanishes in (5.8).

6. On the normal bulk velocity: Mean curvature Flow and the Mullins-Sekerka model

It can be observed that the Cahn-Hilliard energy approximates the surface energy as the interfacial zone becomes thinner and the gradients of c become steeper. Thus, we will first discuss the limit procedures that can be used to derive mean curvature flow from the Allen-Cahn equation resp. Mullins-Sekerka flow from Cahn-Hilliard equation and then demonstrate how these can be derived within our thermodynamic approach to sharp interfaces in the next section.

Let us first note that both, the Allen-Cahn as well as the Cahn-Hilliard equation, can be derived in the framework of maximum rate of entropy production [16, 15] based on the energy function

$$E = u(\eta, \varrho, c) + \frac{1}{2}\sigma \left|\nabla c\right|^2 + \frac{1}{2}\left|\boldsymbol{v}\right|^2 . \tag{6.1}$$

Similarly, in a mathematical formulation, they are the L^2- and H^{-1}- gradient flows of the energy functional based on (6.1). The deeper connection between the theories of maximum rate of entropy production and of gradient flows is outlined in [13]. Finally, for a more detailed mathematical presentation of the sharp interface limits presented below, refer to [31, 25] for the Allen-Cahn equation and to [2, 18, 27] for the (Navier-Stokes-) Mullins-Sekerka model.

6.1. **Asymptotics in the Allen-Cahn equation: Mean curvature flow.** The (non convective) Allen-Cahn equation is given through

$$\varepsilon \partial_t c^\varepsilon - \varepsilon \Delta c^\varepsilon + \frac{1}{\varepsilon} f'(c^\varepsilon) = 0$$

where $f : \mathbb{R} \to \mathbb{R}$ usually is given as the double well potential $f(x) = (1 - x^2)^2$. More physical models for f can be found in [4, 13]. We know from a series of works on the topic ([31, 25] and references therein) that as $\varepsilon \to 0$, the sequence c^ε converges to some characteristic function c attaining only the values ± 1 such that we can define the surface

$$\Gamma := \partial \left\{x \in \Omega \,:\, c(x) = 1\right\} \cap \partial \left\{x \in \Omega \,:\, c(x) = -1\right\} .$$

It is then shown that $\sqrt{\varepsilon}\partial_t c^\varepsilon \to 2\partial_t\Gamma$ and $\sqrt{\varepsilon}\left(\Delta c^\varepsilon - \frac{1}{\varepsilon^2}f'(c^\varepsilon)\right) \to \sigma\kappa$, where $\sigma = \int_{-1}^{1} f$. In particular, the limit equation reads

$$\partial_t\Gamma = \sigma\kappa\,.$$

Associated with the gradient-flow theory of the Allen-Cahn equation is the free energy functional

$$\mathcal{E}^\varepsilon := \int_\Omega \left(\varepsilon\,|\nabla c^\varepsilon|^2 + \frac{1}{\varepsilon}f(c^\varepsilon)\right)\,, \tag{6.2}$$

with dissipation

$$\Xi^\varepsilon := \int_\Omega \varepsilon\left(\Delta c^\varepsilon - \frac{1}{\varepsilon^2}f'(c^\varepsilon)\right)^2\,.$$

Then, in the limit $\varepsilon \to 0$ with $\mathcal{E}^\varepsilon \to \mathcal{E}$ and $\Xi^\varepsilon \to \Xi$, we find

$$\mathcal{E} = \int_\Gamma \sigma\,, \qquad \Xi = \int_\Gamma (\sigma\kappa)^2$$

In case of the convective Allen-Cahn equation,

$$\varepsilon\partial_t c^\varepsilon + \varepsilon\boldsymbol{v}\cdot\nabla c^\varepsilon - \sigma\varepsilon\Delta c^\varepsilon + \frac{1}{\varepsilon}f'(c^\varepsilon) = 0$$

the limit equation reads

$$\partial_t\Gamma + \boldsymbol{v}\cdot\boldsymbol{n}_\Gamma = \sigma\kappa\,.$$

In order to understand the implications of these results, note that the Allen-Cahn equation is non-conservative, i.e. it describes a phase transition such as water to ice. It is the nature of such processes, that the amount of the several species is not conserved and that the interface Γ moves even if there is no convective mass transport.

6.2. **Asymptotics in the Cahn-Hilliard equation: Mullins-Sekerka flow.** In contrast with the former subsection, the (non-convective) Cahn-Hilliard equation is given through

$$\begin{aligned}
\partial_t c^\varepsilon &= \Delta v^\varepsilon\,. && (x,t)\in\Omega\times(0,+\infty)\\
v^\varepsilon &= -\left(-\varepsilon\Delta c^\varepsilon + \frac{1}{\varepsilon}f'(c^\varepsilon)\right) && (x,t)\in\Omega\times(0,+\infty)\\
\frac{\partial c^\varepsilon}{\partial n} &= \frac{\partial v^\varepsilon}{\partial n} = 0 && (x,t)\in\partial\Omega\times(0,+\infty)\\
c^\varepsilon(x,0) &= c_0^\varepsilon(x) && x\in\Omega
\end{aligned}$$

It was shown by Pego [27] that this problem formally converges to

$$\begin{aligned}
\partial_t\Gamma &= -\frac{1}{2}\Delta_\Gamma(\sigma\kappa)\,. \quad (x,t)\ \text{on}\Gamma(t)\,,\ t\in[0,T]\\
\Gamma(0) &= \Gamma_0
\end{aligned} \tag{6.3}$$

as $\varepsilon\to 0$, where we use the notation from subsection 3.4.

Once more, the ε-energy functional is given through (6.2) while the dissipation functional for each ε is given through

$$\Xi^\varepsilon := \int_\Omega \left|\nabla\left(\Delta c^\varepsilon - \frac{1}{\varepsilon^2}f'(c^\varepsilon)\right)\right|^2\,.$$

As for the Allen-Cahn equation, we can study the convective case given through

$$\partial_t c^\varepsilon + \boldsymbol{v}\cdot\nabla c^\varepsilon = \Delta\boldsymbol{v}^\varepsilon$$

with the limit equation

$$\partial_t\Gamma + \boldsymbol{v}\cdot\boldsymbol{n}_\Gamma = -\Delta_\Gamma\left(\sigma\kappa\right)\,.$$

Using the notation from section 3.4, the dissipation functional this time formally converges to

$$\Xi := \int_\Omega |\nabla w_{\sigma\kappa}|^2 = -\int_\Gamma \sigma\kappa\Delta_\Gamma\left(\sigma\kappa\right)\,.$$

The sharp interface limit including Navier-Stokes equation can be found in [2].

7. The Thermodynamics of discontinuous normal velocity

Before we start discussing discontinuous normal velocity at Γ in the sense of (2.4), i.e.

$$\boldsymbol{v} = \boldsymbol{v}_1 + \delta\boldsymbol{v}_1 = \boldsymbol{v}_2 + \delta\boldsymbol{v}_2 \qquad \text{on } \Gamma\,, \tag{7.1}$$

we have to be aware of the physical difficulties that arise from such assumption. In particular, we are left with one degree of freedom in order to relate either $\boldsymbol{v}_{1,n}$ and $\boldsymbol{v}_{2,n}$ or $\delta\boldsymbol{v}_1$ and $\delta\boldsymbol{v}_2$. In order to make this more clear, let us first have a look at the corresponding local rates of entropy production and mass conservation.

In order to keep calculations simple and readable, we assume that the bulk velocity has no-slip boundary condition on $\partial\Omega$, i.e. $\boldsymbol{v}_1|_{\partial\Omega} \equiv \mathbf{0}$, $\boldsymbol{v}_2|_{\partial\Omega} \equiv \mathbf{0}$ and $\delta\boldsymbol{v}_{1,\tau} = \delta\boldsymbol{v}_{2,\tau} = \mathbf{0}$. This leads to the following condition at the contact line:

$$\delta\boldsymbol{v} := \boldsymbol{v} = \delta\boldsymbol{v}_1 = \delta\boldsymbol{v}_2\,. \tag{7.2}$$

Thus, inserting this ansatz into the calculations from section 5, we get

(7.3)

$$\xi_\Gamma := \left(\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)_n - \kappa\sigma_\Gamma\boldsymbol{n}_\Gamma\right)\boldsymbol{v}_n + \left(\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)_\tau\right)\cdot\boldsymbol{v}_{1,\tau} + \boldsymbol{T}_{1,n}^{\boldsymbol{\Gamma}}\cdot\delta\boldsymbol{v}_1 - \boldsymbol{T}_{2,n}^{\boldsymbol{\Gamma}}\cdot\delta\boldsymbol{v}_2 - (\boldsymbol{h}_\Gamma + E_\Gamma\boldsymbol{v})\cdot\frac{\nabla\vartheta}{\vartheta}\,,$$

$$\xi_\gamma := -\left(\sigma_\Gamma\nu_\Gamma + \sigma_1\nu_{\Gamma_1} + \sigma_2\nu_{\Gamma_2} + \sigma_\gamma\boldsymbol{\kappa}_\gamma\right)\cdot\delta\boldsymbol{v} + \vartheta\frac{\partial\eta_\gamma}{\partial\nu_\Gamma}\cdot\partial_t\nu_\Gamma$$

Now, Newton's third law in tangential direction reads $\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)_\tau = 0$, while in normal direction we find $\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)_n - \kappa\sigma_\Gamma\boldsymbol{n}_\Gamma = \mathbf{0}$. For the remainder of this section, we deal only with the governing equations on Γ, while we shift the discussion of the equations on γ to subsection 2.10.

As we saw in section 6, the discontinuous normal velocity may result in a net mass transport through Γ, this being a consequence of phase transitions. On the other hand, the effect of phase separation, will lead to a Mullins-Sekerka type movement of Γ which, by its nature, is mass conservative for each species. We will thus first have a look on the constraint of global mass conservation and conservation of each fluid before deriving the thermodynamical models. In particular, we have to relate $\delta\boldsymbol{v}_i$ to the net mass transport in an appropriate way.

7.1. Global and local mass conservation.

Global mass conservation in a simple system without any discontinuity of the type (7.1) reads

$$0 = \frac{d}{dt}\left(\int_{\Omega_1}\varrho_1 + \int_{\Omega_2}\varrho_2\right) \tag{7.4}$$

where Reynold's theorem applied to the mass of each single fluid implies in case $\delta\boldsymbol{v}_i = \mathbf{0}$

$$\int_{\Omega_1}\partial_t\varrho_1 + \operatorname{div}\left(\varrho_1\boldsymbol{v}_1\right) = 0 \qquad \text{and} \qquad \int_{\Omega_2}\partial_t\varrho_2 + \operatorname{div}\left(\varrho_2\boldsymbol{v}_2\right) = 0\,.$$

However, once we assume (7.1) with $\delta\boldsymbol{v}_i \neq \mathbf{0}$, there is a local net mass transport through Γ, as ϱ_i cannot move faster than $\boldsymbol{v}_i$. Thus, we obtain with respect to (7.4)

$$\frac{d}{dt}\int_{\Omega_1}\varrho_1 = \int_\Gamma m_1\,, \qquad \frac{d}{dt}\int_{\Omega_2}\varrho_2 = \int_\Gamma m_2\,,$$

where m_i is related to a local mass flux through $m_i = \boldsymbol{m}_i\cdot\boldsymbol{n}_\Gamma$. Note that m_1 and m_2 are related through

$$\int_\Gamma\left(m_2 + m_1\right) = 0\,,$$

and a purely reactive normal mass flux (e.g. for phase transitions / chemical reactions) is characterized by $m_1 + m_2 = 0$. On the other hand, we might locally find that $m_1 + m_2 \neq 0$, e.g. in case of Mullins-Sekerka flow. From Remark 3.6 we infer that the mass $\int_{\Omega_1}\varrho_1$ is conserved if and only if there is g_m such that $-\Delta_\Gamma g_m = m_1$.

However, as we saw above, the local rate of entropy production on Γ depends on $\delta\boldsymbol{v}_i$ rather than m_i. On the other hand, we can expect that $\delta\boldsymbol{v}_i = \frac{m_i}{\tilde{m}_i(\varrho_1,\varrho_2)}\boldsymbol{n}_\Gamma$, where $\tilde{m}_i(\varrho_1\varrho_2)$ depends on the quantities ϱ_1 and ϱ_2 in a possibly nonlinear way[3]. We will discuss this issue depending on the physical situation below.

[3]To get a feeling for this nonlinearity, note that in case of phase transition with incompressible fluid 1, compressible fluid 2 and a non-negligible difference $\varrho_1 - \varrho_2$, we would find $m_{i,0}(\varrho_1,\varrho_2) = \varrho_1$, while in the mass conservative case, we can expect $m_{i,0}(\varrho_1,\varrho_2) = \varrho_i$.

7.2. **Mean curvature flow: First approach.** We assume that $\frac{d}{dt}\int_{\Omega_1}\varrho_1 \neq 0$ and that $\delta\boldsymbol{v}_i = \frac{m_i}{\tilde{m}_i(\varrho_1,\varrho_2)}\boldsymbol{n}_\Gamma$. Then, we infer from (7.1) that

$$\delta\boldsymbol{v}_1 = -\frac{\tilde{m}_2\left(\varrho_1,\varrho_2\right)}{\tilde{m}_1\left(\varrho_1,\varrho_2\right)}\delta\boldsymbol{v}_2$$

which far away from the contact line can be assumed to be become $\delta\boldsymbol{v}_1 = -\frac{\varrho_2}{\varrho_1}\delta\boldsymbol{v}_2$ if we suppose $\tilde{m}_i\left(\varrho_1,\varrho_2\right) = \varrho_i$ far from γ. Note that due to (7.2), the relation between m_1 and m_2 need to guaranty that $\frac{\tilde{m}_1}{\tilde{m}_2} = 1$ close to γ. At Γ, we then find for the rate of entropy production on Γ

$$\begin{aligned}\xi_\Gamma := &\left(\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)_n - \kappa\sigma_\Gamma\boldsymbol{n}_\Gamma\right)\boldsymbol{v}_n + \left(\left(\boldsymbol{T}_2^{\boldsymbol{\Gamma}} - \boldsymbol{T}_1^{\boldsymbol{\Gamma}}\right)_\tau\right)\cdot\boldsymbol{v}_{1,\tau} - \left(\boldsymbol{h}_\Gamma + E_\Gamma\boldsymbol{v}\right)\cdot\frac{\nabla\vartheta}{\vartheta}\\ &+\left(\boldsymbol{T}_{2,n}^{\boldsymbol{\Gamma}}\left(1-\frac{\tilde{m}_1(\varrho_1,\varrho_2)}{\tilde{m}_2(\varrho_1,\varrho_2)}\right) - \kappa\sigma_\Gamma\boldsymbol{n}_\Gamma\right)\delta\boldsymbol{v}_1\,,\end{aligned}$$

and assuming that the dissipation is locally given through the function

$$\xi_\Gamma(\delta\boldsymbol{v}_1) = \alpha_\Gamma^{-1}\left|\delta\boldsymbol{v}_1\right|^2$$

we get the following generalized mean curvature flow

$$\delta\boldsymbol{v}_1 = \alpha_\Gamma\left(\boldsymbol{T}_{2,n}^{\boldsymbol{\Gamma}}\left(1-\frac{\tilde{m}_1(\varrho_1,\varrho_2)}{\tilde{m}_2(\varrho_1,\varrho_2)}\right) - \kappa\sigma_\Gamma\boldsymbol{n}_\Gamma\right)\,,$$

and from this the mass fluxes m_1 and m_2. Note that the second term in brackets yields the classical mean curvature flow, while the first term stems from interactions with the stress acting on the surface.

7.3. **Mean curvature flow: Second approach.** In a different approach, we assume that $\boldsymbol{v} = \boldsymbol{v}_1 + \delta\boldsymbol{v}$ as well as $\boldsymbol{v}_1 = \boldsymbol{v}_2$ on Γ and that $\delta\boldsymbol{v} = \frac{m_1}{m_{1,0}(\varrho_1,\varrho_2)}\boldsymbol{n}_\Gamma = \frac{m_2}{m_{2,0}(\varrho_1,\varrho_2)}\boldsymbol{n}_\Gamma$. Then, we get from a similar calculation the final mean curvature flow

$$\delta\boldsymbol{v}_n = -\alpha_\Gamma\kappa\sigma_\Gamma\boldsymbol{n}_\Gamma\,,$$

and from this the mass fluxes m_1 and m_2. Note that with the initial assumption $\boldsymbol{v}_1 = \boldsymbol{v}_2$ there is an issue involved that we will discuss in the next subsection.

7.4. **Mullins-Sekerka flow.** We assume that $\frac{d}{dt}\int_{\Omega_1}\varrho_1 = 0$. Like in the previous subsection, we assume that $\boldsymbol{v} = \boldsymbol{v}_1 + \delta\boldsymbol{v}$ as well as $\boldsymbol{v}_1 = \boldsymbol{v}_2$ on Γ and that $\delta\boldsymbol{v} = \frac{m_1}{m_{1,0}(\varrho_1,\varrho_2)}\boldsymbol{n}_\Gamma = \frac{m_2}{m_{2,0}(\varrho_1,\varrho_2)}\boldsymbol{n}_\Gamma$. These assumptions imply that the continuity assumption on the velocity field, usually applied to multiphase flows, remains valid. In particular, it states that the diffusive oscillations at the interface are of minor influence on the normal velocity field. With $\delta\boldsymbol{v} = \frac{m_1}{m_{1,0}(\varrho_1,\varrho_2)}\boldsymbol{n}_\Gamma$ as well as $m_1 = -\Delta_\Gamma g_m$, we find

$$\xi_\Gamma = \frac{\kappa\sigma_\Gamma}{m_{1,0}(\varrho_1,\varrho_2)}\Delta_\Gamma g_m\,,$$

which yields in combination with g_f being the solution to $-\Delta_\Gamma g_f = \frac{\kappa\sigma_\Gamma}{m_{1,0}(\varrho_1,\varrho_2)}$ that the contribution of ξ_Γ to the global entropy production is

$$\Xi_\Gamma = \int_\Gamma \frac{\kappa\sigma_\Gamma}{m_{1,0}(\varrho_1,\varrho_2)}\Delta_\Gamma g_m = -\int_\Omega \nabla w_{g_f}\cdot\nabla w_{g_m}\,.$$

If we assume that the rate of entropy production due to ξ_Γ is given through the quadratic dependence

$$\Xi_\Gamma(m_1) = \int_\Omega \left|\nabla w_{g_m}\right|^2\,,$$

this finally yields

$$g_m = -\frac{\kappa\sigma_\Gamma}{m_{1,0}(\varrho_1,\varrho_2)}\,.$$

Appendix A. Proof of Proposition 3.5

For any function

$$\begin{aligned} f:\gamma(t) &\to \mathbb{R} \\ x &\mapsto f(x) \end{aligned}$$

we define for $x \in \gamma(t)$ and s such that $x = \widetilde{\gamma}_t(s)$:

$$\partial_\tau f(x) = \frac{d}{dr}(f(\widetilde{\gamma}_t(r))\Big|_{r=s} \qquad \text{or, equivalently,} \qquad \nabla_\gamma f := \partial_\tau f(x)\boldsymbol{\tau}\,.$$

If $f:\mathbb{R}^3 \to \mathbb{R}$ is differentiable, we find

$$\partial_\tau f(x) = \nabla f(\widetilde{\gamma}_t(s)) \cdot \boldsymbol{\tau}\,.$$

By standard, we denote for any $y \in \mathbb{R}^3$ $\operatorname{dist}(y,\gamma)$ the distance of y to γ. We furthermore assume γ is regular enough for there is δ such that with

$$D_\delta := \left\{ y \in \mathbb{R}^3 \,:\, \operatorname{dist}(y,\gamma) < \delta \right\},$$

there is for any $y \in D_\delta$ a unique $\tilde{y} \in \gamma$ such that $|y - \tilde{y}| = \operatorname{dist}(y,\gamma)$. We denote the mapping $y \mapsto \tilde{y}$ by P_γ, which has the same regularity as γ. For any function $g:\gamma \to \mathbb{R}^d$, $d = 1,2,3$, we define $\hat{g}(\cdot) := g(P_\gamma(\cdot))$ which then is a mapping $\hat{g}:D_\delta \to \mathbb{R}^d$. Note that on γ, we find $\partial_\tau f = \nabla \hat{f} \cdot \boldsymbol{\tau}$ and $\operatorname{div}_\tau \boldsymbol{\upsilon} = \operatorname{div} \hat{\boldsymbol{\upsilon}}$.

By standard calculations, as they may be found e.g. in [7], we now find

$$\frac{d}{dt}\mathcal{E}(\gamma(t)) = \int_{\gamma(t)} \partial_t f(t) + \operatorname{div}_\tau \left(\hat{f}(t)\, \hat{\boldsymbol{\upsilon}}(t) \right),$$

which finishes the proof in view of the following lemma:

Lemma A.1.

$$\int_\gamma \nabla_\gamma f = \int_\gamma f \boldsymbol{\kappa}\,.$$

Proof. For any continuously differentiable function $g:D_\delta \to \mathbb{R}$, we find

$$\int_{D_\delta} \nabla g = \int_{\partial D_\delta} g \boldsymbol{N}_\delta d\mathcal{H}^{n-1}\,.$$

Thus, we find

$$\begin{aligned} \left(\int_\gamma \nabla_\gamma f \, d\gamma \right)_i &= \frac{1}{\pi\delta^2} \int_{D_\delta} \left(\hat{f}_j \hat{\boldsymbol{\tau}}_j \right) \hat{\boldsymbol{\tau}}_i \\ &= \frac{1}{\pi\delta^2} \int_{\partial D_\delta} \hat{\boldsymbol{\tau}}_j \hat{\boldsymbol{\tau}}_i \hat{f} \boldsymbol{N}_{\delta,j} - \frac{1}{\pi\delta^2} \int_{D_\delta} f\, \partial_j \left(\hat{\boldsymbol{\tau}}_j \hat{\boldsymbol{\tau}}_i \right) \\ &= -\frac{1}{\pi\delta^2} \int_{D_\delta} f\, \hat{\boldsymbol{\tau}}_i \partial_j \hat{\boldsymbol{\tau}}_j - \frac{1}{\pi\delta^2} \int_{D_\delta} f\, \hat{\boldsymbol{\tau}}_j \partial_j \hat{\boldsymbol{\tau}}_i \\ &= -\frac{1}{\pi\delta^2} \int_{D_\delta} f\, \hat{\boldsymbol{\kappa}}_i \end{aligned}$$

where we used $\hat{\boldsymbol{\tau}} \cdot \boldsymbol{N}_\delta = 0$ and the following two results:

$$\hat{\boldsymbol{\kappa}}_i = \widehat{\widetilde{\gamma}''} = \left(\left(\nabla \widehat{\widetilde{\gamma}'} \right) \widehat{\widetilde{\gamma}'} \right)_i = \sum_j \left(\partial_j \widehat{\widetilde{\gamma}'}_i \right) \widehat{\widetilde{\gamma}'}_j$$

$$\sum_j \partial_j \hat{\boldsymbol{\tau}}_j = \operatorname{tr}\left(\nabla \widehat{\widetilde{\gamma}'} \right) = 0$$

where the last equality follows from the fact that the trace is independent on changes of the coordinates and for a choice $e_1 = \boldsymbol{\tau}$, $e_2 = \boldsymbol{n}_1$, $e_3 = \boldsymbol{n}_2$ with $\boldsymbol{n}_1 \cdot \boldsymbol{\tau} = 0$, $\boldsymbol{n}_2 \cdot \boldsymbol{\tau} = 0$, $\boldsymbol{n}_1 \cdot \boldsymbol{n}_2 = 0$, we find

$$\nabla \widehat{\widetilde{\gamma}'} = \begin{pmatrix} 0 & 0 & 0 \\ \boldsymbol{\kappa}_2 & 0 & 0 \\ \boldsymbol{\kappa}_3 & 0 & 0 \end{pmatrix}.$$

□

References

[1] H. Abels, H. Garcke, and G. Grün. Thermodynamically consistent, frame indifferent diffuse interface models for incompressible two-phase flows with different densities. *Mathematical Models and Methods in Applied Sciences*, 22(03), 2012.

[2] H. Abels and M. Röger. Existence of weak solutions for a non-classical sharp interface model for a two-phase flow of viscous, incompressible fluids. In *Annales de l'Institut Henri Poincare (C) Non Linear Analysis*, volume 26, pages 2403–2424. Elsevier, 2009.

[3] Helmut Abels and Matthias Röger. Existence of weak solutions for a non-classical sharp interface model for a two-phase flow of viscous, incompressible fluids. Preprint, 2008.

[4] Helmut Abels and Mathias Wilke. Convergence to equilibrium for the Cahn-Hilliard equation with a logarithmic free energy. *Nonlinear Analysis: Theory, Methods & Applications*, 67(11):3176–3193, 2007.

[5] N.K. Adam. *The physics and chemistry of surfaces*, volume 109. Clarendon Press Oxford, 1941.

[6] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley. Wetting and spreading. *Reviews of modern physics*, 81(2):739, 2009.

[7] G. C. Buscaglia and R. F. Ausas. Variational formulations for surface tension, capillarity and wetting. *Computer Methods in Applied Mechanics and Engineering*, 2011.

[8] H. Callen. *Thermodynamics and an introduction to thermostatics*. Wiley, London, 1985.

[9] P.G. De Gennes, F. Brochard-Wyart, and D. Quéré. *Capillarity and wetting phenomena: drops, bubbles, pearls, waves*. Springer, 2003.

[10] E. B. Dussan V. and S.H. Davis. On the motion of a fluid-fluid interface along a solid surface. *Journal of Fluid Mechanics*, 65(01):71–95, 1974.

[11] Annegret Glitzky and Alexander Mielke. A gradient structure for systems coupling reaction-diffusion effects in bulk and interfaces. *preprint online*, 2011.

[12] M. Heida. On the derivation of thermodynamically consistent boundary conditions for the Cahn-Hilliard-Navier-Stokes system. *submitted to IJES*, 2011.

[13] M. Heida. On gradient flows of nonconvex functionals in Hilbert spaces with Riemannian metric and application to Cahn-Hilliard equations. *submitted*, 2012.

[14] M. Heida, J. Málek, and K.R. Rajagopal. The derivation of thermodynamically consistent boundary conditions for Korteweg-Fourier fluids. *in preparation*.

[15] M. Heida, J. Málek, and K.R. Rajagopal. On the development and generalizations of Allen-Cahn and Stefan equations within a thermodynmic framework. *to be submitted to Zeitschrift für Angewandte Mathematik und Physik (ZAMP)*, 63(4):759–776, 2012.

[16] M. Heida, J. Málek, and K.R. Rajagopal. On the development and generalizations of Cahn-Hilliard equations within rational thermodynamic framework. *Zeitschrift für Angewandte Mathematik und Physik (ZAMP)*, 63(1):145–169, 2012.

[17] C. Huh and LE Scriven. Hydrodynamic model of steady movement of a solid/liquid/fluid contact line. *Journal of Colloid and Interface Science*, 35(1):85–101, 1971.

[18] J. Lowengrub and L. Truskinovsky. Quasi-incompressible Cahn-Hilliard fluids and topological transitions. *Procedings of the Royal Society in London, Series A, Mathematical and Physical and Engineering Sciences*, 454(1978):2617–2654, 1998.

[19] J. Málek and K.R. Rajagopal. Incompressible rate type fluids with pressure and shear-rate dependent material moduli. *Nonlinear Analysis: Real World Applications*, 8(1):156–164, 2007.

[20] Josef Malek and K.R. Rajagopal. Compressible generalized newtonian fluids. 2009.

[21] M. Mercker, M. Ptashnyk, J. Kühnle, D. Hartmann, M. Weiss, and W. Jäger. A multiscale approach to curvature modulated sorting in biological membranes. *Journal of Theoretical Biology*, 301:67–82, 2012.

[22] Moritz Mercker. Models, numerics and simulations of deforming biological surfaces, 2012.

[23] Alexander Mielke. A gradient structure for reaction–diffusion systems and for energy-drift-diffusion systems. *Nonlinearity*, 24(4):1329, 2011.

[24] Alexander Mielke. Thermomechanical modeling of energy-reaction-diffusion systems, including bulk-interface interactions. *preprint online*, 2011.

[25] L. Mugnai and M. Röger. Convergence of perturbed allen cahn equations to forced mean curvature flow. *preprint online at mis.mpg.de*, 2009.

[26] J. Oudar. *Physics and chemistry of surfaces*. Blackie, 1975.

[27] R.L. Pego. Front migration in the nonlinear Cahn-Hilliard equation. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, 422(1863):261–278, 1989.

[28] T. Qian, X. Wang, and P. Sheng. Molecular scale contact line hydrodynamics of immiscible flows. *Physical Reviews E*, 68(1):016306, Jul 2003.

[29] T. Qian, X.P. Wang, and P. Sheng. A variational approach to moving contact line hydrodynamics. *Journal of Fluid Mechanics*, 564:333–360, 2006.

[30] K. R. Rajagopal. On implicit constitutive theories for fluids. *Journal of Fluid Mechanics*, 550:243–249, 2006.

[31] S. Serfaty. Gamma-convergence of gradient flows on Hilbert and metric spaces and applications. *Disc. Cont. Dyn. Systems, A*, 31:1427–1451, 2009.

[32] Y.D. Shikhmurzaev. The moving contact line on a smooth solid surface. *International Journal of Multiphase Flow*, 19(4):589–610, 1993.

[33] H.A. Stone, A.D. Stroock, and A. Ajdari. Engineering flows in small devices. *Annu. Rev. Fluid Mech.*, 36:381–411, 2004.

[34] C. Truesdell. *Rational thermodynamics*, volume 53. Springer, Berlin, 1985.

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