

Derivation and numerics of thin-film models with moving contact lines for binary mixtures

A thesis submitted for the degree of
MSc in Mathematical and Theoretical Physics

Candidate number: 1030548



Trinity 2019

“Who in the world am I? Ah, that’s the great puzzle.”

— Lewis Carroll, Alice in Wonderland

Acknowledgements

I would like to thank my co- and external supervisors Professor Andreas Münch and Dr. Dirk Peschka for answering the many questions I had over the course of my MSc. I would like to especially thank my direct supervisor Dr. Georgy Kitavtsev for meeting with me many times over the course of the year to guide my progress. This project was incredibly interesting and I learned a great deal.

Thank you Arjun, Jonathan, and Gunnar for the occasional enlightening theoretical physics discussions. But mostly for complaining with me.

Thank you Jean for listening to me at my worst moments and for being excellent company. I know that you will be successful in your future prospects.

Thank you Mariana for helping me make the figures for this dissertation, generously sharing your steaks, and teaching me about everything besides physics.

Thank you Edward for the fruitful conversations during many nights in Michaelmas term. Your work ethic and integrity blows me away.

Thank you Brian for the countless hours spent in monotony with me. I would not have finished this MSc without sharing some of my misery with you.

I would like to thank my brother Bruno and both of my parents for being there for me every step of the way. I am forever in your debt.

Finally, I must thank Ard and Karen, whom saved my life once and twice, respectively.

Excluding figures, this dissertation is 60 pages long.

Abstract

Many hydrodynamical systems in nature can be described in terms of dissipative energy transfer processes. In order to describe such systems, it is essential that we have a systematic way of deriving their equations of motion that is thermodynamically consistent. In this work, we present a framework to formulate the evolution of this general class of hydrodynamical systems as gradient flows in appropriate phase spaces, which automatically ensures several physically significant mathematical properties. We then apply this framework to establish the connection between thin-film binary mixtures composed of Newtonian and inviscid fluid phases to their respective gradient flow dynamics. Furthermore, our approach leads to the unique result that one can always express the bulk equations of motion as an explicit asymmetric momentum-conservation system by imposing conditions on the mixing free energy density of the binary mixture. Finally, we also present an algorithm to numerically model the time evolution of a thin-film monofluid and binary mixture droplet.

Contents

1	Introduction	1
2	Onsager's variational principle	4
2.1	Physical formalism	4
2.2	Abstract formalism of Onsager's variational principle	5
2.2.1	Gradient flows	5
2.2.2	Minimum dissipation principle	6
2.2.3	Solution stability	6
2.3	General procedure	7
3	Monofluids	9
3.1	Bulk equations	11
3.2	Thin-Film Approximation	15
3.2.1	Solving the thin-film equations	20
3.3	Modelling the thin-film evolution	21
3.3.1	The weak formulation	21
3.3.2	Finding an appropriate update rule	22
3.3.3	Finite element analysis of the thin-film equations	25
3.3.4	Extensions of the model	29
3.3.5	Numerical simulation	31
4	Binary Mixtures	37
4.1	Bulk equations	38
4.1.1	Deriving an asymmetric bulk system	42
4.2	Thin-film approximation	45
4.2.1	Solving the thin-film equations	50
4.2.2	Coupled gradient flow	51
4.3	Modelling the binary mixture evolution	52
4.3.1	Weak form of binary mixture thin-film equation	52
4.3.2	Finite element analysis of binary mixture model	54

5 Discussion and conclusion	56
5.1 Final remarks	56
5.2 Conclusion and future work	57
A Mathematical Methods	58
B Simple application of Onsager's variational principle	59
C Continuum mechanics	62
C.1 Stress	62
C.2 Deformation in highly viscous fluids	62
C.3 Stoke's flow	63
C.4 Dissipation relations	64
C.5 Computer code	65

List of Figures

1.1 Illustration of a thin-film droplet with left and right contact angles θ_L and θ_R , respectively.	2
3.1 Illustration of a liquid droplet on a smooth solid substrate and surrounded by a gas. The liquid-gas, liquid-solid, and solid-gas interfaces are denoted by Λ_{lg} , Λ_{ls} , and Λ_{sg} , respectively.	9
3.2 Illustration of a film with a time-independent support and time-dependent free surface Λ	10
3.3 Illustration of the variable H which has a constant support during consecutive time-steps.	25
3.4 Evolution towards stationary droplet with $S_L = S_R = 1.0$ and $\zeta_n = \zeta_\tau = 0$	33
3.5 Volume over time for droplet in figure 3.4.	33
3.6 Evolution towards travelling wave solution with $S_L = S_R = 1.0$, $\zeta_n = 0$, and $\zeta_\tau = 10$	34
3.7 Evolution towards travelling wave solution with $S_L = S_R = 1.0$, $\zeta_n = 0$, and $\zeta_\tau = 100$	34

3.8	Evolution towards stationary droplet with $S_L = S_R = 1.0$, $\zeta_n = 50$, and $\zeta_\tau = 0$.	35
3.9	Marangoni effect demonstration with $S_L = 0$, $S_R = 2.0$, and $\zeta_n =$ $\zeta_\tau = 0$.	36
3.10	Dewetting demonstration with $S_L = S_R = 1.0$ and $\zeta_n = \zeta_\tau = 0$.	36
B.1	Illustration of a fluid rising with height $h(t)$ in a capillary filled with particles.	59

Notation

The following mathematical notation holds unless otherwise specified:

V^*	dual space of the vector space V
$\langle \cdot, \cdot \rangle_H$	inner product in H
$(A, x) := Ax$	mapping A acting on an element x of a space
$\text{div}(v)$	divergence of vector field v
$A : B$	$A_{ij}B_{ij}$ in Einstein notation for rank-2 tensors A and B
$\dot{s} := \frac{\partial s}{\partial t}$	partial derivative of s with respect to time
$\partial_\phi := \frac{\partial}{\partial \phi}$	partial derivative with respect to ϕ
$\iint_{\Omega} F(\mathbf{x}) \, d\mathbf{x}$	integral of $F(\mathbf{x})$ over the 2D domain Ω
$\int_{\Lambda} F(\mathbf{x}) \, d\Lambda$	integral of $F(\mathbf{x})$ over the 1D curve Λ
$\frac{\delta J}{\delta f(x)}$	Fréchet derivative of J with respect to f at the point x

1

Introduction

Lubrication theory is the study of fluid domains where typical length scales H in one dimension are much smaller than typical length scales L in the other dimensions; this is known as the *thin-film approximation* [22]. The main idea is to asymptotically expand the Navier-Stokes equations with respect to the small ratio $\epsilon = \frac{H}{L}$ to attain a thin fluid layer [23]. Thin-film approximations are useful with regards to mathematical modelling, as they effectively reduce the system dimensionality by one. They can be used to model a vast array of physical phenomena, from large scale lava flows [28] to cytoplasm dynamics related to amoeboid cell motion [25].

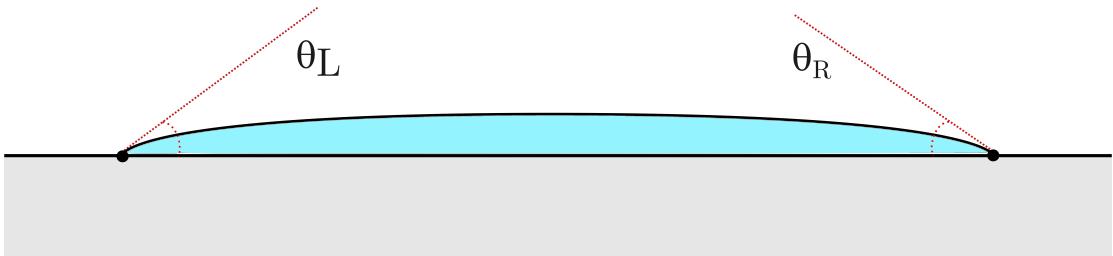


Figure 1.1: Illustration of a thin-film droplet with left and right contact angles θ_L and θ_R , respectively.

A theoretical formulation for lubrication theory was first developed by Reynolds in 1886 [3] to study the boundary and surface action of viscous fluids. Motivated by the frequent observation of these processes in commonplace scenarios, our understanding of lubrication mechanisms has made great advancements over the past century [42]. Research in lubrication theory has resulted in numerous useful biological applications, such as in studies of the tear film covering of the cornea [12, 26], mucus and intra-airway gas transport in the pulmonary system [19], and

instability of cell membranes [14, 11]. Lubrication theory has also seen engineering applications, such as in space systems [18], lubricated load-bearing joints [37], nanofluidics [33], and paint coating [21].

Evolving liquid thin-film droplets (see, for example, figure 1.1) host a platform for studying a large range of interesting dynamics, such as travelling waves [47, 17], wetting [41, 10], instabilities in rupturing films [24, 16], Marangoni convection [46, 57], and singularities at moving contact lines [7, 8, 59]. Many of these processes are well understood for simple fluids consisting of one composition (in this text referred to as *monofluids*). However, more complex fluid films such as active gels [56] and binary mixtures [32] exhibit unique phenomena, such as topological defects [48] and phase separation. These features interact with film effects such as surface tension, resulting in complicated processes that are not yet fully understood [49].

In order to understand these more complex dynamics, it would be advantageous to have a general mathematical framework from which one may derive equations of motion in a systematic way. In 1931, Lars Onsager formulated a procedure, known as *Onsager's variational principle* [5, 6], which can be used to derive the equations of motion for *dissipative* systems, i.e. systems that lose energy through irreversible dissipative processes. This principle, which is founded on a physical basis, has a mathematical foundation known as *gradient flows*, which describes equations with a specific gradient structure. If one can formulate the equations of motion in terms of this gradient structure, then the mathematical theory of gradient flows guarantees the thermodynamic consistency and stability of solutions. This approach has been applied for instance in liquid crystal [40] and two-phase fluid [25] models.

In this text, we shall perform the following tasks. In chapter 2, we present Onsager's variational principle and establish its connection to gradient flows, highlighting the usefulness of its mathematical structure. In chapter 3, we apply Onsager's variational principle to a monofluid system with a free surface. We shall first derive the full non-approximated case and then derive the thin-film case. Afterwards, we will numerically model the evolution of a thin-film monofluid droplet. In chapter 4, we apply Onsager's variational principle to a binary mixture system with a free surface. Once again, we will first derive the non-approximated case and then derive the thin-film case. In chapter 5, we will make a few remarks and discuss the implications of our results.

2

Onsager's variational principle

2.1 Physical formalism

Onsager's variational principle applies for dissipative systems in the linear response regime; in hydrodynamics, this corresponds to highly viscous flows absent of inertia. These systems can be described in terms of a *free energy* functional F and a *dissipation* functional Φ . The free energy functional accounts for the non-dissipative effects affecting the system, such as capillarity and gravity. The dissipation functional is defined as $\Phi = \frac{1}{2}D$, where D is the actual dissipation of the system; it accounts for irreversible energy transfers, such as energy lost through viscous flow. A simplifying assumption we shall use for Onsager's variational principle is that the system is isothermal [55].

The procedure for Onsager's variational principle is outlined as follows. Consider a set of N time-dependent state variables $\mathbf{x}(t) = (x_1(t), x_2(t), \dots, x_N(t))$ that fully describe the system, with corresponding rates $\dot{\mathbf{x}} = (\dot{x}_1, \dot{x}_2, \dots, \dot{x}_N)$. Define the functionals

$$\Phi = \frac{1}{2} \zeta_{ij} \dot{x}_i \dot{x}_j, \quad \dot{F} = \frac{\partial F}{\partial x_i} \dot{x}_i \quad (2.1)$$

in Einstein notation, where Φ is the dissipation functional, \dot{F} is the total time derivative of the free energy functional $F(\mathbf{x}(t))$ and $\zeta_{ij} \in \mathbb{R}$ is an element of the friction matrix [45]. The friction matrix ζ is symmetric and positive definite; for a proof of both properties that invokes hydrodynamics, see section C.4.

We then construct the *Rayleighian* functional $R = \dot{F} + \Phi$ and minimize it with respect to the rates \dot{x} , which yields the equation of motion of the system

$$-\sum_j \zeta_{ij} \dot{x}_j - \frac{\partial F}{\partial x_i} = 0 \quad (2.2)$$

A key feature is that $\dot{F} = -2\Phi \leq 0$, i.e. $F(x(t))$ always decreases over time.

2.2 Abstract formalism of Onsager's variational principle

2.2.1 Gradient flows

Onsager's variational principle is closely related to the gradient flow mathematical formalism which is described as follows.

Let \mathcal{X} be a Hilbert space equipped with a real inner product which induces a metric. Define a state $x(t) \in \mathcal{X}$ with each point $x(t)$ having a corresponding tangent vector $\dot{x} \in T_x \mathcal{X}$. Let the states be driven by a smooth free energy functional $F : \mathcal{X} \rightarrow \mathbb{R}$ through curves parametrized by $t \in \mathbb{R}$. Let $\zeta(x) : T_x \mathcal{X} \rightarrow T_x^* \mathcal{X}$ and $\xi(x) : T_x^* \mathcal{X} \rightarrow T_x \mathcal{X}$ be duality maps between the tangent space $T_x \mathcal{X}$ and cotangent space $T_x^* \mathcal{X}$. The equation of motion (2.2) is in the form of a gradient flow [50], given by

$$\begin{aligned}\zeta \dot{x} &= -\frac{\delta F}{\delta x} \\ \dot{x} &= -\xi \frac{\delta F}{\delta x}\end{aligned}\tag{2.3}$$

where $\frac{\delta F}{\delta x} \in T_x^* \mathcal{X}$ is notation for the Fréchet derivative of F at x . Assume that the duality maps are positive-definite, i.e. ζ and ξ both satisfy

$$(Aq, q) \geq 0 \quad \forall q \in V\tag{2.4}$$

for $q \neq 0$ and $A : V \rightarrow V^*$ with appropriate vector space V . Assume that they are also both symmetric such that

$$(q, Ap) = (p, Aq) \quad \forall q, p \in V\tag{2.5}$$

and invertible such that $\zeta = \xi^{-1}$. The positive-definiteness implies that F decreases along solutions, since

$$\begin{aligned}\frac{d}{dt} F &= \dot{F} = \left(\frac{\delta F}{\delta x}, \dot{x} \right) = - \left(\frac{\delta F}{\delta x}, \xi \frac{\delta F}{\delta x} \right) \\ &= -(\zeta \dot{x}, \dot{x}) < 0\end{aligned}\tag{2.6}$$

for all $\dot{x} \neq 0$. By defining the convex symmetric bilinear form $\Phi : T_x \mathcal{X} \times T_x \mathcal{X} \rightarrow \mathbb{R}$ as $\Phi(p, p) = \frac{1}{2}(p, \zeta p)$, the solution \dot{x} can be equivalently written as

$$\dot{x} = \operatorname{argmin}_{p \in T_x \mathcal{X}} \left(\Phi(p, p) + \dot{F}(p) \right)\tag{2.7}$$

where $\dot{F} : T_x \mathcal{X} \rightarrow \mathbb{R}$ is a linear functional defined as $\dot{F}(p) = \left(\frac{\delta F}{\delta x}, p \right)$ [50].

2.2.2 Minimum dissipation principle

To apply the structure of gradient flow to problems in fluid dynamics, we require the Helmholtz minimum dissipation theorem, a result attained by Hermann von Helmholtz in 1868 [2].

Theorem 2.2.1 (Helmholtz minimum dissipation theorem) *For a given viscosity and boundary conditions, the velocity field of an incompressible fluid experiencing steady Stoke's flow will generate the minimum possible dissipation rate [27].*

Theorem 2.2.1 implies that there exists specific processes preferred by nature that generate tangent vectors $\dot{x} \in T_x \mathcal{X}$ in such a way as to produce the minimum possible dissipation rate. These processes are not necessarily related to the states themselves [50]. Let these processes w exist in the *process space* $P_x \mathcal{X}$, and assume that for each $x \in \mathcal{X}$ there exists an operator $\mathcal{W}(x) : P_x \mathcal{X} \rightarrow T_x \mathcal{X}$ such that $\mathcal{W}(x)w = \dot{x}$ [50].

Let us re-define the dissipation functional Φ such that it is always minimized by the given process, i.e. for $p \in T_x \mathcal{X}$

$$\Phi(p, p) \rightarrow \min_{w \in P_x \mathcal{X}} (\Phi(w, w))$$

The solution $v \in P_x \mathcal{X}$ can then be written as

$$v = \operatorname{argmin}_{w \in P_x \mathcal{X}} \left(\Phi(w, w) + \dot{F}(\mathcal{W}(x)w) \right) \quad (2.8)$$

for a given free energy functional F . The corresponding tangent vector can then be found through $\dot{x} = \mathcal{W}(x)v$.

2.2.3 Solution stability

Suppose the solution to equation (2.3) has an equilibrium $x = x_e$ corresponding to $\dot{x} = 0$. If we then assume that the free energy functional locally (i.e. in a neighbourhood around x_e) satisfies the conditions

1. $F(x) = 0 \iff x = x_e$
2. $F(x) > 0 \iff x \neq x_e$
3. $\dot{F}(x) \leq 0 \iff x \neq x_e$

then $F(x)$ is a *Lyapunov* functional and system (2.3) is guaranteed to have Lyapunov stability [29]. Note that condition 3 is equivalent to equation (2.6), and conditions 1 and 2 can be satisfied by choosing an appropriate gauge. Furthermore, if condition 3 is replaced with $\dot{F}(x) < 0 \iff x \neq x_e$, the system is guaranteed to have local asymptotic stability in a neighbourhood around x_e [29]. Therefore, the framework provided by gradient flows is useful because it guarantees the stability of solutions for flows driven by a generic class of free energy functionals that often appear in dynamical systems.

2.3 General procedure

Hydrodynamical systems are often subject to some constraint, such as fluid incompressibility. In such cases, we introduce a Lagrange multiplier into the Rayleighian via a constraint term C . Let \mathcal{X} and \mathcal{Y} be Hilbert spaces equipped with a real inner product. The Rayleighian functional subject to the constraint $C(v, p) = 0$ for $v \in \mathcal{X}$ and $p \in \mathcal{Y}$ is

$$R(v, p) = \Phi(v, v) + \dot{F}(v) + C(v, p) \quad (2.9)$$

The optimality condition requires taking the Gateaux derivative of the Rayleighian at $(v, p) \in (\mathcal{X}, \mathcal{Y})$. This yields

$$\delta R(v)[\phi] = 2\Phi(v, \phi) + \dot{F}(\phi) + C(\phi, p) = 0 \quad \forall \phi \in \mathcal{X} \quad (2.10)$$

upon optimizing with respect to $v \in \mathcal{X}$ and

$$\delta R(p)[\theta] = C(v, \theta) = 0 \quad \forall \theta \in \mathcal{Y} \quad (2.11)$$

upon optimizing with respect to $p \in \mathcal{Y}$. Equation (2.10) determines the evolution of the dissipative system.

Existence and uniqueness of constrained solutions

Let V and Q be real Hilbert spaces, and let $\mathcal{F} \in V^*$ and $\mathcal{C} \in Q^*$ exist in the corresponding dual spaces. Let $a : V \times V \rightarrow \mathbb{R}$ and $b : V \times Q \rightarrow \mathbb{R}$ be bilinear forms. We shall restrict this presentation to a homogenous constraint $\mathcal{C}(\theta) = 0 \quad \forall \theta \in Q$, although the conditions corresponding to existence and uniqueness of the inhomogeneous problem may be extended straightforwardly.

The problem is stated as follows: for a given $(\mathcal{F}, \mathcal{C}) \in (V^*, Q^*)$, find $(v, p) \in (V, Q)$ such that

$$\begin{aligned} a(v, \phi) + b(\phi, p) &= \mathcal{F}(\phi) \\ b(v, \theta) &= 0 \end{aligned} \tag{2.12}$$

for every $(\phi, \theta) \in (V, Q)$.

Theorem 2.3.1 (Ladyzhenskaya-Babuška-Brezzi) *Suppose that $a(\cdot, \cdot)$ and $b(\cdot, \cdot)$ are bounded, bilinear forms. Suppose that $a(\cdot, \cdot)$ is coercive on the kernel of $b(\cdot, \cdot)$, i.e.*

$$a(\phi, \phi) \geq \alpha \|\phi\|_V \text{ s.t. } b(\phi, \theta) = 0 \quad \forall (\phi, \theta) \in (V, Q) \tag{2.13}$$

for some $0 < \alpha \in \mathbb{R}$. Additionally, suppose that there exists some $0 < \beta \in \mathbb{R}$ such that

$$\beta \leq \inf_{\substack{\theta \in Q \\ \theta \neq 0}} \sup_{\substack{\phi \in V \\ \phi \neq 0}} \frac{b(\phi, \theta)}{\|\phi\|_V \|\theta\|_Q} \tag{2.14}$$

Then there exists a unique solution pair $(v, p) \in (V, Q)$ for the saddle-point problem described by (2.12).

Theorem 2.3.1 then states the conditions necessary for existence and uniqueness of the constrained version of Onsager's variational principle. For a proof, see [9].

Prescription summary

Onsager's variational principle is conducted to attain the equations of motion as follows:

1. Rayleighian construction

1.1. Determine the free energy functional F .

1.1.1. Compute its total time derivative \dot{F} .

1.2. Determine the dissipation functional Φ .

1.3. Determine any constraints C .

1.4. Sum all components to attain the Rayleighian $R = \dot{F} + \Phi + C$.

2. Rayleighian minimization

2.1. Compute a Gateaux derivative of the Rayleighian R at $v \in P_x \mathcal{X}$ in the direction $\delta v \in P_x \mathcal{X}$ for each vector in the process space $P_x \mathcal{X}$.

2.2. Collect terms corresponding to each Gateaux derivative.

This prescription will be followed for the remainder of the text.

3

Monofluids

Consider a two dimensional isotropic, incompressible, and Newtonian fluid droplet occupying a domain

$$\Omega(t) = \{(x, z) \in \mathbb{R}^2 : 0 < z < h(x, t)\} \quad (3.1)$$

with a surface $\partial\Omega(t)$ surrounded by a gas and smooth solid substrate (see figure 3.1 for an illustration). The parameter $h(x, t)$ represents the distance from the liquid-solid interface to the liquid-gas interface at each point x . The fluid covers an area

$$\omega(t) = \{x \in \mathbb{R} : x_- < x < x_+\} \quad (3.2)$$

of the solid substrate (this area is known as the *support*) with boundary $\partial\omega(t)$. The height is driven by a free energy F ; our goal is to model the height distribution of the film over time. We assume that the droplet is a monofluid, i.e. that it consists of a single composition.

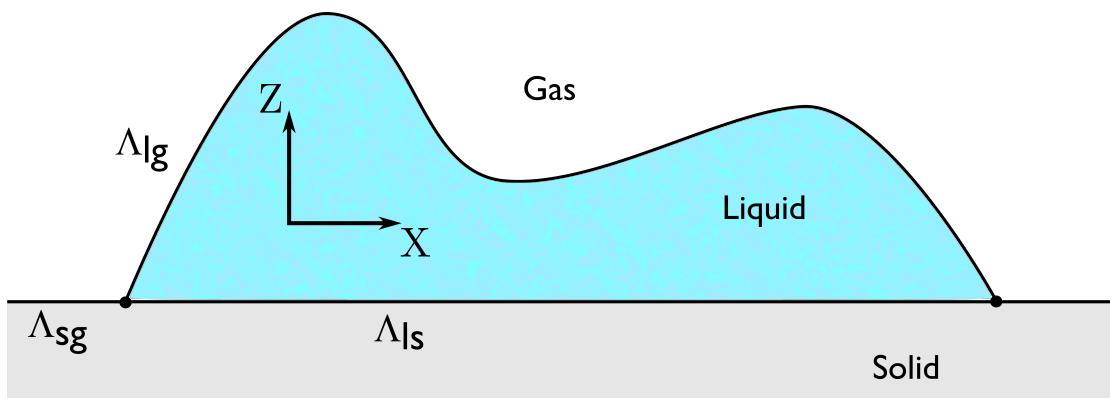


Figure 3.1: Illustration of a liquid droplet on a smooth solid substrate and surrounded by a gas. The liquid-gas, liquid-solid, and solid-gas interfaces are denoted by Λ_{lg} , Λ_{ls} , and Λ_{sg} , respectively.

We shall first consider a fluid with a support ω that is confined by two fixed walls as shown in figure 3.2. Let x and z be the horizontal and vertical directions respectively, with support boundaries at x_+ and x_- that are stationary with respect to time. We write the flow velocity as $\mathbf{v}(x, z, t) = u(x, z, t)\hat{\mathbf{x}} + w(x, z, t)\hat{\mathbf{z}}$.

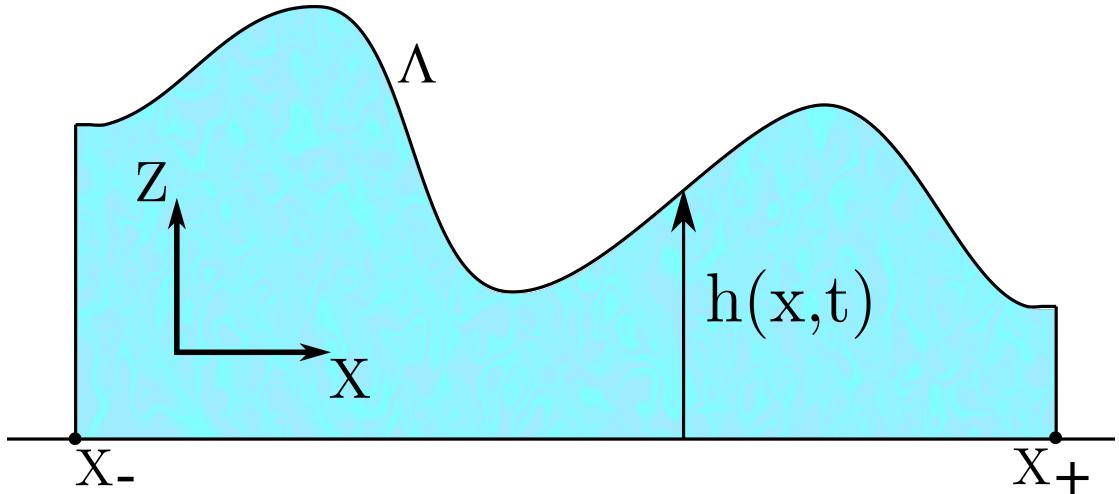


Figure 3.2: Illustration of a film with a time-independent support and time-dependent free surface Λ .

The boundary conditions are

$$\partial_x h|_{\partial\omega} = 0, \quad (3.3)$$

$$u|_{\partial\omega} = 0, \quad (3.4)$$

$$\mathbf{v}|_{z=0} = 0 \quad (3.5)$$

The last condition is a *slip* condition. In the current case, we assume a no-slip condition at the liquid-solid interface.

Kinematic construction

There is a free surface, hereafter denoted Λ , located at $z = h(x, t)$. Taking the time derivative of both sides of $z = h(x, t)$ yields the additional *kinematic* condition for the evolution of $h(x, t)$:

$$w(x, h(x, t), t) = \dot{h}(x, t) + u(x, h(x, t), t) \partial_x h(x, t) \quad (3.6)$$

We can equivalently re-write the kinematic condition by using the no-slip condition:

$$\dot{h}(x, t) = -u(x, h(x, t), t) \partial_x h(x, t) + \int_0^{h(x, t)} \frac{\partial w(x, h(x, t), t)}{\partial z} dz$$

Using the incompressibility condition $0 = \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z}$, this becomes

$$\dot{h}(x, t) = -u(x, h(x, t), t) \partial_x h(x, t) - \int_0^{h(x, t)} \frac{\partial u(x, h(x, t), t)}{\partial x} dz$$

Using Leibniz's integral rule, this can be expressed as

$$\dot{h}(x, t) = -\frac{\partial}{\partial x} \int_0^{h(x, t)} u(x, z, t) dz \quad (3.7)$$

which yields a continuity equation for the film.

3.1 Bulk equations

When we minimize the Rayleighian without applying the thin-film approximation, we refer to the resulting evolution equations as the *bulk* system. In this section we shall derive the bulk equations for a monofluid and compare our results with the well-established literature in order to validate Onsager's variational principle.

Rayleighian construction

Consider a state space \mathcal{X} and a tangent space $T_q\mathcal{X}$ at each $q \in \mathcal{X}$. At the free surface Λ , let $h \in \mathcal{X}$, $\dot{h} \in T_h\mathcal{X}$, and let the tangent vectors be generated by the fluid velocity normal and tangential to the free surface. The process space is defined by

$$P_h\mathcal{X} = \{\mathbf{v} \cdot \mathbf{n}, \mathbf{v} \cdot \boldsymbol{\tau} \in \mathbb{R} : \Lambda(t) \rightarrow \mathbb{R}\} \quad (3.8)$$

where $\mathbf{n}(x, t)$ and $\boldsymbol{\tau}(x, t)$ are normal and tangent unit vectors at Λ , respectively. In the domain Ω , let $\rho \in \mathcal{X}$ be the fluid density and $\dot{\rho} \in T_\rho\mathcal{X}$ be the partial derivative of the fluid density with respect to time. Changes in fluid density in the domain are generated by the velocity flow field \mathbf{v} , so the process space is

$$P_\rho\mathcal{X} = \{\mathbf{v} \in \mathbb{R}^2 : \Omega(t) \rightarrow \mathbb{R}\} \quad (3.9)$$

The mapping $\mathcal{W}(\rho) : P_\rho\mathcal{X} \rightarrow T_\rho\mathcal{X}$ is defined by the conservation law

$$\dot{\rho} = \mathcal{W}(\rho)\mathbf{v} = -\nabla \cdot (\rho\mathbf{v})$$

We must then compute $\delta R(\mathbf{v} \cdot \mathbf{n})[\delta \mathbf{v} \cdot \mathbf{n}] = 0$ and $\delta R(\mathbf{v} \cdot \boldsymbol{\tau})[\delta \mathbf{v} \cdot \boldsymbol{\tau}] = 0$ at Λ and $\delta R(\mathbf{v})[\delta \mathbf{v}] = 0$ at Ω .

Constraints

To include the incompressibility constraint $\nabla \cdot \mathbf{v} = 0$, we introduce a Lagrange multiplier $p(x, z, t)$. The constraint is of the form

$$C = - \int_{x_-}^{x_+} \int_0^{h(x,t)} p(x, z, t) \nabla \cdot \mathbf{v} \, dx dz$$

Let us denote integrals over the domain Ω and free surface Λ by $\iint_{\Omega} \cdot \, d\mathbf{x}$ and $\int_{\Lambda} \cdot \, d\Lambda$, respectively. Integration by parts yields

$$C = \iint_{\Omega} \nabla p \cdot \mathbf{v} \, d\mathbf{x} - \int_{\partial\Omega} p \mathbf{v} \cdot \mathbf{n} \, d\partial\Omega \quad (3.10)$$

where $\int_{\partial\Omega} \cdot \, d\partial\Omega$ denotes a line integral over the full perimeter of the domain Ω , and \mathbf{n} is the corresponding outward-facing unit vector for the domain. Note that boundary conditions (3.4) and (3.5) imply that $\mathbf{v} \cdot \mathbf{n} = 0$ on all boundaries except at Λ . Furthermore, the outward-facing unit normal vector to Λ can be expressed as

$$\mathbf{n}(x, t) = \frac{(-\partial_x h, 1)}{\sqrt{1 + (\partial_x h)^2}} \quad (3.11)$$

And the normal velocity at Λ is

$$\mathbf{v}(x, h(x, t), t) \cdot \mathbf{n}(x, t) = \frac{-u\partial_x h + w}{\sqrt{1 + (\partial_x h)^2}} = \frac{\dot{h}}{\sqrt{1 + (\partial_x h)^2}} \quad (3.12)$$

where we have used the kinematic condition (3.6). Equation (3.10) can then be expressed as

$$C = \iint_{\Omega} \nabla p \cdot \mathbf{v} \, d\mathbf{x} - \int_{\Lambda} p \mathbf{v} \cdot \mathbf{n} \, d\Lambda \mid_{z=h(x,t)}$$

Free energy

The energy stored in an interface is dependent on its curvature and the surface tension force $\sigma_{\theta\phi}$ between phases θ and ϕ , which are typically solid (s), liquid (l), or gas (g). The total free energy of the surfaces of the droplet in figure 3.1 is

$$F = \sum_{i=1}^3 \int_{\Lambda_i} \sigma_i \, d\Lambda_i$$

where $\sum_{i=1}^3$ is the summation of all three interfaces, $\int_{\Lambda_i} \cdot \, d\Lambda_i$ is the parametrized integral over these surfaces, and σ_i is a constant surface tension for each interface in units of Newtons (hereafter denoted as N). Let σ_{lg} , σ_{ls} , and σ_{sg} denote the surface

tension force for the liquid-gas, liquid-solid, and solid-gas interfaces, respectively. The free energy is

$$F = \int_{\Lambda_{lg}} \sigma_{lg} d\Lambda_{lg} + \int_{\Lambda_{ls}} \sigma_{ls} d\Lambda_{ls} - \int_{\Lambda_{sg}} \sigma_{sg} d\Lambda_{sg} \quad (3.13)$$

The arc-length parametrizations at the interfaces are $d\Lambda_{lg} = \left(\sqrt{1 + (\partial_x h)^2} \right) dx$, $d\Lambda_{ls} = dx$, and $d\Lambda_{sg} = dx$. Hence, the free energy is

$$F = \int_{x_-}^{x_+} \left(\sigma_{lg} \sqrt{1 + |\partial_x h|^2} + \sigma_{ls} - \sigma_{sg} \right) dx \quad (3.14)$$

Since we are assuming that all surfaces are stationary except for the free surface Λ , the free energy will only be measured relative to this liquid-gas surface, which has a surface tension that will be written as σ from now on. Therefore, the free energy is written as

$$F = \int_{x_-}^{x_+} \sigma \left(\sqrt{1 + |\partial_x h|^2} \right) dx \quad (3.15)$$

The time derivative of the free energy is

$$\begin{aligned} \dot{F} &= \sigma \int_{x_-}^{x_+} \partial_x \dot{h} \frac{\partial}{\partial(\partial_x h)} (1 + |\partial_x h|^2)^{\frac{1}{2}} dx \\ &= \sigma \int_{x_-}^{x_+} \partial_x \dot{h} (1 + |\partial_x h|^2)^{-\frac{1}{2}} \partial_x h dx \end{aligned} \quad (3.16)$$

We can integrate by parts and use the boundary condition (3.3), resulting in

$$\dot{F} = -\sigma \int_{x_-}^{x_+} \dot{h} (1 + |\partial_x h|^2)^{-\frac{3}{2}} \partial_x^2 h dx \quad (3.17)$$

Furthermore, substituting equation (3.12) and the parametrization for $d\Lambda$ yields

$$\dot{F} = -\sigma \int_{\Lambda} \mathbf{v} \cdot \mathbf{n} \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} d\Lambda \quad (3.18)$$

Energy dissipation

In section C.4, it was shown that an isotropic, incompressible, Newtonian viscous fluid flowing with velocity \mathbf{v} in a domain Ω has a dissipation function given by

$$\Phi = \iint_{\Omega} \frac{\eta}{4} \left(\nabla \mathbf{v} + (\nabla \mathbf{v})^T \right)^2 dx \quad (3.19)$$

where η is the viscosity coefficient in units of Pa · s. Expanding the dissipation function yields

$$\Phi = \frac{\eta}{2} \iint_{\Omega} \left(\nabla \mathbf{v} : \nabla \mathbf{v} + (\nabla \mathbf{v})^T : \nabla \mathbf{v} \right) dx \quad (3.20)$$

where $\nabla \mathbf{v} : \nabla \mathbf{v}$ represents the operation $\frac{\partial v_i}{\partial x_j} \frac{\partial v_i}{\partial x_j}$ in Einstein notation.

Minimizing the Rayleighian

The Rayleighian R is

$$\begin{aligned} R &= \dot{F} + \Phi + C \\ &= - \int_{\Lambda} \sigma \mathbf{v} \cdot \mathbf{n} \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} d\Lambda \\ &\quad + \frac{\eta}{2} \iint_{\Omega} (\nabla \mathbf{v} : \nabla \mathbf{v} + (\nabla \mathbf{v})^T : \nabla \mathbf{v}) dx \\ &\quad + \iint_{\Omega} \nabla p \cdot \mathbf{v} dx - \int_{\Lambda} p \mathbf{v} \cdot \mathbf{n} d\Lambda \end{aligned} \quad (3.21)$$

The variation of \dot{F} is

$$\delta \dot{F} = -\sigma \int_{\Lambda} \delta \mathbf{v} \cdot \mathbf{n} \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} d\Lambda \quad (3.22)$$

The variation of C is

$$\delta C = \iint_{\Omega} \nabla p \cdot \delta \mathbf{v} dx - \int_{\Lambda} p \delta \mathbf{v} \cdot \mathbf{n} d\Lambda \quad (3.23)$$

The variation of Φ is

$$\delta \Phi = \eta \iint_{\Omega} (\nabla \mathbf{v} : \nabla \delta \mathbf{v} + (\nabla \mathbf{v})^T : \nabla \delta \mathbf{v}) dx \quad (3.24)$$

We can integrate by parts to attain

$$\begin{aligned} \delta \Phi &= -\eta \iint_{\Omega} (\nabla \cdot \nabla \mathbf{v} + \nabla \cdot (\nabla \mathbf{v})^T) \cdot \delta \mathbf{v} dx \\ &\quad + \eta \int_{\partial \Omega} (\nabla \mathbf{v} \cdot \mathbf{n} + (\nabla \mathbf{v})^T \cdot \mathbf{n}) \cdot \delta \mathbf{v} d\partial \Omega \\ &= -\eta \int_{x_-}^{x_+} \int_0^{h(x,t)} \nabla \cdot (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) \cdot \delta \mathbf{v} dx dz \\ &\quad + \eta \int_{\partial \Omega} (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) : \delta \mathbf{v} \mathbf{n} d\partial \Omega \end{aligned} \quad (3.25)$$

where \mathbf{n} is the corresponding outward-facing unit vector. Boundary conditions (3.4) and (3.5) imply that $\delta \mathbf{v} = 0$ at all boundaries except at Λ . We ignore the boundaries at the stationary walls x_- and x_+ , as the equations that arise from these conditions will not be useful in modelling the droplet. Furthermore, the outward-facing unit normal vector \mathbf{n} to this boundary can be expressed as (3.11), while the unit tangent vector along this boundary can be expressed as

$$\boldsymbol{\tau}(x, t) = \frac{(1, \partial_x h)}{\sqrt{1 + (\partial_x h)^2}} \quad (3.26)$$

Let us decompose the function $\delta\mathbf{v}$ in terms of components tangential and normal to the free surface Λ as $\delta\mathbf{v} = (\delta\mathbf{v} \cdot \boldsymbol{\tau})\boldsymbol{\tau} + (\delta\mathbf{v} \cdot \mathbf{n})\mathbf{n}$. We will also use the notation $\mathbf{T} = (\nabla\mathbf{v} + (\nabla\mathbf{v})^T)$ for the viscous stress tensor. The energy dissipation becomes

$$\begin{aligned}\delta\Phi = & -\eta \iint_{\Omega} \nabla \cdot \mathbf{T} \cdot \delta\mathbf{v} \, d\mathbf{x} \\ & + \eta \int_{\Lambda} \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{n} (\delta\mathbf{v} \cdot \mathbf{n}) \, d\Lambda \\ & + \eta \int_{\Lambda} \boldsymbol{\tau} \cdot \mathbf{T} \cdot \mathbf{n} (\delta\mathbf{v} \cdot \boldsymbol{\tau}) \, d\Lambda\end{aligned}\quad (3.27)$$

The total variation of R with respect to \mathbf{v} is then

$$\begin{aligned}\delta R = & \dot{\delta F} + \delta\Phi + \delta C = 0 \\ = & -\sigma \int_{\Lambda} \delta\mathbf{v} \cdot \mathbf{n} \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} \, d\Lambda \\ & - \eta \iint_{\Omega} \nabla \cdot \mathbf{T} \cdot \delta\mathbf{v} \, d\mathbf{x} \\ & + \eta \int_{\Lambda} \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{n} (\delta\mathbf{v} \cdot \mathbf{n}) \, d\Lambda \\ & + \eta \int_{\Lambda} \boldsymbol{\tau} \cdot \mathbf{T} \cdot \mathbf{n} (\delta\mathbf{v} \cdot \boldsymbol{\tau}) \, d\Lambda \\ & + \iint_{\Omega} \nabla p \cdot \delta\mathbf{v} \, d\mathbf{x} - \int_{\Lambda} p \delta\mathbf{v} \cdot \mathbf{n} \, d\Lambda\end{aligned}\quad (3.28)$$

Collecting $\delta\mathbf{v} \cdot \mathbf{n}$ and $\delta\mathbf{v} \cdot \boldsymbol{\tau}$ terms at Λ yields

$$\sigma \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} = -p + \eta \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{n} \quad \text{at } \Lambda \quad (3.29)$$

$$0 = \eta \boldsymbol{\tau} \cdot \mathbf{T} \cdot \mathbf{n} \quad \text{at } \Lambda \quad (3.30)$$

respectively. Collecting $\delta\mathbf{v}$ terms at Ω yields

$$0 = \nabla p - \eta \nabla \cdot \mathbf{T} \quad \text{in } \Omega \quad (3.31)$$

Equation (3.31) is the Stoke's flow equation [34], implying that p is the local pressure. Onsager's variational principle has successfully reproduced a well known result. Let us now derive the thin-film equations of the monofluid.

3.2 Thin-Film Approximation

Suppose that the typical length scales in the horizontal and vertical characteristic dimensions of the film are L and H , respectively. We shall assume that the height of the film is much smaller than its length, i.e. $\epsilon = \frac{H}{L} \ll 1$.

Scalings

We shall nondimensionalize all variables and determine the appropriate scalings. The lengths x, z and their derivatives scale according to

$$x = \bar{x}L, \quad \frac{\partial}{\partial x} = \frac{1}{L} \frac{\partial}{\partial \bar{x}} \quad \text{and} \quad z = \bar{z}H, \quad \frac{\partial}{\partial z} = \frac{1}{H} \frac{\partial}{\partial \bar{z}} \quad (3.32)$$

where \bar{x} and \bar{z} are both dimensionless and of order $\mathcal{O}(1)$. The fluid directional velocities will scale according to $u = \bar{u}U$ and $w = \bar{w}W$, where U and W are typical scales of the components of the velocities, and \bar{u} and \bar{w} are of order $\mathcal{O}(1)$. The fluid incompressibility implies

$$\begin{aligned} 0 &= \nabla \cdot \mathbf{v} = \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \\ &= \frac{U}{L} \frac{\partial \bar{u}}{\partial \bar{x}} + \frac{W}{H} \frac{\partial \bar{w}}{\partial \bar{z}} \end{aligned} \quad (3.33)$$

We require

$$0 = \frac{\partial \bar{u}}{\partial \bar{x}} + \frac{\partial \bar{w}}{\partial \bar{z}} \quad (3.34)$$

which implies that $W = \frac{UH}{L} = U\epsilon$.

Other variables scale as

$$t = \bar{t}T = \bar{t}\frac{L}{U}, \quad h = \bar{h}H, \quad \dot{h} = \dot{\bar{h}}U\epsilon \quad (3.35)$$

where \bar{h} is dimensionless and of order $\mathcal{O}(1)$.

Rayleighian Construction

In section 3.1, we found expressions for the time derivative of the free energy, energy dissipation, and constraint required to construct the Rayleighian. Let us conduct the Rayleigh-Onsager approach by applying the thin-film approximation first, and then minimizing the resulting leading order Rayleighian.

Constraints

The Lagrange multiplier $p(x, z, t)$ scales as $p = \bar{p}P$, where \bar{p} is dimensionless and of order $\mathcal{O}(1)$. The constraint is given by

$$\begin{aligned} C &= \int_{x_-}^{x_+} \int_0^{h(x,t)} \nabla(p(x, z, t)) \cdot \mathbf{v} \, dx dz - \int_{x_-}^{x_+} p(x, h, t) \dot{h} \, dx \\ &= \int_{x_-}^{x_+} \int_0^{h(x,t)} \left(\frac{UP}{L} \frac{\partial \bar{p}}{\partial \bar{x}} \bar{u} + \frac{UP}{L} \frac{\partial \bar{p}}{\partial \bar{z}} \bar{w} \right) LH \, d\bar{x} d\bar{z} - \int_{x_-}^{x_+} \frac{UHP}{L} \bar{p} \dot{\bar{h}} L \, d\bar{x} \\ &= \iint_{\Omega} UHP \bar{\nabla} \bar{p} \cdot \bar{\mathbf{v}} \, d\bar{x} - \int_{x_-}^{x_+} UHP \bar{p} \dot{\bar{h}} \, d\bar{x} \end{aligned} \quad (3.36)$$

where $\bar{\nabla} = (\partial_{\bar{x}}, \partial_{\bar{z}})$ represents the gradient with respect to dimensionless variables. Substituting condition (3.6) yields

$$C = \iint_{\Omega} U L \epsilon P \bar{\nabla} \bar{p} \cdot \bar{v} d\bar{x} - \int_{x_-}^{x_+} U L \epsilon P \bar{p} (\bar{w} - \bar{u} \partial_{\bar{x}} \bar{h}) d\bar{x} \quad (3.37)$$

Free energy

The time derivative of the free energy is given by

$$\dot{F} = -\sigma \int_{x_-}^{x_+} \dot{h} \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} dx \quad (3.38)$$

Substituting appropriate scalings yields

$$\dot{F} = -\sigma \int_{x_-}^{x_+} \dot{\bar{h}} U \epsilon \frac{\partial_{\bar{x}}^2 \bar{h} \frac{\epsilon}{L}}{(1 + |\partial_{\bar{x}} \bar{h}|^2 \epsilon^2)^{\frac{3}{2}}} L d\bar{x} \quad (3.39)$$

Hence,

$$\dot{F} = -\sigma \int_{x_-}^{x_+} \dot{\bar{h}} \partial_{\bar{x}}^2 \bar{h} \epsilon^2 U d\bar{x} + \mathcal{O}(\epsilon^2) \quad (3.40)$$

Substituting condition (3.6) yields

$$\dot{F} \approx -\sigma \int_{x_-}^{x_+} (\bar{w} - \bar{u} \partial_{\bar{x}} \bar{h}) \partial_{\bar{x}}^2 \bar{h} \epsilon^2 U d\bar{x} \quad (3.41)$$

Energy dissipation

The energy dissipation is given by

$$\begin{aligned} \Phi &= \frac{\eta}{2} \int_{x_-}^{x_+} \int_0^{h(x,t)} \left(\nabla \mathbf{v} : \nabla \mathbf{v} + (\nabla \mathbf{v})^T : \nabla \mathbf{v} \right) dx dz \\ &= \frac{\eta}{2} \iint_{\Omega} \left(\left(\frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial w}{\partial x} \right)^2 + \left(\frac{\partial u}{\partial z} \right)^2 + \left(\frac{\partial w}{\partial z} \right)^2 \right. \\ &\quad \left. + \left(\frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial w}{\partial x} \right) \left(\frac{\partial u}{\partial z} \right) + \left(\frac{\partial w}{\partial x} \right) \left(\frac{\partial u}{\partial z} \right) + \left(\frac{\partial w}{\partial z} \right)^2 \right) dx dz \\ &= \frac{\eta}{2} \iint_{\Omega} \left(2 \frac{U^2}{L^2} \left(\frac{\partial \bar{u}}{\partial \bar{x}} \right)^2 + \frac{\epsilon^2 U^2}{L^2} \left(\frac{\partial \bar{w}}{\partial \bar{x}} \right)^2 \right. \\ &\quad \left. + \frac{U^2}{\epsilon^2 L^2} \left(\frac{\partial \bar{u}}{\partial \bar{z}} \right)^2 + 2 \frac{U^2}{L^2} \left(\frac{\partial \bar{w}}{\partial \bar{z}} \right)^2 + 2 \frac{U^2}{L^2} \left(\frac{\partial \bar{w}}{\partial \bar{x}} \right) \left(\frac{\partial \bar{u}}{\partial \bar{z}} \right) \right) L H d\bar{x} \\ &= \frac{\eta}{2} \iint_{\Omega} \frac{U^2}{\epsilon} \left(\frac{\partial \bar{u}}{\partial \bar{z}} \right)^2 d\bar{x} + \mathcal{O}(\epsilon) \end{aligned} \quad (3.42)$$

Minimizing the Rayleighian

The variation of C is

$$\delta C = \iint_{\Omega} U L \epsilon P \bar{\nabla} \bar{p} \cdot \delta \bar{v} \, d\bar{x} - \int_{x_-}^{x_+} U L \epsilon P \bar{p} (\delta \bar{w} - \delta \bar{u} \partial_{\bar{x}} \bar{h}) \, d\bar{x} \quad (3.43)$$

The variation of \dot{F} is

$$\delta \dot{F} = -\sigma \int_{x_-}^{x_+} (\delta \bar{w} - \delta \bar{u} \partial_{\bar{x}} \bar{h}) \partial_{\bar{x}}^2 \bar{h} \epsilon^2 U \, d\bar{x} \quad (3.44)$$

The variation of the leading order Φ is

$$\begin{aligned} \delta \Phi &= \eta \iint_{\Omega} \frac{U^2}{\epsilon} \left(\frac{\partial \bar{u}}{\partial \bar{z}} \right) \left(\frac{\partial \delta \bar{u}}{\partial \bar{z}} \right) d\bar{x} \\ &= -\eta \iint_{\Omega} \frac{U^2}{\epsilon} \left(\frac{\partial^2 \bar{u}}{\partial \bar{z}^2} \right) \delta \bar{u} \, d\bar{x} + \eta \int_{x_-}^{x_+} \frac{U^2}{\epsilon} \left(\frac{\partial \bar{u}}{\partial \bar{z}} \right) \delta \bar{u} \, d\bar{x} \Big|_{z=h(x,t)} \end{aligned} \quad (3.45)$$

The variation of R is

$$\begin{aligned} \delta R &= \delta \dot{F} + \delta \Phi + \delta C = 0 \\ &= -\sigma \int_{x_-}^{x_+} (\delta \bar{w} - \delta \bar{u} \partial_{\bar{x}} \bar{h}) \partial_{\bar{x}}^2 \bar{h} \epsilon^2 U \, d\bar{x} \\ &\quad - \eta \iint_{\Omega} \frac{U^2}{\epsilon} \left(\frac{\partial^2 \bar{u}}{\partial \bar{z}^2} \right) \delta \bar{u} \, d\bar{x} + \eta \int_{x_-}^{x_+} \frac{U^2}{\epsilon} \left(\frac{\partial \bar{u}}{\partial \bar{z}} \right) \delta \bar{u} \, d\bar{x} \Big|_{z=h(x,t)} \\ &\quad + \iint_{\Omega} U L \epsilon P \bar{\nabla} \bar{p} \cdot \delta \bar{v} \, d\bar{x} - \int_{x_-}^{x_+} U L \epsilon P \bar{p} (\delta \bar{w} - \delta \bar{u} \partial_{\bar{x}} \bar{h}) \, d\bar{x} \end{aligned} \quad (3.46)$$

Collecting δu terms in Ω yields

$$0 = U L \epsilon P \frac{\partial \bar{p}}{\partial \bar{x}} - \eta \frac{U^2}{\epsilon} \frac{\partial^2 \bar{u}}{\partial \bar{z}^2} \quad \text{in } \Omega \quad (3.47)$$

We notice that the only way both terms of equation (3.47) can be of the same order is if $P \sim \eta \frac{U}{L \epsilon^2}$. Let us define the dimensionless *Reynolds number* R_e given by

$$R_e = \frac{\rho U L}{\eta} \quad (3.48)$$

where ρ is the constant fluid density. We are then in the regime in which

$$\bar{\eta} = \frac{\eta U \epsilon^2}{P L} = \frac{P R_e \epsilon^2}{\rho U^2} \sim \mathcal{O}(1) \quad (3.49)$$

The term $R_e \epsilon^2 = \tilde{R}_e$ is sometimes referred to as the *reduced Reynolds number* [53].

Collecting $\delta\bar{w}$ and $\delta\bar{u}$ terms at Λ yields

$$\sigma \partial_x^2 \bar{h} \epsilon^3 = -\eta U \bar{p} \quad \text{at } \Lambda \quad (3.50)$$

$$0 = \sigma \partial_{\bar{x}} \bar{h} \partial_x^2 \bar{h} \epsilon^3 + \eta U \bar{p} \partial_{\bar{x}} \bar{h} + \eta U \frac{\partial \bar{u}}{\partial \bar{z}} \quad \text{at } \Lambda \quad (3.51)$$

Note that equations (3.50) and (3.51) are unbalanced in terms of order unless we assume that we are in the regime

$$\mathcal{C}_A = \frac{\eta U}{\sigma} \sim \mathcal{O}(\epsilon^3) \quad (3.52)$$

where \mathcal{C}_A is the *capillary number* [54]. This assumption physically implies that the fluid viscous drag forces are negligible compared to surface tension forces. This is not unusual in small domains where the ratio between the surface area and volume is large, as in thin films. Therefore, we assume that we are in the regime

$$\bar{\sigma} = \frac{\sigma \epsilon^3}{\eta U} \sim \mathcal{O}(1) \quad (3.53)$$

Note that in two dimensions, the units are

$$[\sigma] = \text{N}, \quad [\eta] = \frac{\text{N} \cdot \text{s}}{\text{m}}$$

which implies that $\bar{\sigma}$ and $\bar{\eta}$ are dimensionless.

Summing equations (3.50) and (3.51) yields $\partial_z \bar{u} = 0$ at Λ . Hereafter, we shall omit bar notation for dimensionless variables, i.e. we let $\bar{h} \rightarrow h$, $\bar{\sigma} \rightarrow \sigma$, etc. and assume everything is already dimensionless to increase readability. The full set of equations is

$$\sigma \partial_x^2 h = -p \quad \text{at } \Lambda \quad (3.54)$$

$$0 = \frac{\partial u}{\partial z} \quad \text{at } \Lambda \quad (3.55)$$

$$0 = \frac{\partial p}{\partial z} \quad \text{in } \Omega \quad (3.56)$$

$$0 = \frac{\partial p}{\partial x} - \eta \frac{\partial^2 u}{\partial z^2} \quad \text{in } \Omega \quad (3.57)$$

Equation (3.57) is the Stoke's flow equation for incompressible Newtonian fluids, implying that $p = \frac{\delta F}{\delta h}$ is in fact the pressure. Equation (3.56) indicates that the pressure is at hydrostatic equilibrium in the vertical direction. To have a full description of the thin-film system, these equations are combined with the

boundary, kinematic, and incompressibility conditions:

$$\begin{aligned}\partial_x h|_{\partial\omega} &= 0 \\ u|_{\partial\omega} &= 0 \\ u|_{z=0} &= w|_{z=0} = 0 \\ (w - \dot{h} - u\partial_x h)|_{z=h} &= 0 \\ \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} &= 0\end{aligned}\tag{3.58}$$

3.2.1 Solving the thin-film equations

Equation (3.56) implies that $p = p(x, t)$. Integrating equation (3.57) with respect to z and using the conditions (3.54), (3.55), and (3.58) yields

$$u = -\frac{\sigma}{\eta} \partial_x^3 h \left(\frac{1}{2} z^2 - h z \right)\tag{3.59}$$

Substituting equation (3.7) yields

$$\dot{h} = -\frac{\partial}{\partial x} \left(\frac{\sigma h^3}{3\eta} \partial_x^3 h \right)\tag{3.60}$$

Although it will not be performed in this text, the derivation extends to three dimensions similarly [22].

We may place emphasis on the slip condition by defining the *mobility coefficient* $m(h) = \frac{h^3}{3\eta}$. The mobility coefficient typically takes the form $m(h) \propto h^\nu$ for $0 < \nu \leq 3$ depending on the slip condition at the liquid-solid interface [31]. It is important to note that for a time-dependent support $\omega(t)$ the condition $\nu = 3$, corresponding to a no-slip condition at the liquid-solid interface, yields a singular viscous dissipation rate at the moving solid-liquid-gas interface. In fact, an approach involving purely conventional hydrodynamics cannot describe this region; see [59] for a discussion on the assumed sharp wedge geometry, and see [39] for a review.

Gradient formulation

We note that since $-\sigma \partial_x^2 h = \frac{\delta F}{\delta h}$, equation (3.60) is in gradient flow form and can be written in three dimensions as

$$\dot{h} = -\nabla \cdot \left(\frac{h^3 \sigma}{3\eta} \nabla \Delta h \right) = \nabla \cdot \left(\frac{h^3}{3\eta} \nabla \frac{\delta F}{\delta h} \right)\tag{3.61}$$

The gradient flow form can be written in terms of the mobility coefficient as

$$\dot{h} = \nabla \cdot (m(h) \nabla p)\tag{3.62}$$

3.3 Modelling the thin-film evolution

3.3.1 The weak formulation

Now that we have derived the height evolution equation in its strong form, we aim to model the height distribution evolution numerically using the finite element method. We now let the support be time-dependent and aim to express this free boundary problem in the weak formulation. For the moment, we assume that no external force densities such as gravity are affecting the evolution. We will also relax the no-slip condition and consider a general mobility coefficient. In three dimensions, the relevant dimensionless equations are

$$\dot{h} = \nabla \cdot (m(h) \nabla p) \quad (3.63)$$

and

$$F(h) = \int_{\omega(t)} \left(S + \frac{1}{2} (\nabla h)^2 \right) d\mathbf{x} \quad (3.64)$$

where $S = -\frac{\sigma_{sg} - \sigma_{ls} - \sigma_{lg}}{\sigma_{lg}}$ is the negative spreading coefficient up to a factor of σ_{lg}^{-1} [45]. We have re-defined the dimensionless version of equation (3.14) such that $F \rightarrow \frac{F}{\sigma_{lg}}$ and Taylor expanded assuming that $\partial_x h \ll 1$. Note that $d\mathbf{x}$ represents an infinitesimal element of the support $\omega(t)$. We first multiply both sides of equation (3.63) by a test function $\phi(x, y) \in H^1(\omega(t))$ and then integrate over the support. The boundary term resulting from an integration by parts is zero since $m(h) = 0$ on $\partial\omega(t)$, resulting in

$$\int_{\omega(t)} (\dot{h}\phi + m(h)\nabla p \cdot \nabla\phi) d\mathbf{x} = 0 \quad (3.65)$$

According to Reynold's transport theorem (see theorem A.0.1), the time derivative of the free energy is

$$\dot{F} = \int_{\omega(t)} (\nabla h \cdot \nabla \dot{h}) d\mathbf{x} + \int_{\partial\omega(t)} \left(S + \frac{1}{2} (\nabla h)^2 \right) \mathbf{v} \cdot \mathbf{n} ds$$

where $\mathbf{n} = -\frac{\nabla h}{|\nabla h|}$ is an outward-facing unit normal vector on the boundary and ds is an infinitesimal element of the support boundary $\partial\omega(t)$. Taking the total time derivative of both sides of the boundary condition $h(\mathbf{x}, t) = 0$ on $\omega(t)$ results in

$$\frac{dh}{dt} = \dot{h} + \mathbf{v} \cdot \nabla h = 0 \quad \text{on } \partial\omega(t) \quad (3.66)$$

which defines $\mathbf{v} \cdot \mathbf{n} = \frac{\dot{h}}{|\nabla h|}$, on the boundaries. This constrains the flow velocity normal to the boundary $\partial\omega(t)$, but says nothing about how the flow velocity

tangent to the boundary should behave. The time derivative of the free energy can now be written as

$$\dot{F} = \int_{\omega(t)} (\nabla h \cdot \nabla \dot{h}) d\mathbf{x} + \int_{\partial\omega(t)} |\nabla h|^{-1} \left(S + \frac{1}{2}(\nabla h)^2 \right) \dot{h} ds \quad (3.67)$$

If we take a Gateaux derivative of $F(h)$ with respect to h in an arbitrary ϕ direction, we attain

$$\delta F(h)[\phi] = \int_{\omega(t)} (\nabla h \cdot \nabla \phi) d\mathbf{x} + \int_{\partial\omega(t)} (\nabla h)^{-1} \left(S + \frac{1}{2}(\nabla h)^2 \right) \phi ds \quad (3.68)$$

We can now express p in another way by using its definition and write

$$\begin{aligned} p &= \frac{\delta F}{\delta h} \\ \int p \phi d\mathbf{x} &= \int \frac{\delta F}{\delta h} \phi d\mathbf{x} \equiv \delta F(h)[\phi] \end{aligned} \quad (3.69)$$

Note that the right hand side of equation (3.69) is equivalent to equation (3.68). Therefore, p is expressed in the weak form as

$$\int_{\omega(t)} p \phi d\mathbf{x} = \int_{\omega(t)} (\nabla h \cdot \nabla \phi) d\mathbf{x} + \int_{\partial\omega(t)} |\nabla h|^{-1} \left(S + \frac{1}{2}|\nabla h|^2 \right) \phi ds \quad (3.70)$$

Performing an integration by parts on the first term of the right-hand side of equation (3.70) yields

$$\int_{\omega(t)} p \phi d\mathbf{x} = - \int_{\omega(t)} \nabla^2 h \phi d\mathbf{x} + \int_{\partial\omega(t)} |\nabla h|^{-1} \left(S - \frac{1}{2}|\nabla h|^2 \right) \phi ds$$

Equating both sides implies that the pressure is $p = -\nabla^2 h$ in ω and that the contact angle is $|\nabla h| = \sqrt{2S}$ on $\partial\omega$. Since S is the *negative* spreading coefficient up to a factor, $S > 0$ and $S \leq 0$ imply partial and full wetting, respectively [45]. Our current formulation does not yield physical contact angles for $S < 0$, so we will focus on the $S \geq 0$ case.

3.3.2 Finding an appropriate update rule

Consistent support violation

Attempting to apply the update rule $h(t_0 + \tau) = h(t_0) + \tau \dot{h}(t_0)$ makes no sense since the height distributions $h(t_0 + \tau)$ and $h(t_0)$ are defined on different supports. To avoid this issue, we need a quantity which has a support that does not change from time t_0 to time $t_0 + \tau$.

At time t_0 , the fluid material points P on the support are confined to positions $\mathbf{r} = \mathbf{X} \in \omega(t_0)$. At times $t > t_0$, the material points will be located at $\mathbf{r} = \mathbf{x}(\mathbf{X}, t) \in \omega(t)$. These points will deform during each time-step via a mapping $\psi(t) : \omega(t) \rightarrow \mathbb{R}^2$ such that

$$\psi(\mathbf{X}, t) = \mathbf{x}(\mathbf{X}, t) \quad (3.71)$$

The mapping ψ can be defined in terms of the deformation vector as $\psi(\mathbf{X}) = \mathbf{X} + \mathbf{u}(\mathbf{X})$. For a small time-step $\tau \ll 1$, the deformation vector can be expressed as $\mathbf{u}(\mathbf{X}) = \tau \dot{\mathbf{X}} = \tau \dot{\psi}(\mathbf{X})$ for some generator $\dot{\psi}$, resulting in the mapping.

$$\psi(\mathbf{X}) = \mathbf{X} + \tau \dot{\psi}(\mathbf{X}) \quad (3.72)$$

At time $t = t_0$, we have knowledge of the shape of the support $\omega(t_0)$ and of the height distribution $h(t_0, \mathbf{X})$. If we knew the map ψ at time $t = t_0$, we would be able to predict how the support deforms for time $t = t_0 + \tau$. The height distribution corresponding to such a deformed support at time $t = t_0$ is $h(t_0, \psi(\mathbf{X})) = H(t_0, \mathbf{X})$. The height distributions $H(t_0, \mathbf{X})$ and $H(t_0 + \tau, \mathbf{X})$ are defined on the same support. Therefore, it is the height H for which we may apply the update rule

$$H \rightarrow H + \tau \dot{H} \quad (3.73)$$

Arbitrary Lagrangian-Eulerian transformation

One possible way to model the support would be to set a configuration of points (known as the *mesh*) fixed in space upon which the height distribution is discretely defined. This is the *Eulerian* paradigm.

We could instead construct a mesh with points that follow the associated material particle at each time-step. This is *Lagrangian* paradigm.

Since we only know the velocity of the material particles at the support boundary $\partial\omega(t)$, we will use the *Arbitrary Lagrangian-Eulerian* (ALE) paradigm, where the Lagrangian paradigm is only applied to a portion of the mesh points (in this case, the support boundaries) [30]. To do this, we need an update rule for the mesh points to transform them as $\mathbf{X} \rightarrow \mathbf{x}$. The mapping ψ defines the update rule

$$\mathbf{X} \rightarrow \mathbf{X} + \tau \dot{\psi} \quad (3.74)$$

We will integrate over the undeformed support \mathbf{X} first, update the support (i.e. let $\mathbf{X} \rightarrow \mathbf{x}$), and then integrate over the deformed support \mathbf{x} in the next iteration.

The update rule

To apply the update rules (3.73) and (3.74), we must first determine $\dot{\psi}$ and \dot{H} . Let us revisit the kinematic condition

$$\mathbf{v} \cdot \mathbf{n} = \frac{\dot{h}}{|\nabla h|} \quad \text{on } \partial\omega(t) \quad (3.75)$$

where ∇ is always defined with respect to the \mathbf{X} coordinates unless otherwise specified. The generator $\dot{\psi}$ is expressed as

$$\mathbf{v} = \dot{\psi}(\mathbf{X})$$

Once we have found \dot{h} and ∇h , we can find $\dot{\psi} \cdot \mathbf{n}$ at the boundaries through

$$\dot{\psi} \cdot \mathbf{n} = \frac{\dot{h}}{|\nabla h|} \quad \text{on } \partial\omega(t) \quad (3.76)$$

Afterwards, we interpolate between the boundaries to determine the update rule for the points in between. In the one dimensional case, this process does not require a constraint on the tangential component $\dot{\psi} \cdot \mathbf{t}$ since such a component does not exist. However, for the two dimensional case, this constraint is required in order to properly define the update rule for all of the points in the mesh. The constraint for the tangential component is arbitrary, and mainly chosen to select an appropriate mesh scheme and increase computational accuracy [30].

To find \dot{H} , let us begin from the definition $H(t, \mathbf{X}) = h(t, \psi(\mathbf{X}))$ and calculate the partial time derivative, given by

$$\dot{H}(t, \mathbf{X}) = \dot{h} + \frac{\partial h}{\partial \psi} \cdot \dot{\psi}$$

Note that for $\tau \ll 1$, we attain

$$\begin{aligned} \frac{\partial h}{\partial X_i} &= \frac{\partial h}{\partial \psi_j} \frac{\partial \psi_j}{\partial X_i} = \frac{\partial h}{\partial \psi_j} \left(\delta_{ij} + \tau \frac{\partial \dot{\psi}_j}{\partial X_i} \right) \\ \frac{\partial h}{\partial X_i} &\approx \frac{\partial h}{\partial \psi_i} \end{aligned}$$

in Einstein notation. This results in

$$\dot{H} = \dot{h} + \nabla h \cdot \dot{\psi} \quad (3.77)$$

Note that this implies that $\dot{H} = 0$ on $\partial\omega(t)$. Once we have found $\dot{\psi}$ for all points of the mesh, we can also find \dot{H} for the corresponding point. This completes the requirements for the update rules. See figure 3.3 for a schematic diagram of the update rule for H between time-steps.

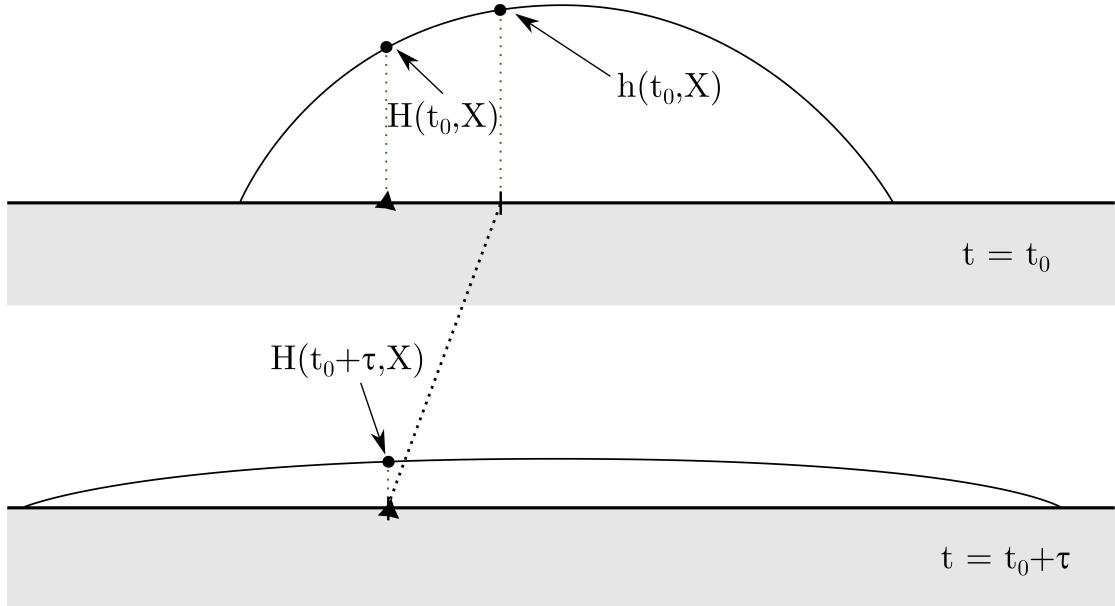


Figure 3.3: Illustration of the variable H which has a constant support during consecutive time-steps.

3.3.3 Finite element analysis of the thin-film equations

We are now ready to devise a numerical scheme to solve the weak formulation of the thin-film evolution equation. We time-discretize equation (3.70) semi-implicitly [51] by making the replacement $\nabla h \rightarrow \nabla(h + \tau \dot{h})$ to stabilize the algorithm [44], yielding

$$\begin{aligned} & \int_{\omega(t)} (p\phi - \tau \nabla \dot{h} \cdot \nabla \phi) dx \\ &= \int_{\omega(t)} (\nabla h \cdot \nabla \phi) dx + \int_{\partial\omega(t)} |\nabla h|^{-1} \left(S + \frac{1}{2} |\nabla h|^2 \right) \phi ds \quad (3.78) \end{aligned}$$

We will perform finite element decomposition in the one dimensional case. The support will be decomposed geometrically into N intervals. We shall choose a set of nodal basis functions $\phi_i(x_j) = \delta_{ij}$ where each ϕ_i is piecewise linear. Therefore, we make a Galerkin approximation with the basis functions, constructing the space $V_h \in V$ such that $V_h = \text{span}(\phi_1, \phi_2, \dots, \phi_N)$ [62]. We will first solve equations (3.65) and (3.78) for p and \dot{h} . The functions \dot{h} , h , p , and ϕ are decomposed as

linear combinations of the basis functions as follows

$$\begin{aligned}\dot{h} &= \sum_{i=1}^N u_i \phi_i & h &= \sum_{i=1}^N h_i \phi_i & \dot{H} &= \sum_{i=1}^N U_i \phi_i \\ p &= \sum_{i=1}^N p_i \phi_i & \phi &= \sum_{i=1}^N v_i \phi_i\end{aligned}$$

Substituting the decompositions into equation (3.65) yields

$$\sum_{i=1}^N \left(\int_{\omega(t)} \phi_i \phi_j dx \right) u_i + \sum_{i=1}^N \left(\int_{\omega(t)} m(h) \nabla \phi_i \cdot \nabla \phi_j dx \right) p_i = 0$$

If we define $M_{ij} = \left(\int_{\omega(t)} \phi_i \phi_j dx \right)$ and $\tilde{S}_{ij} = \left(\int_{\omega(t)} m(h) \nabla \phi_i \cdot \nabla \phi_j dx \right)$, we attain

$$M_{ij} u_i + \tilde{S}_{ij} p_i = 0 \quad (3.79)$$

in Einstein notation. Substituting the decompositions into equation (3.78) yields

$$\begin{aligned}\sum_{i=1}^N \left(\int_{\omega(t)} \phi_i \phi_j dx \right) p_i - \tau \sum_{i=1}^N \left(\int_{\omega(t)} \nabla \phi_i \cdot \nabla \phi_j dx \right) u_i \\ = \sum_{i=1}^N \left(\int_{\omega(t)} \nabla \phi_i \cdot \nabla \phi_j dx \right) h_i + \int_{\partial \omega(t)} |\nabla h|^{-1} \left(S + \frac{1}{2} |\nabla h|^2 \right) \phi_j ds \quad (3.80)\end{aligned}$$

Note that, since h is piecewise linear, we cannot evaluate ∇h pointwise [43]. We must find the weak derivative [43], g , of h as follows

$$\int_{\omega(t)} \nabla h \phi dx = \int_{\omega(t)} g \phi dx$$

If we decompose g as $g = \sum_{i=1}^N g_i \phi_i$, we can write

$$\begin{aligned}\int_{\omega(t)} \nabla \left(\sum_{i=1}^N h_i \phi_i \right) \sum_{j=1}^N v_j \phi_j dx &= \int_{\omega(t)} \sum_{i=1}^N g_i \phi_i \sum_{j=1}^N v_j \phi_j dx \\ \sum_{i=1}^N \left(\int_{\omega(t)} \nabla \phi_i \phi_j dx \right) h_i &= \sum_{i=1}^N \left(\int_{\omega(t)} \phi_i \phi_j dx \right) g_i \\ C_{ij} h_i &= M_{ij} g_i\end{aligned}$$

where we have defined $C_{ij} = \left(\int_{\omega(t)} \nabla \phi_i \phi_j dx \right)$. The weak derivative is then

$$\mathbf{g} = M^{-1} C \mathbf{h} \quad (3.81)$$

where $\mathbf{g} = (g_1, g_2, \dots, g_N)^T$ and $\mathbf{h} = (h_1, h_2, \dots, h_N)^T$. When in weak form, we can now substitute $\nabla h = g$.

Let us define $\tilde{b}_j = \left(\int_{\partial\omega(t)} |\nabla h|^{-1} (S + \frac{1}{2} |\nabla h|^2) \phi_j ds \right)$, noting that $\tilde{b}_j = 0$ for $j \neq 1, N$ in the one dimensional case. Furthermore, substituting $\nabla h = g$ yields

$$\begin{aligned}\tilde{b}_j &= \delta_{j1}|g|^{-1} \left(S + \frac{1}{2}|g|^2 \right) \Big|_{x_-} + \delta_{jN}|g|^{-1} \left(S + \frac{1}{2}|g|^2 \right) \Big|_{x_+} \\ &= \delta_{j1}|g_j|^{-1} \left(S + \frac{1}{2}|g_j|^2 \right) + \delta_{jN}|g_j|^{-1} \left(S + \frac{1}{2}|g_j|^2 \right)\end{aligned}$$

Defining $S_{ij} = \left(\int_{\omega(t)} \nabla \phi_i \cdot \nabla \phi_j dx \right)$, we can write equation (3.80) as

$$M_{ij} p_i - \tau S_{ij} u_i = S_{ij} h_i + \tilde{b}_j \quad (3.82)$$

We can combine equations (3.79) and (3.82) into a matrix representation by defining

$$A = \begin{bmatrix} M & \tilde{S} \\ -\tau S & M \end{bmatrix} \quad \boldsymbol{\chi} = \begin{bmatrix} \mathbf{u} \\ \mathbf{p} \end{bmatrix} \quad \mathbf{b} = \begin{bmatrix} 0 \\ S\mathbf{h} + \tilde{\mathbf{b}} \end{bmatrix} \quad (3.83)$$

where $\mathbf{u} = (u_1, u_2, \dots, u_N)^T$ and $\mathbf{p} = (p_1, p_2, \dots, p_N)^T$. We must then solve for $\boldsymbol{\chi}$ through $A\boldsymbol{\chi} = \mathbf{b}$.

With this formulation, we can solve for \dot{h} and ∇h . The only requirement left for the update rule is to find $\dot{\psi}$, which we do by interpolating between the boundaries. In one dimension, we can linearly interpolate and express $\dot{\psi}$ (which is now one-dimensional) explicitly as

$$\dot{\psi}(X) = (\dot{\psi}_+ - \dot{\psi}_-) \xi(X) + \dot{\psi}_- \quad (3.84)$$

where $\xi(X) = \frac{X-X_-}{X_+-X_-}$ such that $0 = \xi(X_-) < \xi(X) < \xi(X_+) = 1$. The values X_\pm represent the locations of both boundaries. The kinematic condition $\dot{\psi}_- = -\frac{\dot{h}}{\partial_x h} \Big|_{X_-}$ and $\dot{\psi}_+ = -\frac{\dot{h}}{\partial_x h} \Big|_{X_+}$ defines the velocity normal to the boundaries.

Assembly algorithm

One way to construct the matrices M_{ij} , S_{ij} , C_{ij} , and \tilde{S}_{ij} would be to range over all values $1 < i, j < N$, and compute one element in each matrix for every iteration. However, this operation is very wasteful: every evaluation of element i, j requires an integration over all of the cells K , resulting in many cells being visited multiple times.

Since most basis functions do not intersect, the resulting matrices will be composed of mostly zeros. Therefore, we only need to compute the elements i, j for neighbouring basis functions, and so we can instead iterate over each cell once. For each cell, we will compute the local matrices that contain all of the contributions

of the basis functions for that cell. In the nodal basis, each cell will have at most two basis functions contributing to the local matrix. All of the local matrices will first be computed on the same reference cell \hat{K} (which in the one dimensional case is the interval $\hat{x} = [0, 1]$) which will afterwards be transformed into the actual physical cell K by computing the corresponding Jacobian $J(\hat{x})$ [58].

Let \hat{x} refer to coordinates on the reference cell, and let x refer to coordinates on the physical cell. In addition, let $\phi_i^{\hat{K}} = \phi_i^{\hat{K}}(\hat{x})$ be a basis function defined on the reference cell. In the one dimension, the reference cell \hat{K} will be the interval $\hat{x} = [0, 1]$. Let $\phi^{\hat{K}} = (\phi_1^{\hat{K}}, \phi_2^{\hat{K}}) = (1 - \hat{x}, \hat{x})$ and $\nabla_{\hat{K}}\phi^{\hat{K}} = (\nabla_{\hat{K}}\phi_1^{\hat{K}}, \nabla_{\hat{K}}\phi_2^{\hat{K}}) = (-1, 1)$. When computed on their reference cells, the matrices are

$$M_{ij}^{\hat{K}} = \int_0^1 \phi_i^{\hat{K}} \phi_j^{\hat{K}} d\hat{x} \quad S_{ij}^{\hat{K}} = \int_0^1 \nabla_{\hat{K}}\phi_i^{\hat{K}} \cdot \nabla_{\hat{K}}\phi_j^{\hat{K}} d\hat{x} \quad (3.85)$$

$$C_{ij}^{\hat{K}} = \int_0^1 \nabla_{\hat{K}}\phi_i^{\hat{K}} \phi_j^{\hat{K}} d\hat{x} \quad \tilde{S}_{ij}^{\hat{K}} = \int_0^1 m(h) \nabla_{\hat{K}}\phi_i^{\hat{K}} \cdot \nabla_{\hat{K}}\phi_j^{\hat{K}} d\hat{x} \quad (3.86)$$

where $\nabla_{\hat{K}}$ is a derivative with respect to the reference cell coordinates. Further computation is straightforward, and reveals that

$$M_{ij}^{\hat{K}} = \begin{bmatrix} \frac{1}{3} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{3} \end{bmatrix} \quad S_{ij}^{\hat{K}} = \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \quad C_{ij}^{\hat{K}} = \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{bmatrix} \quad (3.87)$$

Note that $\tilde{S}_{ij}^{\hat{K}}$ cannot yet be computed, since we have not specified the mobility. However, since the basis functions are linear, their derivatives are not coupled into the integrand, which greatly simplifies the calculation. For example, if $m(h) = h^2$ we can write \tilde{S} on the physical cell as $\tilde{S}_{ij}^K = M_{lm}^{\hat{K}} h_l h_m S_{ij}^{\hat{K}}$ in Einstein notation.

Let us perform the calculation to transform back to the physical cell K . For S , this gives

$$\begin{aligned} S_{ij}^K &= \int_K \nabla_K \phi_i^K \cdot \nabla_K \phi_j^K dx \\ &= \int_{\hat{K}} \nabla_K \phi_i^K \cdot \nabla_K \phi_j^K |J(\hat{x})| d\hat{x} = \int_{\hat{K}} \nabla_{\hat{K}} \phi_i^{\hat{K}} \cdot \nabla_{\hat{K}} \phi_j^{\hat{K}} \frac{\partial \hat{x}}{\partial x} \frac{\partial \hat{x}}{\partial x} \frac{\partial x}{\partial \hat{x}} d\hat{x} \\ &= \int_{\hat{K}} \nabla_{\hat{K}} \phi_i^{\hat{K}} \cdot \nabla_{\hat{K}} \phi_j^{\hat{K}} \frac{\partial \hat{x}}{\partial x} d\hat{x} \end{aligned}$$

where $\frac{\partial \hat{x}}{\partial x} = \frac{\Delta \hat{x}}{\Delta x} = \frac{1}{\Delta x}$ and Δx is the length of the corresponding physical cell. Therefore, in order to complete the transformation we need to compute $S_{ij}^K = \frac{S_{ij}^{\hat{K}}}{\Delta x}$. The computations for the transformations of the other matrices are similar. We attain

$$M_{ij}^K = M_{ij}^{\hat{K}} \Delta x \quad C_{ij}^K = C_{ij}^{\hat{K}}$$

Solution algorithm

We are finally ready to outline the numerical algorithm. It proceeds as follows, starting at time t_0 :

1. At time $t = t_0$, compute the length of each physical cell Δx .
2. Use Δx to transform all local matrices to their corresponding physical cells.
3. Insert these transformed matrices into the sparse matrix A .
4. Compute $\mathbf{g} = M^{-1}C\mathbf{h}$ and therefore $\tilde{\mathbf{b}}$.
5. Solve the system $A\boldsymbol{\chi} = \mathbf{b}$ to find \mathbf{u} .
6. Construct $\dot{\psi}$ as outlined in section 3.3.3.
7. Compute $\mathbf{U} = \mathbf{u} + \mathbf{g}.*\dot{\psi}$, where $.*$ is element-wise vector multiplication.
8. Update the support $\mathbf{X} = \mathbf{X} + \tau\dot{\psi}$ and height $\mathbf{h} = \mathbf{h} + \tau\mathbf{U}$.

3.3.4 Extensions of the model

External potentials

Let us now allow the dynamics of the liquid film to be affected by some external potential, such as one arising from gravity. The free energy would acquire an additional term, in three dimensions given by

$$F_g = \iiint_{\Omega} \mathcal{F}(h, z) \, dx dy dz \quad (3.88)$$

where $\mathcal{F}(h, z)$ is some gravitational energy density. According to the mean value theorem, the average energy density $\tilde{\mathcal{F}}(h)$ is $\frac{1}{h} \int_0^h \mathcal{F}(h, z) \, dz = \tilde{\mathcal{F}}(h)$. Since we assumed that the film height was very small compared to its length, we can make the approximation $\mathcal{F}(h, z) \approx \tilde{\mathcal{F}}(h)$ and therefore $F_g \approx \int_{\omega(t)} h \mathcal{F}(h) \, d\mathbf{x}$, where now $d\mathbf{x} = dx dy$ for a two dimensional support. We shall use the definition $f(h) := h \mathcal{F}(h)$ hereafter. This will change the resulting thin-film equation into

$$\dot{h} = \nabla \cdot \left(m(h) \nabla \left(-\sigma \Delta h + \frac{\partial f}{\partial h} \right) \right) \quad (3.89)$$

where now $p = -\sigma \Delta h + \frac{\partial f}{\partial h}$.

We shall perform a finite element analysis including gravity with a one dimensional support $\omega(t)$ such that $d\mathbf{x} = dx$. We can model an external gravitational potential using

$$f(h) = \zeta_n h^2 - \zeta_\tau h x \quad (3.90)$$

where ζ_n and ζ_τ are dimensionless constants measuring the strength of the gravitational potential normal and tangential to the solid substrate, respectively. Note that with this choice, greater values for ζ_n and ζ_τ correspond to decreasing potential energies in the $-z$ direction and $+x$ direction respectively.

Using $\frac{\partial f}{\partial h} = 2\zeta_n h - \zeta_\tau x$ and adding F_g to the original free energy, equation (3.78) becomes

$$\begin{aligned} \int_{\omega(t)} \left(p\phi - \tau \nabla h \cdot \nabla \phi \right) d\mathbf{x} &= \int_{\omega(t)} (\nabla h \cdot \nabla \phi) d\mathbf{x} \\ &+ \int_{\omega(t)} (2\zeta_n h - \zeta_\tau x) \phi d\mathbf{x} + \int_{\partial\omega(t)} |\nabla h|^{-1} \left(S + \frac{1}{2} |\nabla h|^2 \right) \phi ds \end{aligned} \quad (3.91)$$

Note that our choice of gravitational energy density f results in $f(h) = 0$ at the boundaries $\partial\omega(t)$. We decompose x in terms of linear combinations of the basis functions ϕ as

$$x = \sum_{i=1}^N x_i \phi_i \quad (3.92)$$

and define $\mathbf{x} = (x_1, x_2, \dots, x_N)^T$. Let us define the gravitational matrix as

$$\mathcal{G}_{ij} = M_{ij} (2\zeta_n h_i - \zeta_\tau x_i) \quad (3.93)$$

in Einstein notation. Equation (3.82) becomes modified to become

$$M_{ij} p_i - \tau S_{ij} u_i = S_{ij} h_i + \mathcal{G}_{ij} + \tilde{b}_j \quad (3.94)$$

In matrix form, we must then solve for $\boldsymbol{\chi}$ in the system $A\boldsymbol{\chi} = \mathbf{b}$ with matrices in the form

$$A = \begin{bmatrix} M & \tilde{S} \\ -\tau S & M \end{bmatrix} \quad \boldsymbol{\chi} = \begin{bmatrix} \mathbf{u} \\ \mathbf{p} \end{bmatrix} \quad \mathbf{b} = \begin{bmatrix} 0 \\ S\mathbf{h} + \mathcal{G} + \tilde{\mathbf{b}} \end{bmatrix} \quad (3.95)$$

Non-uniform spreading

We can let S take non-uniform values on the boundaries, which physically corresponds to varying surface tensions along the gas-liquid-solid contact line. For a one dimensional support, we can choose

$$S(x) = \begin{cases} S_L, & x = x_- \\ S_R, & x = x_+ \end{cases} \quad (3.96)$$

which changes the definition of \tilde{b}_j , now given by

$$\tilde{b}_j = \delta_{j1} |g_j|^{-1} \left(S_L + \frac{1}{2} |g_j|^2 \right) + \delta_{jN} |g_j|^{-1} \left(S_R + \frac{1}{2} |g_j|^2 \right) \quad (3.97)$$

3.3.5 Numerical simulation

Depending on our choice for S_L , S_R , ζ_n , and ζ_τ , we attain different thin-film dynamics. All numerical solutions were computed with $m(h) = h^2$ to avoid the contact line singularity. Matrix algebra was computed using NumPy [61] and SciPy [60] on Python [63]. Graphs were produced using Matplotlib [38].

Simple stationary distribution

The numerical solution for $S_L = S_R = 1.0$, and $\zeta_n = \zeta_\tau = 0$ with initial height distribution $h_0 = \frac{1}{2} - |x_0 - \frac{1}{2}|$ for a uniform initial support distribution $0 < x_0 < 1$ is shown in figure 3.4 at various times. The height distribution achieves a steady state as $t \rightarrow \infty$; the analytic stationary distribution for this case is

$$h(x) = a \frac{1}{\sqrt{2}} \left(1 - \frac{1}{a^2} \left(x - \frac{1}{2} \right)^2 \right) \quad (3.98)$$

where $a = \sqrt{\frac{\sqrt{18}}{16}}$ and the support is uniformly distributed in $x \in (1/2 - a, 1/2 + a)$ [51]. The numerical solution quickly converges to the analytic stationary distribution, and at time $t = 10$ the two are virtually indistinguishable. The algorithm also conserves most of the volume of the droplet, with only $7.770 \times 10^{-3}\%$ of the total volume lost from $t = 0$ to $t = 10$. Figure 3.5 illustrates the volume loss curve over time for this droplet, calculated by integrating the droplet height with Simpson's rule (see section C.5 for computer code). Most of the volume is lost in the first few time-steps as the droplet loses its initial shape, and then stabilizes as it approaches its stationary state.

Travelling waves

Figures 3.6 and 3.7 illustrate the numerical solution of a droplet under the effects of a tangential gravitational force in the $+x$ direction of differing strengths. From $t = 0$ to $t = 30$, the droplet affected by the weaker and stronger tangential gravitational force gains $1.701 \times 10^{-3}\%$ and loses $7.349 \times 10^{-2}\%$ of its total volume, respectively. In both situations, the droplet approaches a travelling wave configuration for $t \rightarrow \infty$. The droplet in the strong tangential gravity case approaches a steady state that is more asymmetrical compared to the droplet in the weak tangential gravity case.

Let us analyze the stability of the travelling wave solution for the droplet affected by only a tangential gravity with a strength characterized by the parameter

ζ_τ . Consider a flat thin-film distribution of height h_0 with a small wave perturbation $\epsilon \ll 1$, i.e.

$$h(x, t) = h_0 + \epsilon e^{i\psi x + \gamma t} \quad (3.99)$$

where ψ is the spatial wavenumber and γ is the growth rate of the waves. Substituting this expression into the thin film equation corresponding to a tangential gravity term gives

$$\gamma = -\psi (h_0^2 \sigma \psi^3 + i2h_0 \zeta_\tau) + \mathcal{O}(\epsilon) \quad (3.100)$$

which implies that since $\text{Re}(\gamma) \leq 0$, perturbations always decay with time. Substituting this into equation (3.99) yields

$$h(x, t) = h_0 + \epsilon e^{-\sigma h_0^2 \psi^4 t + i\psi(x - 2h_0 \zeta_\tau t)} \quad (3.101)$$

which has the form of a decaying wave travelling in the $+x$ direction with velocity $V = 2h_0 \zeta_\tau$.

Miscellaneous scenarios

Figure 3.8 illustrates the numerical solution for a droplet under the effects of a normal gravitational force in the $-z$ direction. Figure 3.9 illustrates the droplet evolution for $S_L < S_R$ without the effects of gravity. The droplet moves in the $-x$ direction as a result of the Marangoni effect [1], which arises from surface tension gradients. The right-most contact line has a lower surface tension corresponding to the gas-liquid-solid interface than the left-most contact line, and hence the droplet is “pulled” from right to left. Figure 3.10 illustrates the process of a dewetting droplet with an initial support length $L = 50$.

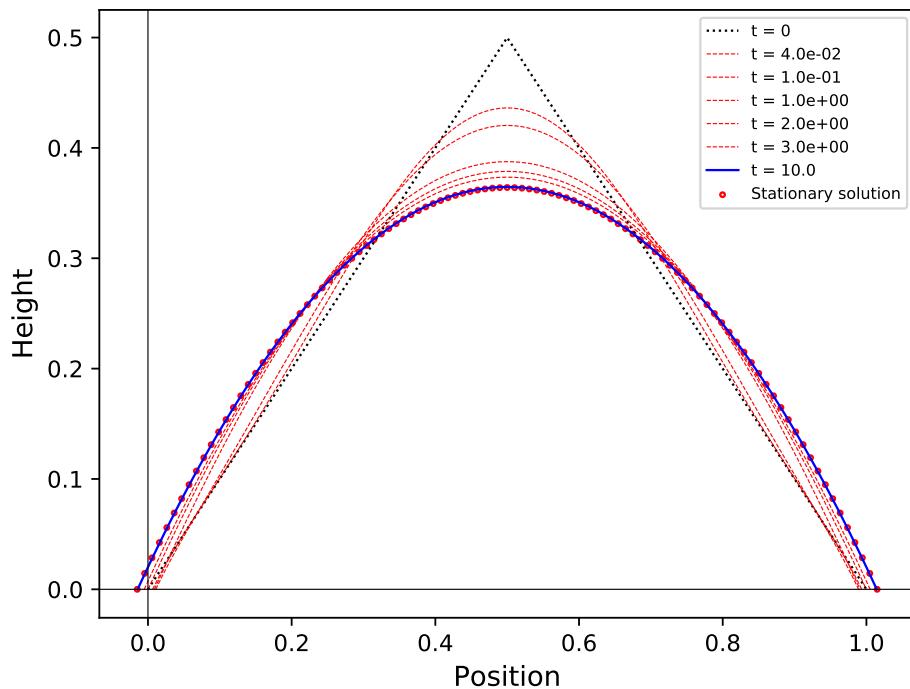


Figure 3.4: Evolution towards stationary droplet with $S_L = S_R = 1.0$ and $\zeta_n = \zeta_\tau = 0$.

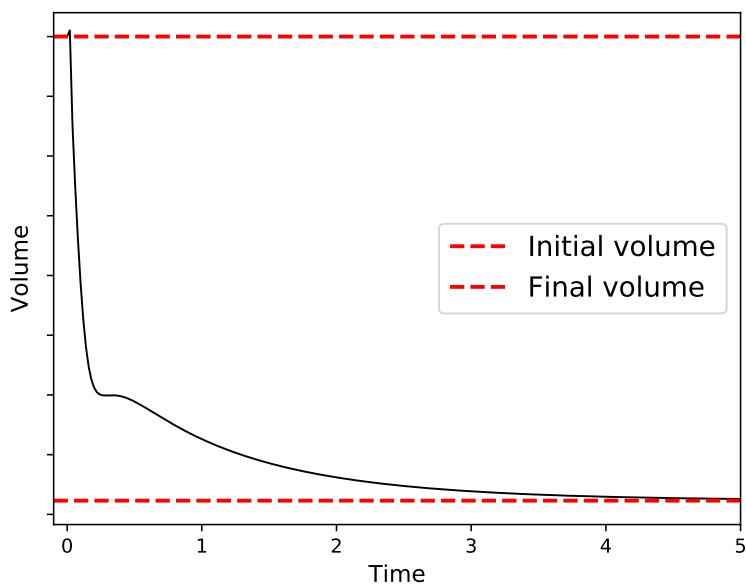


Figure 3.5: Volume over time for droplet in figure 3.4.

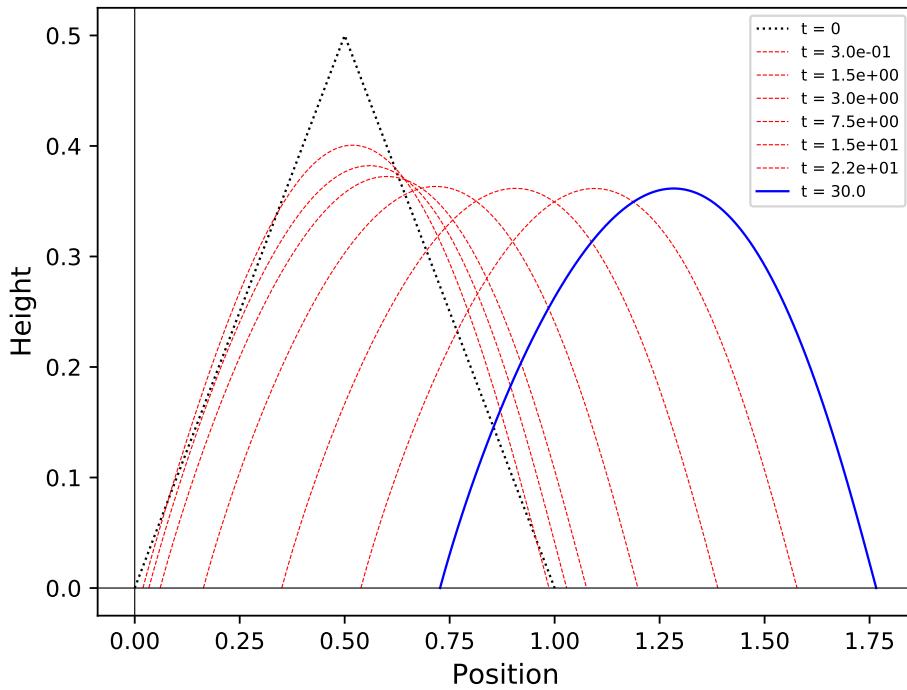


Figure 3.6: Evolution towards travelling wave solution with $S_L = S_R = 1.0$, $\zeta_n = 0$, and $\zeta_\tau = 10$.

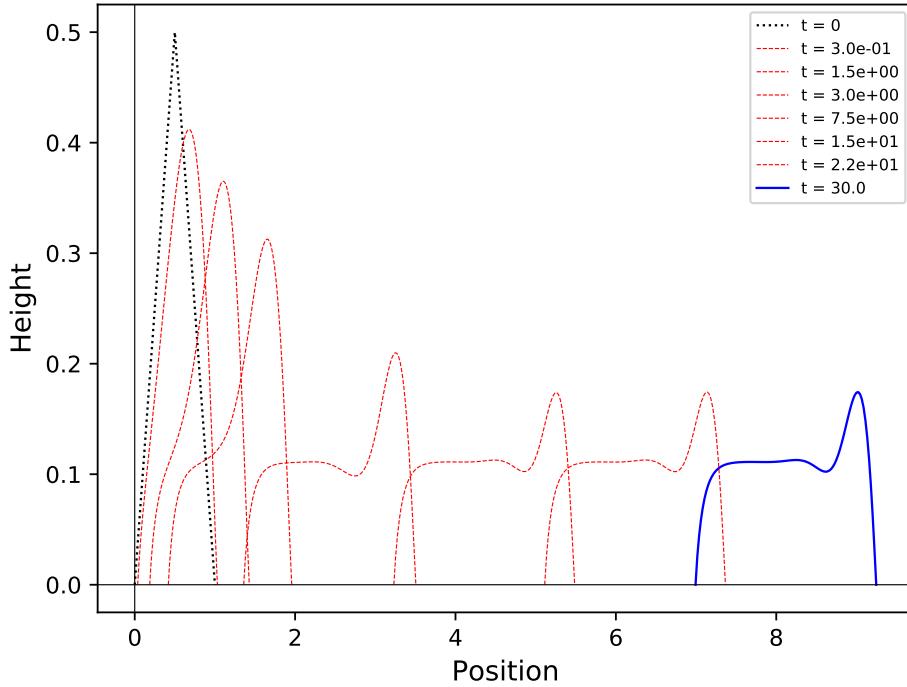


Figure 3.7: Evolution towards travelling wave solution with $S_L = S_R = 1.0$, $\zeta_n = 0$, and $\zeta_\tau = 100$.

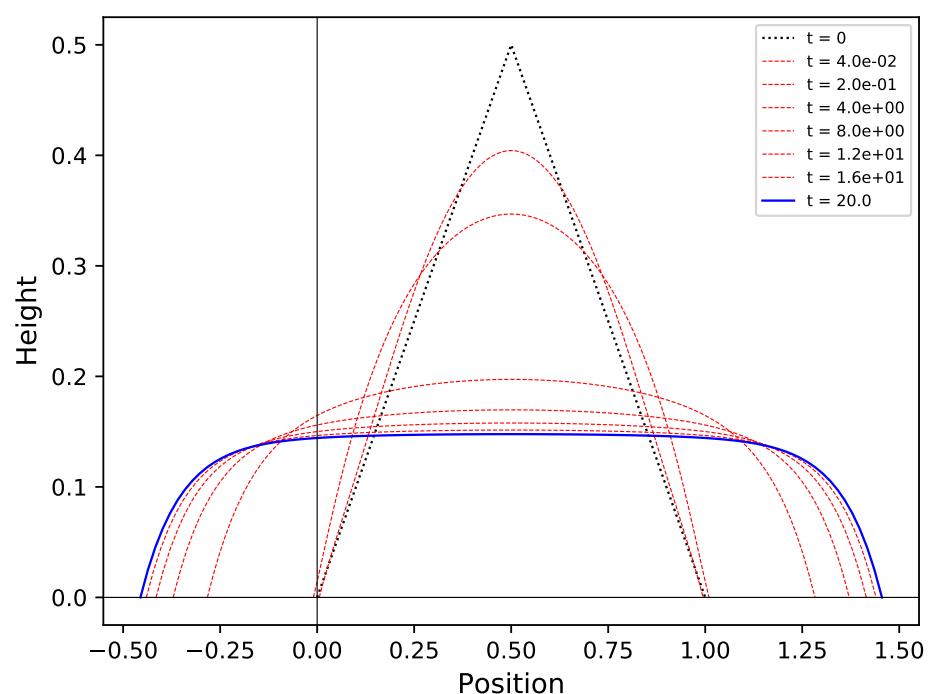


Figure 3.8: Evolution towards stationary droplet with $S_L = S_R = 1.0$, $\zeta_n = 50$, and $\zeta_\tau = 0$.

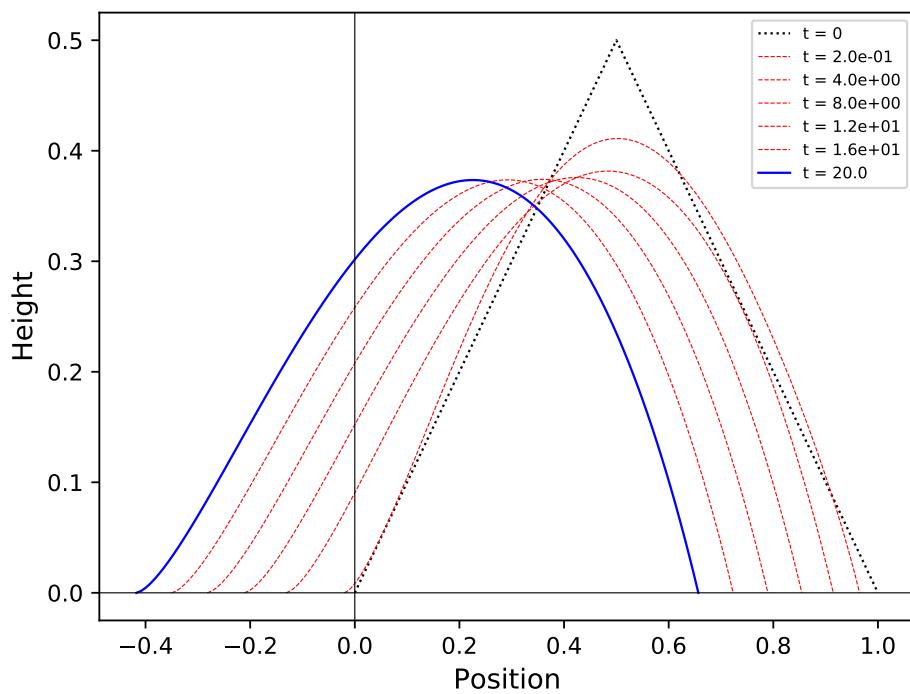


Figure 3.9: Marangoni effect demonstration with $S_L = 0$, $S_R = 2.0$, and $\zeta_n = \zeta_\tau = 0$.

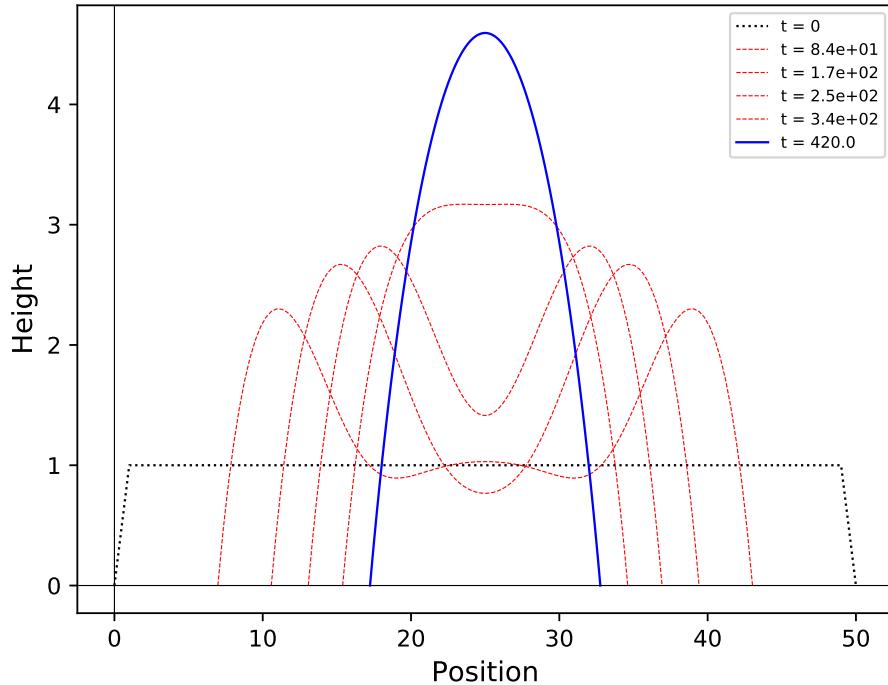


Figure 3.10: Dewetting demonstration with $S_L = S_R = 1.0$ and $\zeta_n = \zeta_\tau = 0$.

4

Binary Mixtures

Let us now consider binary mixtures consisting of two distinct components: an inviscid fluid component (occasionally referred to as the *solvent* phase) and a Newtonian fluid component (the *network* phase) [35]. Our analysis of this mixture shall follow a similar approach to [49] and [52]. The inviscid and Newtonian components have velocities $\mathbf{v}_1(x, z, t) = (u_1, w_1)$ and $\mathbf{v}_2(x, z, t) = (u_2, w_2)$, respectively, and relative concentrations $\theta_1 = (1 - \theta)$ and $\theta_2 = \theta$, respectively, where $0 \leq \theta(x, z, t) \leq 1$. We assume that both components have equal molar mass and volume and that the total mass density ρ is constant with respect to space and time [52].

For binary mixtures, we shall always consider a fluid with a time-independent support that is confined by two fixed boundaries at $x = x_+$ and $x = x_-$. The fluid has a free surface Λ at $z = h(x, t)$. Let x and z be the horizontal and vertical directions respectively.

Kinematic construction

The individual fluid components obey individual mass conservation equations:

$$\frac{\partial(1 - \theta)}{\partial t} + \nabla \cdot ((1 - \theta)\mathbf{v}_1) = 0, \quad \frac{\partial\theta}{\partial t} + \nabla \cdot (\theta\mathbf{v}_2) = 0 \quad (4.1)$$

Summing both conservation equations yields

$$\nabla \cdot \mathbf{v} = 0 \quad (4.2)$$

where $\mathbf{v} := \mathbf{v}_1(1 - \theta) + \mathbf{v}_2\theta = (u, w)$ is the mean velocity of the binary mixture. Replacing equations (4.1) with the mean velocity yields

$$\frac{\partial\theta}{\partial t} + \mathbf{v} \cdot \nabla\theta = -\nabla \cdot \mathbf{j} \quad (4.3)$$

where $\mathbf{j} := \theta(1 - \theta)(\mathbf{v}_2 - \mathbf{v}_1) = (j_x, j_z)$ is the mean diffusive flux. We then have a relation between the mean velocity and diffusive flux, given by

$$\mathbf{v}_2 = \mathbf{v} + \frac{1}{\theta} \mathbf{j} \quad (4.4)$$

The boundary conditions are

$$\partial_x h|_{\partial\omega} = 0, \quad (4.5)$$

$$u|_{\partial\omega} = 0, \quad (4.6)$$

$$\mathbf{v}_1|_{z=0} = \mathbf{v}_2|_{z=0} = \mathbf{v}|_{z=0} = 0 \quad (4.7)$$

$$\mathbf{v}_1|_{z=h(x,t)} = \mathbf{v}_2|_{z=h(x,t)} = \mathbf{v}|_{z=h(x,t)} \quad (4.8)$$

Conditions (4.7) and (4.8) represent no-slip conditions at the liquid-solid and liquid-gas interfaces, respectively. The free surface Λ at $z = h(x, t)$ obeys the kinematic condition given by

$$w(x, h(x, t), t) = \dot{h}(x, t) + u(x, h(x, t), t) \partial_x h(x, t) \quad (4.9)$$

In addition, there exists two conservation laws: the height h continuity equation, given by

$$\dot{h}(x, t) = -\frac{\partial}{\partial x} \int_0^{h(x,t)} u \, dz \quad (4.10)$$

and the effective solute thickness Ψ continuity equation, given by

$$\dot{\Psi}(x, t) = -\frac{\partial}{\partial x} \int_0^{h(x,t)} (u\theta + j_x) \, dz \quad (4.11)$$

where $\Psi = \int_0^h \theta \, dz$ [49].

4.1 Bulk equations

Rayleighian construction

Consider a state space \mathcal{X} and a tangent space $T_q \mathcal{X}$ at each $q \in \mathcal{X}$. At the free surface Λ , let $h \in \mathcal{X}$, $\dot{h} \in T_h \mathcal{X}$, and let the tangent vectors be generated by the fluid velocity normal and tangential to the free surface. Because of the slip condition (4.8) at the liquid-gas interface, the process space is defined by

$$P_h \mathcal{X} = \{\mathbf{v} \cdot \mathbf{n}, \mathbf{v} \cdot \boldsymbol{\tau} \in \mathbb{R} : \Lambda(t) \rightarrow \mathbb{R}\} \quad (4.12)$$

In the domain Ω , let $\theta_1, \theta_2 \in \mathcal{X}$ be the relative concentration for the solvent and network phases, respectively, and $\dot{\theta}_1, \dot{\theta}_2 \in T_{\theta_1, \theta_2} \mathcal{X}$ be the partial derivative

of these relative concentrations with respect to time. Changes in each relative concentration in the domain are generated by the respective velocity flow field \mathbf{v}_1 and \mathbf{v}_2 , so the process space is

$$P_{\theta_1, \theta_2} \mathcal{X} = \{\mathbf{v}_1, \mathbf{v}_2 \in \mathbb{R}^2 : \Omega(t) \rightarrow \mathbb{R}\} \quad (4.13)$$

The mapping $\mathcal{W}(\theta_1, \theta_2) : P_{\theta_1, \theta_2} \mathcal{X} \rightarrow T_{\theta_1, \theta_2} \mathcal{X}$ is in fact the conservation equations defined in (4.1). We must then compute $\delta R(\mathbf{v} \cdot \mathbf{n})[\delta \mathbf{v} \cdot \mathbf{n}] = 0$ and $\delta R(\mathbf{v} \cdot \boldsymbol{\tau})[\delta \mathbf{v} \cdot \boldsymbol{\tau}] = 0$ at Λ and $\delta R(\mathbf{v}_1)[\delta \mathbf{v}_1] = 0$ and $\delta R(\mathbf{v}_2)[\delta \mathbf{v}_2] = 0$ at Ω .

Constraints

To include the incompressibility constraint $\nabla \cdot \mathbf{v} = 0$, we introduce a Lagrange multiplier $p(x, z, t)$. The constraint is of the form

$$C = - \iint_{\Omega} p(x, z, t) \nabla \cdot \mathbf{v} \, d\mathbf{x}$$

After performing integration by parts, the constraint can be expressed as

$$C = \iint_{\Omega} (\nabla p \cdot \mathbf{v}_1(1 - \theta) + \nabla p \cdot \mathbf{v}_2(\theta)) \, d\mathbf{x} - \int_{\Lambda} p \mathbf{v} \cdot \mathbf{n} \, d\Lambda \quad (4.14)$$

where \mathbf{n} is the corresponding outward-facing unit vector.

Free energy

We shall consider a free energy F which depends on the evolving surface via a constant surface tension σ in units of N . The free energy of the mixing of both phases must be considered via a volume integral of the free energy density $g(\theta)$ in units of $\frac{J}{m^2}$ [52]. The chemical potential of the fluid is then

$$\frac{\delta F}{\delta \theta} = \frac{\partial g}{\partial \theta} := g'(\theta) \quad (4.15)$$

by definition. The free energy is

$$F = \int_{x_-}^{x_+} \sigma \sqrt{1 + |\partial_x h|^2} \, dx + \iint_{\Omega} g(\theta) \, d\mathbf{x} \quad (4.16)$$

The time derivative of the free energy is

$$\begin{aligned}
\dot{F} &= \sigma \int_{x_-}^{x_+} \partial_x h \frac{\partial}{\partial(\partial_x h)} (1 + |\partial_x h|^2)^{\frac{1}{2}} dx \\
&\quad + \iint_{\Omega} \frac{\partial g}{\partial \theta} \frac{\partial \theta}{\partial t} d\mathbf{x} + \int_{x_-}^{x_+} g|_{z=h(x,t)} \dot{h} dx \\
&= \int_{x_-}^{x_+} \left(\sigma \partial_x h (1 + |\partial_x h|^2)^{-\frac{1}{2}} \partial_x h + g \dot{h} \right) dx - \iint_{\Omega} g' (\nabla \cdot \mathbf{j} + \mathbf{v} \cdot \nabla \theta) d\mathbf{x} \\
&= \int_{x_-}^{x_+} \left(-\sigma \dot{h} \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} + g \dot{h} \right) dx - \int_{\partial\Omega(t)} g' \mathbf{j} \cdot \mathbf{n} d\partial\Omega \\
&\quad - \iint_{\Omega} (g' \mathbf{v} \cdot \nabla \theta - \mathbf{j} \cdot \nabla g'(\theta)) d\mathbf{x}
\end{aligned}$$

where the first term was integrated by parts and rearranged, and \mathbf{n} is the unit normal vector to the free surface. Note that $\mathbf{j} \cdot \mathbf{n} = \theta(1 - \theta)(\mathbf{v}_2 \cdot \mathbf{n} - \mathbf{v}_1 \cdot \mathbf{n})$ vanishes at the free surface. After expanding, \dot{F} can be written as

$$\begin{aligned}
\dot{F} &= \int_{\Lambda} \mathbf{v} \cdot \mathbf{n} \left(-\sigma \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} + g(\theta) \right) d\Lambda \\
&\quad - \iint_{\Omega} (g'(\theta) (\mathbf{v}_1(1 - \theta) + \mathbf{v}_2\theta) \cdot \nabla \theta - \theta(1 - \theta)(\mathbf{v}_2 - \mathbf{v}_1) \cdot \nabla g'(\theta)) d\mathbf{x} \quad (4.17)
\end{aligned}$$

Energy dissipation

The Newtonian component will contribute a similar energy dissipation term as the monofluid in chapter 3. The inviscid component will not dissipate heat. We must also include the dissipation arising due to the friction corresponding to the relative motion of both fluids, with a friction coefficient $\tilde{\mu}_s(\theta)$ in units of $\frac{\text{J}\cdot\text{s}}{\text{m}^4}$. The concentration of particles at any given position is $\theta(1 - \theta)$ [45]. The dissipation functional is therefore written as

$$\Phi = \iint_{\Omega} \frac{\mu_n(\theta)}{4} \left(\nabla \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T \right)^2 d\mathbf{x} + \frac{\mu_s}{2} \iint_{\Omega} \theta(1 - \theta) |\mathbf{v}_2 - \mathbf{v}_1|^2 d\mathbf{x} \quad (4.18)$$

where $\mu_n(\theta)$ is the dynamic viscosity coefficient of the Newtonian fluid in units of $\frac{\text{J}\cdot\text{s}}{\text{m}^2}$. Note that we have defined

$$\tilde{\mu}_s(\theta) = \mu_s \theta(1 - \theta)$$

Expanding the dissipation functional yields

$$\begin{aligned}
\Phi &= \iint_{\Omega} \frac{\mu_n(\theta)}{2} \left(\nabla \mathbf{v}_2 : \nabla \mathbf{v}_2 + \nabla \mathbf{v}_2 : (\nabla \mathbf{v}_2)^T \right) d\mathbf{x} \\
&\quad + \frac{\mu_s}{2} \iint_{\Omega} \theta(1 - \theta) (\mathbf{v}_2 \cdot \mathbf{v}_2 + \mathbf{v}_1 \cdot \mathbf{v}_1 - 2\mathbf{v}_1 \cdot \mathbf{v}_2) d\mathbf{x} \quad (4.19)
\end{aligned}$$

Minimizing the Rayleighian

The Rayleighian is

$$\begin{aligned}
R &= \dot{F} + \Phi + C \\
&= \int_{\Lambda} \mathbf{v} \cdot \mathbf{n} \left(-\sigma \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} + g \right) d\Lambda \\
&\quad - \iint_{\Omega} (g' (\mathbf{v}_1(1 - \theta) + \mathbf{v}_2\theta) \cdot \nabla \theta - \theta(1 - \theta)(\mathbf{v}_2 - \mathbf{v}_1) \cdot \nabla g') d\mathbf{x} \\
&\quad + \iint_{\Omega} \frac{\mu_n}{2} \left(\nabla \mathbf{v}_2 : \nabla \mathbf{v}_2 + \nabla \mathbf{v}_2 : (\nabla \mathbf{v}_2)^T \right) d\mathbf{x} \\
&\quad + \frac{\mu_s}{2} \iint_{\Omega} \theta(1 - \theta) (\mathbf{v}_2 \cdot \mathbf{v}_2 + \mathbf{v}_1 \cdot \mathbf{v}_1 - 2\mathbf{v}_1 \cdot \mathbf{v}_2) d\mathbf{x} \\
&\quad + \iint_{\Omega} (\nabla p \cdot \mathbf{v}_1(1 - \theta) + \nabla p \cdot \mathbf{v}_2(\theta)) d\mathbf{x} - \int_{\Lambda} p \mathbf{v} \cdot \mathbf{n} d\Lambda
\end{aligned} \tag{4.20}$$

The variation of \dot{F} is

$$\begin{aligned}
\delta \dot{F} &= \int_{\Lambda} \delta \mathbf{v} \cdot \mathbf{n} \left(-\sigma \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} + g \right) d\Lambda \\
&\quad - \iint_{\Omega} (g' (\delta \mathbf{v}_1(1 - \theta) + \delta \mathbf{v}_2\theta) \cdot \nabla \theta - \theta(1 - \theta)(\delta \mathbf{v}_2 - \delta \mathbf{v}_1) \cdot \nabla g') d\mathbf{x}
\end{aligned} \tag{4.21}$$

The variation of C is

$$\delta C = \iint_{\Omega} (\nabla p \cdot \delta \mathbf{v}_1(1 - \theta) + \nabla p \cdot \delta \mathbf{v}_2(\theta)) d\mathbf{x} - \int_{\Lambda} p \delta \mathbf{v} \cdot \mathbf{n} d\Lambda \tag{4.22}$$

For conciseness, let us define $T_2 := (\nabla \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T)$ to be the viscous stress tensor. The variation of Φ is

$$\begin{aligned}
\delta \Phi &= \iint_{\Omega} \mu_n \left(\nabla \mathbf{v}_2 : \nabla \delta \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T : \nabla \delta \mathbf{v}_2 \right) d\mathbf{x} \\
&\quad + \frac{\mu_s}{2} \iint_{\Omega} \theta(1 - \theta) (2\mathbf{v}_2 \cdot \delta \mathbf{v}_2 + 2\mathbf{v}_1 \cdot \delta \mathbf{v}_1 - 2\mathbf{v}_1 \cdot \delta \mathbf{v}_2 - 2\mathbf{v}_2 \cdot \delta \mathbf{v}_1) d\mathbf{x} \\
&= - \iint_{\Omega} \nabla \cdot \left(\mu_n \left(\nabla \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T \right) \right) \cdot \delta \mathbf{v}_2 d\mathbf{x} \\
&\quad + \int_{\partial \Omega} \mu_n \left(\nabla \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T \right) : \delta \mathbf{v}_2 \mathbf{n} d\partial \Omega \\
&\quad + \mu_s \iint_{\Omega} \theta(1 - \theta) (\mathbf{v}_2 \cdot \delta \mathbf{v}_2 + \mathbf{v}_1 \cdot \delta \mathbf{v}_1 - \mathbf{v}_1 \cdot \delta \mathbf{v}_2 - \mathbf{v}_2 \cdot \delta \mathbf{v}_1) d\mathbf{x} \\
&= - \iint_{\Omega} \nabla \cdot (\mu_n T_2) \cdot \delta \mathbf{v}_2 d\mathbf{x} \\
&\quad + \int_{\Lambda} \mu_n (\mathbf{n} \cdot T_2 \cdot \mathbf{n} (\delta \mathbf{v} \cdot \mathbf{n}) + \boldsymbol{\tau} \cdot T_2 \cdot \mathbf{n} (\delta \mathbf{v} \cdot \boldsymbol{\tau})) d\Lambda \\
&\quad + \mu_s \iint_{\Omega} \theta(1 - \theta) (\mathbf{v}_2 - \mathbf{v}_1) \cdot (\delta \mathbf{v}_2 - \delta \mathbf{v}_1) d\mathbf{x}
\end{aligned} \tag{4.23}$$

where we have used $\delta\mathbf{v}_2 \cdot \mathbf{n} = \delta\mathbf{v} \cdot \mathbf{n}$ and $\delta\mathbf{v}_2 \cdot \boldsymbol{\tau} = \delta\mathbf{v} \cdot \boldsymbol{\tau}$ at the free surface.

The total variation of the Rayleighian with respect to \mathbf{v} is then

$$\begin{aligned}
\delta R &= \delta\dot{F} + \delta\Phi + \delta C = 0 \\
&= \int_{\Lambda} \delta\mathbf{v} \cdot \mathbf{n} \left(-\sigma \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} + g \right) d\Lambda \\
&\quad - \iint_{\Omega} (g' (\delta\mathbf{v}_1(1 - \theta) + \delta\mathbf{v}_2\theta) \cdot \nabla\theta - \theta(1 - \theta)(\delta\mathbf{v}_2 - \delta\mathbf{v}_1) \cdot \nabla g') d\mathbf{x} \\
&\quad - \iint_{\Omega} \nabla \cdot (\mu_n \mathbf{T}_2) \cdot \delta\mathbf{v}_2 d\mathbf{x} \\
&\quad + \int_{\Lambda} \mu_n (\mathbf{n} \cdot \mathbf{T}_2 \cdot \mathbf{n} (\delta\mathbf{v} \cdot \mathbf{n}) + \boldsymbol{\tau} \cdot \mathbf{T}_2 \cdot \mathbf{n} (\delta\mathbf{v} \cdot \boldsymbol{\tau})) d\Lambda \\
&\quad + \mu_s \iint_{\Omega} \theta(1 - \theta)(\mathbf{v}_2 - \mathbf{v}_1) \cdot (\delta\mathbf{v}_2 - \delta\mathbf{v}_1) d\mathbf{x} \\
&\quad + \iint_{\Omega} (\nabla p \cdot \delta\mathbf{v}_1(1 - \theta) + \nabla p \cdot \delta\mathbf{v}_2(\theta)) d\mathbf{x} \\
&\quad - \int_{\Lambda} p \delta\mathbf{v} \cdot \mathbf{n} d\Lambda
\end{aligned} \tag{4.24}$$

Collecting $\delta\mathbf{v} \cdot \mathbf{n}$ and $\delta\mathbf{v} \cdot \boldsymbol{\tau}$ at Λ yields

$$\sigma \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} = -p + \mu_n \mathbf{n} \cdot \mathbf{T}_2 \cdot \mathbf{n} + g \quad \text{at } \Lambda \tag{4.25}$$

$$0 = \mu_n \boldsymbol{\tau} \cdot \mathbf{T}_2 \cdot \mathbf{n} \quad \text{at } \Lambda \tag{4.26}$$

respectively. Collecting $\delta\mathbf{v}_2$ and $\delta\mathbf{v}_1$ on Ω yields

$$\begin{aligned}
0 &= -(1 - \theta)g' \nabla\theta - \theta(1 - \theta)\nabla g' \\
&\quad - \mu_s \theta(1 - \theta)(\mathbf{v}_2 - \mathbf{v}_1) + (1 - \theta)\nabla p \quad \text{on } \Omega
\end{aligned} \tag{4.27}$$

$$\begin{aligned}
0 &= -\theta g' \nabla\theta + \theta(1 - \theta)\nabla g' - \nabla \cdot (\mu_n \mathbf{T}_2) \\
&\quad + \mu_s \theta(1 - \theta)(\mathbf{v}_2 - \mathbf{v}_1) + \theta \nabla p \quad \text{on } \Omega
\end{aligned} \tag{4.28}$$

respectively.

4.1.1 Deriving an asymmetric bulk system

Summing equations (4.27) and (4.28) on the domain Ω yields

$$0 = -g' \nabla\theta + \nabla p - \nabla \cdot (\mu_n \mathbf{T}_2) \tag{4.29}$$

which is the generalized version of the monofluid Stoke's flow that we arrived at in equation (3.31). The Lagrange multiplier p can be interpreted as an effective

hydrostatic pressure [20, Chapter I.9] which we are free to choose via an appropriate gauge [25]. We may, for instance, let $p \rightarrow p + g$ to attain the more familiar form

$$0 = \nabla p - \nabla \cdot (\mu_n T_2) \quad (4.30)$$

Our aim in this section is to attain an asymmetric bulk system which explicitly implies momentum conservation in terms of equal and opposite forces between the network and solvent stress tensors. Consider both fluids flowing such that there exists a free interface between the phases in a certain sense. In general, the fluids will attempt to mix in a way that maximizes their entropy. The pressures between the phases will be described by the osmotic pressure $\Pi(\theta)$ which is related closely to the free energy density of mixing $g(\theta)$ [52].

As discussed in [13], two-phase flows can be modelled with respect to an interphase pressure p_{ns} as well as macroscopic intra-phase pressures [36] p_n and p_s corresponding to the network and solvent phases, respectively. The effective hydrostatic pressure p is then added to each of these pressures. We can also define the mean pressure $P = \theta p_n + (1-\theta)p_s$ [35]. To relate these various pressures, we define the *contractile* pressure $\Upsilon(\theta) = p_s - p_n$ and *solvation* pressure $\Theta(\theta) = p_s - p_{ns}$ [13], which describe the relative pressures on (and between) each phase. Once we establish the three pressures p_s , p_n , and p_{ns} , there exists two degrees of freedom which are removed by imposing two relations among them [13].

We shall choose our Lagrange multiplier p to represent the network pressure such that $p = p_n$. We can relate the network, solvent, and mean pressures through

$$p_n = P - (1 - \theta)\Upsilon, \quad p_n = p_s - \Upsilon \quad (4.31)$$

Substituting this relation into equation (4.29) yields

$$0 = \nabla P - \nabla \cdot (\mu_n T_2) + (\Upsilon - (1 - \theta)\Upsilon' - g') \nabla \theta \quad (4.32)$$

where $\Upsilon' = \frac{\partial \Upsilon}{\partial \theta}$. We can write this equation in a form that resembles the monofluid Stoke's equation by imposing the condition

$$\Upsilon - (1 - \theta)\Upsilon' - g' = 0 \quad (4.33)$$

which removes one degree of freedom. We can solve for Υ to yield

$$\Upsilon = -\frac{1}{(1 - \theta)}g + \frac{A}{(1 - \theta)} \quad (4.34)$$

for some constant of integration A , which can be evaluated via boundary conditions as $A = \Upsilon(0) + g(0)$, where $\Upsilon(0)$ is Υ evaluated at $\theta = 0$.

After making the replacement $p = p_n$, equations (4.27) and (4.28) can respectively be rearranged to yield

$$\nabla \cdot ((1 - \theta)(-p_n \mathbb{1})) = -\mu_s \mathbf{j} + (p_n - (1 - \theta)g' - \theta(1 - \theta)g'') \nabla \theta \quad (4.35)$$

and

$$\nabla \cdot \left(\theta \left(-p_n \mathbb{1} + \frac{1}{\theta} \mu_n T_2 \right) \right) = \mu_s \mathbf{j} - (p_n + \theta g' - \theta(1 - \theta)g'') \nabla \theta \quad (4.36)$$

Using the relation $p_n = p_s - \Upsilon$ and rearranging terms, equation (4.35) becomes

$$\begin{aligned} \nabla \cdot ((1 - \theta)(-p_s \mathbb{1})) \\ = -\mu_s \mathbf{j} + (p_n + \theta g' - \theta(1 - \theta)g'') \nabla \theta - g' \nabla \theta - \nabla \cdot ((1 - \theta)\Upsilon \mathbb{1}) \end{aligned} \quad (4.37)$$

Substituting the expression for the contractile pressure given by equation (4.34) yields

$$\nabla \cdot ((1 - \theta)(-p_s \mathbb{1})) = -\mu_s \mathbf{j} + (p_n + \theta g' - \theta(1 - \theta)g'') \nabla \theta \quad (4.38)$$

Equations (4.38) and (4.36) are now in a form that, with the correct choice of variables, can be formulated as an asymmetric system.

Let us define

$$\begin{aligned} \Sigma_s &:= -p_s \mathbb{1}, & D &:= -\mu_s \theta(1 - \theta)(\mathbf{v}_2 - \mathbf{v}_1) + p_{ns} \nabla \theta \\ \Sigma_n &:= -p_n \mathbb{1} + \frac{\mu_n}{\theta} T_2, & p_{ns} &:= p_n + \theta g' - \theta(1 - \theta)g'' \end{aligned} \quad (4.39)$$

where Σ_s and Σ_n are respectively the solvent and network stress tensors [35]. D is the interphase force acting on the network phase, and is composed of two terms: the term $p_{ns} \nabla \theta$ represents the force arising from the net static pressure acting on the network phase by the solvent phase, while the first term is the frictional drag force arising from the relative motion of both phases [13]. Note that p_{ns} can be written in terms of the mean pressure P by using the pressure relations, yielding

$$p_{ns} = P + g + \theta g' - \theta(1 - \theta)g'' - \Upsilon(0) - g(0) \quad (4.40)$$

This effectively defines $\Theta(\theta)$ via $p_{ns} = P + \theta \Upsilon - \Theta$, thereby removing another degree of freedom.

We can then re-write equations (4.38) and (4.36) in a fully asymmetric form given by

$$\begin{aligned} \nabla \cdot ((1 - \theta)\Sigma_s) &= D \\ \nabla \cdot (\theta\Sigma_n) &= -D \end{aligned} \quad (4.41)$$

Note that swapping the network and solvent phases in equations (4.41) yields the same asymmetric system. We also have the condition

$$\nabla \cdot \Sigma = 0 \quad (4.42)$$

for a total stress tensor given by

$$\Sigma = \theta \Sigma_n + (1 - \theta) \Sigma_s \quad (4.43)$$

which is valid when there exists no volume forces such as gravity.

4.2 Thin-film approximation

Scalings

By assuming the typical thin-film approximation $\epsilon = \frac{H}{L} \ll 1$, the variables are scaled as follows:

$$x = \bar{x}L, \quad z = \bar{z}\epsilon L, \quad u = \bar{u}U, \quad w = \bar{w}\epsilon U, \quad t = \bar{t}\frac{L}{U}$$

as in chapter 3. The relevant coefficients are scaled as

$$p = \bar{p}P, \quad g = \bar{g}G \quad (4.44)$$

where \bar{p} and \bar{g} are dimensionless variables. We will determine the scaling of the physical parameters σ , μ_n , and μ_s by considering an appropriately selected scaling regime.

Rayleighian construction

In contrast to section 4.1, we will perform a change of variables and instead select the process space

$$P_{\theta_1, \theta_2} \mathcal{X} = \{\mathbf{v}, \mathbf{j} \in \mathbb{R}^2 : \Omega(t) \rightarrow \mathbb{R}\} \quad (4.45)$$

The Rayleighian is then minimized with respect to \mathbf{v} and \mathbf{j} such that $\delta R(\mathbf{v})[\delta \mathbf{v}] = 0$ and $\delta R(\mathbf{j})[\delta \mathbf{j}] = 0$. This will yield the same set of equations with a more concise presentation.

Constraints

The constraint with Lagrange multiplier p is given by

$$\begin{aligned} C &= \iint_{\Omega} \nabla(p(x, z, t)) \cdot \mathbf{v} \, d\mathbf{x} - \int_{x_-}^{x_+} p(x, h, t) \dot{h} \, dx \\ &\approx \iint_{\Omega} UL\epsilon P \bar{\nabla} \bar{p} \cdot \bar{\mathbf{v}} \, d\bar{\mathbf{x}} - \int_{x_-}^{x_+} UL\epsilon P \bar{p} \bar{\mathbf{v}} \cdot \mathbf{n} \, d\bar{x} \end{aligned} \quad (4.46)$$

where $\bar{\nabla}$ represents a derivative with respect to dimensionless variables.

Free energy

The time derivative of the free energy is given by

$$\begin{aligned}\dot{F} = & \int_{x_-}^{x_+} \dot{h} \left(-\sigma \frac{\partial_x^2 h}{(1 + |\partial_x h|^2)^{\frac{3}{2}}} + g \right) dx \\ & - \iint_{\Omega} (g' \mathbf{v} \cdot \nabla \theta - \theta(1 - \theta)(\mathbf{v}_2 - \mathbf{v}_1) \cdot g'' \nabla \theta) d\mathbf{x} \quad (4.47)\end{aligned}$$

Substituting appropriate scalings yields

$$\begin{aligned}\dot{F} \approx & \int_{x_-}^{x_+} \bar{\mathbf{v}} \cdot \mathbf{n} U (-\sigma \partial_{\bar{x}}^2 \bar{h} \epsilon^2 + L \epsilon \bar{g} G) d\bar{x} \\ & - \iint_{\Omega} U L \epsilon (\bar{g}' G \bar{\mathbf{v}} \cdot \bar{\nabla} \theta - \bar{g}'' G \bar{\mathbf{j}} \cdot \bar{\nabla} \theta) d\bar{x} \quad (4.48)\end{aligned}$$

To keep terms of the same order, we choose the scaling

$$G \sim \frac{\sigma \epsilon}{L} \quad (4.49)$$

by assuming that we are in the regime

$$\mathcal{A}_G := \frac{LG}{\sigma \epsilon} \sim \mathcal{O}(1) \quad (4.50)$$

The time derivative of the free energy can then be expressed as

$$\begin{aligned}\dot{F} = & \int_{x_-}^{x_+} \bar{\mathbf{v}} \cdot \mathbf{n} U \sigma \epsilon^2 (-\partial_{\bar{x}}^2 \bar{h} + \mathcal{A}_G \bar{g}) d\bar{x} \\ & - \iint_{\Omega} U L G \epsilon (\bar{g}' \bar{\mathbf{v}} \cdot \bar{\nabla} \theta - \bar{g}'' \bar{\mathbf{j}} \cdot \bar{\nabla} \theta) d\bar{x} \quad (4.51)\end{aligned}$$

Energy dissipation

The dissipation functional is given by

$$\begin{aligned}\Phi = & \iint_{\Omega} \frac{\mu_n(\theta)}{4} \left(\nabla \mathbf{v}_2 + (\nabla \mathbf{v}_2)^T \right)^2 d\mathbf{x} + \frac{\mu_s}{2} \iint_{\Omega} \theta(1 - \theta) |\mathbf{v}_2 - \mathbf{v}_1|^2 d\mathbf{x} \\ = & \iint_{\Omega} U^2 \left(\frac{\mu_n}{2} \frac{1}{L^2} \left(2 \left(\frac{\partial \bar{u}_2}{\partial \bar{x}} \right)^2 + 2 \left(\frac{\partial \bar{w}_2}{\partial \bar{z}} \right)^2 + 2 \left(\frac{\partial \bar{w}_2}{\partial \bar{x}} \right) \left(\frac{\partial \bar{u}_2}{\partial \bar{z}} \right) \right. \right. \\ & \left. \left. + \frac{1}{\epsilon^2} \left(\frac{\partial \bar{u}_2}{\partial \bar{z}} \right)^2 + \epsilon^2 \left(\frac{\partial \bar{w}_2}{\partial \bar{x}} \right)^2 \right) + \frac{\mu_s}{2} \frac{1}{\theta(1 - \theta)} (\bar{j}_x^2 + \epsilon^2 \bar{j}_z^2) \right) L^2 \epsilon d\bar{x} \quad (4.52)\end{aligned}$$

Let us assume that we are in the regime

$$\mathcal{D}_0 := \frac{\mu_s L^2 \epsilon^2}{\mu_n} \sim \mathcal{O}(1) \quad (4.53)$$

The dissipation functional can be expressed as

$$\begin{aligned}\Phi = \iint_{\Omega} \frac{\mu_n U^2 \epsilon}{2} & \left(2 \left(\frac{\partial \bar{u}_2}{\partial \bar{x}} \right)^2 + 2 \left(\frac{\partial \bar{w}_2}{\partial \bar{z}} \right)^2 + 2 \left(\frac{\partial \bar{w}_2}{\partial \bar{x}} \right) \left(\frac{\partial \bar{u}_2}{\partial \bar{z}} \right) + \frac{1}{\epsilon^2} \left(\frac{\partial \bar{u}_2}{\partial \bar{z}} \right)^2 \right. \\ & \left. + \epsilon^2 \left(\frac{\partial \bar{w}_2}{\partial \bar{x}} \right)^2 + \frac{1}{\theta(1-\theta)} \frac{1}{\epsilon^2} \mathcal{D}_0 \bar{j}_x^2 + \frac{1}{\theta(1-\theta)} \mathcal{D}_0 \bar{j}_z^2 \right) d\bar{x}\end{aligned}\quad (4.54)$$

Minimizing the Rayleighian

The variation of C is

$$\delta C = \iint_{\Omega} U H P \bar{\nabla} \bar{p} \cdot \delta \bar{v} d\bar{x} - \int_{x_-}^{x_+} U H P \bar{p} \delta \bar{v} \cdot \mathbf{n} d\bar{x} \quad (4.55)$$

The variation of \dot{F} is

$$\begin{aligned}\delta \dot{F} = \int_{x_-}^{x_+} \delta \bar{v} \cdot \mathbf{n} U \sigma \epsilon^2 (-\partial_{\bar{x}}^2 \bar{h} + \mathcal{A}_G \bar{g}) d\bar{x} \\ - \iint_{\Omega} U L G \epsilon (\bar{g}' \delta \bar{v} \cdot \bar{\nabla} \theta - \bar{g}'' \delta \bar{j} \cdot \bar{\nabla} \theta) d\bar{x} \quad (4.56)\end{aligned}$$

The variation of Φ is

$$\begin{aligned}\delta \Phi = \iint_{\Omega} \mu_n U^2 \epsilon & \left(\left(\frac{\partial \bar{u}_2}{\partial \bar{x}} \right) \left(\frac{\partial \delta \bar{u}_2}{\partial \bar{x}} \right) + \left(\frac{\partial \bar{w}_2}{\partial \bar{z}} \right) \left(\frac{\partial \delta \bar{w}_2}{\partial \bar{z}} \right) + (\bar{\nabla} \bar{v}_2)^T : \bar{\nabla} \delta \bar{v}_2 \right. \\ & \left. + \frac{1}{\epsilon^2} \left(\frac{\partial \bar{u}_2}{\partial \bar{z}} \right) \left(\frac{\partial \delta \bar{u}_2}{\partial \bar{z}} \right) + \epsilon^2 \left(\frac{\partial \bar{w}_2}{\partial \bar{x}} \right) \left(\frac{\partial \delta \bar{w}_2}{\partial \bar{x}} \right) \right. \\ & \left. + \frac{1}{\theta(1-\theta)} \frac{1}{\epsilon^2} \mathcal{D}_0 \bar{j}_x \delta \bar{j}_x + \frac{1}{\theta(1-\theta)} \mathcal{D}_0 \bar{j}_z \delta \bar{j}_z \right) d\bar{x} \\ = \iint_{\Omega} U^2 \epsilon & \left(-\bar{\nabla} \cdot (\mu_n \bar{\nabla} \bar{v}_2)^T \cdot \delta \bar{v}_2 - \frac{\partial}{\partial \bar{x}} \left(\mu_n \frac{\partial \bar{u}_2}{\partial \bar{x}} \right) \delta \bar{u}_2 - \frac{\partial}{\partial \bar{z}} \left(\mu_n \frac{\partial \bar{w}_2}{\partial \bar{z}} \right) \delta \bar{w}_2 \right. \\ & \left. - \frac{1}{\epsilon^2} \frac{\partial}{\partial \bar{z}} \left(\mu_n \frac{\partial \bar{u}_2}{\partial \bar{z}} \right) \delta \bar{u}_2 - \epsilon^2 \frac{\partial}{\partial \bar{x}} \left(\mu_n \frac{\partial \bar{w}_2}{\partial \bar{x}} \right) \delta \bar{w}_2 \right. \\ & \left. + \frac{1}{\theta(1-\theta)} \frac{1}{\epsilon^2} \mu_n \mathcal{D}_0 \bar{j}_x \delta \bar{j}_x + \frac{1}{\theta(1-\theta)} \mu_n \mathcal{D}_0 \bar{j}_z \delta \bar{j}_z \right) d\bar{x} \\ & + \int_{x_-}^{x_+} \mu_n U^2 \epsilon \left(\mathbf{n} \cdot (\bar{\nabla} \bar{v}_2)^T \cdot \delta \bar{v}_2 + \frac{1}{\epsilon^2} \frac{\partial \bar{u}_2}{\partial \bar{z}} \delta \bar{u}_2 + \frac{\partial \bar{w}_2}{\partial \bar{z}} \delta \bar{w}_2 \right) d\bar{x} \Big|_{z=h(x,t)} \quad (4.57)\end{aligned}$$

After substituting equations (4.9), (4.4), and the no-slip condition at the interface (i.e. $\mathbf{v}_1 = \mathbf{v}_2 = \mathbf{v}$ at Λ), the total variation of R with respect to \bar{v} and \bar{j}

is

$$\begin{aligned}
\delta R &= \delta \dot{F} + \delta \Phi + \delta C = 0 \\
&= \int_{x_-}^{x_+} (\delta \bar{w} - \delta \bar{u} \partial_{\bar{x}} \bar{h}) U \sigma \epsilon^2 (-\partial_{\bar{x}}^2 \bar{h} + \mathcal{A}_G \bar{g}) d\bar{x} \\
&\quad - \iint_{\Omega} ULG \epsilon (\bar{g}' \delta \bar{v} \cdot \bar{\nabla} \theta - \bar{g}'' \delta \bar{j} \cdot \bar{\nabla} \theta) d\bar{x} \\
&\quad + \iint_{\Omega} U^2 \epsilon \left(-\bar{\nabla} \cdot (\mu_n \bar{\nabla} \bar{v}_2)^T \cdot \left(\delta \bar{v} + \frac{1}{\theta} \delta \bar{j} \right) - \frac{\partial}{\partial \bar{x}} \left(\mu_n \frac{\partial \bar{u}_2}{\partial \bar{x}} \right) \left(\delta \bar{u} + \frac{1}{\theta} \delta j_x \right) \right. \\
&\quad \left. - \frac{\partial}{\partial \bar{z}} \left(\mu_n \frac{\partial \bar{w}_2}{\partial \bar{z}} \right) \left(\delta \bar{w} + \frac{1}{\theta} \delta j_z \right) - \frac{1}{\epsilon^2} \frac{\partial}{\partial \bar{z}} \left(\mu_n \frac{\partial \bar{u}_2}{\partial \bar{z}} \right) \left(\delta \bar{u} + \frac{1}{\theta} \delta j_x \right) \right. \\
&\quad \left. - \epsilon^2 \frac{\partial}{\partial \bar{x}} \left(\mu_n \frac{\partial \bar{w}_2}{\partial \bar{x}} \right) \left(\delta \bar{w} + \frac{1}{\theta} \delta j_z \right) \right. \\
&\quad \left. + \frac{1}{\theta(1-\theta)} \frac{1}{\epsilon^2} \mu_n \mathcal{D}_0 \bar{j}_x \delta \bar{j}_x + \frac{1}{\theta(1-\theta)} \mu_n \mathcal{D}_0 \bar{j}_z \delta \bar{j}_z \right) d\bar{x} \\
&\quad + \int_{x_-}^{x_+} \mu_n U^2 \epsilon \left(\mathbf{n} \cdot (\bar{\nabla} \bar{v}_2)^T \cdot \delta \bar{v} + \frac{1}{\epsilon^2} \frac{\partial \bar{u}_2}{\partial \bar{z}} \delta \bar{u} + \frac{\partial \bar{w}_2}{\partial \bar{z}} \delta \bar{w} \right) d\bar{x} \\
&\quad + \iint_{\Omega} UL \epsilon P \bar{\nabla} \bar{p} \cdot \delta \bar{v} d\bar{x} - \int_{x_-}^{x_+} UL \epsilon P \bar{p} (\delta \bar{w} - \delta \bar{u} \partial_{\bar{x}} \bar{h}) d\bar{x} \tag{4.58}
\end{aligned}$$

Note that here we have kept lower order terms in the Rayleighian for completeness. However, we will not solve the full system; we will only focus on the leading order terms.

Scaling analysis

Recall from chapter 3 the capillary number

$$\mathcal{C}_{\mathcal{A}} = \frac{\mu_n U}{\sigma}$$

where μ_n is the viscosity coefficient of the Newtonian fluid. Once again, we assume that $\mathcal{C}_{\mathcal{A}}$ scales as $\sim \mathcal{O}(\epsilon^3)$. Making this assumption (i.e. that viscous drag forces are negligible compared to surface tension forces), restricts the analysis to the regime

$$\mathcal{A}_{\mu} := \frac{\mu_n U}{\sigma \epsilon^3} \sim \mathcal{O}(1)$$

To balance terms in the surface integrals, we restrict the analysis to the regime

$$\mathcal{A}_P := \frac{LP}{\sigma \epsilon} \sim \mathcal{O}(1) \tag{4.59}$$

In two dimensions, recall the dimensions of the variables, given by

$$[G] = \frac{J}{m^2} = \frac{N}{m} = [P] \tag{4.60}$$

and of the physical parameters, given by

$$[\mu_n] = \frac{\text{N} \cdot \text{s}}{\text{m}}, \quad [\mu_s] = \frac{\text{N} \cdot \text{s}}{\text{m}^3}, \quad [\sigma] = \text{N} \quad (4.61)$$

Therefore, in two dimensions, \mathcal{D}_0 , \mathcal{A}_G , \mathcal{A}_μ , and \mathcal{A}_P are dimensionless. The scaling regime is equivalent to letting

$$G = \frac{\sigma\epsilon}{L}, \quad G = P, \quad P = \frac{\mu_n U}{L\epsilon^2} \quad (4.62)$$

in which case $\mathcal{A}_G = \mathcal{A}_\mu = \mathcal{A}_P = \bar{\sigma}^{-1} \sim \mathcal{O}(1)$ for dimensionless $\bar{\sigma}$.

Minimization

Dividing equation (4.58) by $U\sigma\epsilon^3$ and expressing the result in terms of dimensionless variables $\bar{\sigma}$ and \mathcal{D}_0 gives the system

$$\begin{aligned} 0 = & \int_{x_-}^{x_+} \bar{\sigma}^{-1} (\delta\bar{w} - \delta\bar{u}\partial_{\bar{x}}\bar{h}) (-\bar{\sigma}\partial_{\bar{x}}^2\bar{h} + \bar{g}) \, d\bar{x} \\ & - \iint_{\Omega} \bar{\sigma}^{-1} (\bar{g}'\delta\bar{\mathbf{v}} \cdot \bar{\nabla}\theta - \bar{g}''\delta\bar{\mathbf{j}} \cdot \bar{\nabla}\theta) \, d\bar{x} \\ & + \iint_{\Omega} \frac{\bar{\sigma}^{-1}}{\mu_n} \left(-\epsilon^2 \bar{\nabla} \cdot (\mu_n \bar{\nabla} \bar{\mathbf{v}}_2)^T \cdot \left(\delta\bar{\mathbf{v}} + \frac{1}{\theta}\delta\bar{\mathbf{j}} \right) - \epsilon^2 \frac{\partial}{\partial\bar{x}} \left(\mu_n \frac{\partial\bar{u}_2}{\partial\bar{x}} \right) \left(\delta\bar{u} + \frac{1}{\theta}\delta\bar{j}_x \right) \right. \\ & \quad \left. - \epsilon^2 \frac{\partial}{\partial\bar{z}} \left(\mu_n \frac{\partial\bar{w}_2}{\partial\bar{z}} \right) \left(\delta\bar{w} + \frac{1}{\theta}\delta\bar{j}_z \right) - \frac{\partial}{\partial\bar{z}} \left(\mu_n \frac{\partial\bar{u}_2}{\partial\bar{z}} \right) \left(\delta\bar{u} + \frac{1}{\theta}\delta\bar{j}_x \right) \right. \\ & \quad \left. - \epsilon^4 \frac{\partial}{\partial\bar{x}} \left(\mu_n \frac{\partial\bar{w}_2}{\partial\bar{x}} \right) \left(\delta\bar{w} + \frac{1}{\theta}\delta\bar{j}_z \right) \right. \\ & \quad \left. + \frac{1}{\theta(1-\theta)} \mathcal{D}_0 \bar{j}_x \delta\bar{j}_x + \frac{1}{\theta(1-\theta)} \epsilon^2 \mathcal{D}_0 \bar{j}_z \delta\bar{j}_z \right) \, d\bar{x} \\ & + \int_{x_-}^{x_+} \bar{\sigma}^{-1} \left(\epsilon^2 \mathbf{n} \cdot (\bar{\nabla} \bar{\mathbf{v}}_2)^T \cdot \delta\bar{\mathbf{v}} + \frac{\partial\bar{u}_2}{\partial\bar{z}} \delta\bar{u} + \epsilon^2 \frac{\partial\bar{w}_2}{\partial\bar{z}} \delta\bar{w} \right) \, d\bar{x} \\ & + \iint_{\Omega} \bar{\sigma}^{-1} \bar{\nabla}\bar{p} \cdot \delta\bar{\mathbf{v}} \, d\bar{x} - \int_{x_-}^{x_+} \bar{\sigma}^{-1} \bar{p} (\delta\bar{w} - \delta\bar{u}\partial_{\bar{x}}\bar{h}) \, d\bar{x} \end{aligned} \quad (4.63)$$

For the following analysis, we make the assumption that the relative concentration θ changes negligibly along the z -direction [35], i.e.

$$\theta \approx \theta(x, t) \quad (4.64)$$

Most crucially, this assumption decouples p and θ which will allow us to find an expression for u_2 with parabolic z -dependence [52].

Collecting $\mathcal{O}(1)$ $\delta\bar{w}$ terms at Λ yields

$$0 = -\bar{\sigma}\partial_{\bar{x}}^2\bar{h} + \bar{g} - \bar{p} \quad \text{at} \quad \Lambda \quad (4.65)$$

Collecting $\mathcal{O}(1)$ $\delta\bar{u}$ terms at Λ yields

$$0 = -\partial_{\bar{x}}\bar{h}(-\bar{\sigma}\partial_{\bar{x}}^2\bar{h} + \bar{g} - \bar{p}) + \frac{\partial\bar{u}_2}{\partial\bar{z}} \quad \text{at } \Lambda \quad (4.66)$$

which, combined with equation (4.65), becomes

$$0 = \frac{\partial\bar{u}_2}{\partial\bar{z}} \quad \text{at } \Lambda \quad (4.67)$$

Collecting $\mathcal{O}(1)$ $\delta\bar{w}$ terms in Ω yields

$$0 = \frac{\partial\bar{p}}{\partial\bar{z}} \quad \text{in } \Omega \quad (4.68)$$

Collecting $\mathcal{O}(1)$ $\delta\bar{u}$ terms in Ω yields

$$0 = -\bar{g}'\frac{\partial\theta}{\partial\bar{x}} - \frac{\partial^2\bar{u}_2}{\partial\bar{z}^2} + \frac{\partial\bar{p}}{\partial\bar{x}} \quad \text{in } \Omega \quad (4.69)$$

Collecting $\mathcal{O}(1)$ $\delta\bar{j}_x$ terms in Ω yields

$$0 = \bar{g}''\frac{\partial\theta}{\partial\bar{x}} - \frac{1}{\theta}\frac{\partial^2\bar{u}_2}{\partial\bar{z}^2} + \frac{1}{\theta(1-\theta)}\mathcal{D}_0\bar{j}_x \quad \text{in } \Omega \quad (4.70)$$

4.2.1 Solving the thin-film equations

Equation (4.68) implies that $\bar{p} = \bar{p}(\bar{x}, \bar{t})$. Therefore, equation (4.69) can be combined with equation (4.65) to attain

$$\frac{\partial^2\bar{u}_2}{\partial\bar{z}^2} = -\bar{\sigma}\partial_{\bar{x}}^3\bar{h}$$

where we cancelled a term by using $\partial_{\bar{x}}\bar{g} = \bar{g}'\partial_{\bar{x}}\theta$. Similar to section 3.2.1, we may solve for $\bar{u}_2(\bar{x}, \bar{z}, \bar{t})$ using the boundary conditions (4.67) and (4.7) to attain the parabolic form

$$\bar{u}_2 = -\bar{\sigma}\partial_{\bar{x}}^3\bar{h}\left(\frac{1}{2}\bar{z}^2 - \bar{h}\bar{z}\right) \quad (4.71)$$

We may use equation (4.70) to isolate $\bar{u}_1(\bar{x}, \bar{z}, \bar{t})$, yielding

$$\bar{u}_1 = \frac{1}{\mathcal{D}_0}\left(\frac{\bar{\sigma}}{\theta}\partial_{\bar{x}}^3\bar{h} + \partial_{\bar{x}}\bar{g}'\right) + \bar{u}_2 \quad (4.72)$$

The flux \bar{j}_x is found to be

$$\bar{j}_x = -\frac{\theta(1-\theta)}{\mathcal{D}_0}\left(\frac{\bar{\sigma}}{\theta}\partial_{\bar{x}}^3\bar{h} + \partial_{\bar{x}}\bar{g}'\right) \quad (4.73)$$

where we have used $g''\partial_{\bar{x}}\theta = \partial_{\bar{x}}g'$. Using relation (4.4), the mean velocity \bar{u} is expressed as

$$\bar{u} = -\bar{\sigma}\partial_{\bar{x}}^3\bar{h}\left(\frac{1}{2}\bar{z}^2 - \bar{h}\bar{z}\right) + \frac{(1-\theta)}{\mathcal{D}_0}\left(\frac{\bar{\sigma}}{\theta}\partial_{\bar{x}}^3\bar{h} + \partial_{\bar{x}}\bar{g}'\right) \quad (4.74)$$

Substituting \bar{u} into the non-dimensional continuity equation (4.10) for the height h yields

$$\begin{aligned}\dot{\bar{h}} &= -\frac{\partial}{\partial \bar{x}} \int_0^{\bar{h}} \left(-\bar{\sigma} \partial_{\bar{x}}^3 \bar{h} \left(\frac{1}{2} \bar{z}^2 - \bar{h} \bar{z} \right) + \frac{(1-\theta)}{\mathcal{D}_0} \left(\frac{\bar{\sigma}}{\theta} \partial_{\bar{x}}^3 \bar{h} + \partial_{\bar{x}} \bar{g}' \right) \right) d\bar{z} \\ &= -\frac{\partial}{\partial \bar{x}} \left(\frac{\bar{\sigma} \bar{h}^3}{3} \partial_{\bar{x}}^3 \bar{h} + \frac{(1-\theta) \bar{h}}{\mathcal{D}_0} \left(\frac{\bar{\sigma}}{\theta} \partial_{\bar{x}}^3 \bar{h} + \partial_{\bar{x}} \bar{g}' \right) \right)\end{aligned}\quad (4.75)$$

After using relation (4.4), converting to non-dimensional variables, and recalling the assumption $\theta = \theta(x, t)$, the continuity equation (4.11) for the effective solute thickness Ψ becomes

$$\frac{\partial}{\partial \bar{t}} (\bar{h} \theta) = -\frac{\partial}{\partial \bar{x}} \int_0^{\bar{h}} \theta \bar{u}_2 d\bar{z} \quad (4.76)$$

where $\bar{\Psi} \approx \bar{h} \theta$. Substituting u_2 gives

$$\begin{aligned}\frac{\partial}{\partial \bar{t}} (\bar{h} \theta) &= -\frac{\partial}{\partial \bar{x}} \int_0^{\bar{h}} \theta \left(-\bar{\sigma} \partial_{\bar{x}}^3 \bar{h} \left(\frac{1}{2} \bar{z}^2 - \bar{h} \bar{z} \right) \right) d\bar{z} \\ &= -\frac{\partial}{\partial \bar{x}} \left(\frac{\theta \bar{\sigma} \bar{h}^3}{3} \partial_{\bar{x}}^3 \bar{h} \right)\end{aligned}\quad (4.77)$$

We shall hereafter omit the bar notation for dimensionless variables. Equation (4.75) can be expressed as

$$\dot{h} = -\frac{\partial}{\partial x} \left(\frac{\mathcal{D}_0 \theta h^3 + 3h(1-\theta)}{3\mathcal{D}_0 \theta} \sigma \partial_x^3 h \right) - \frac{\partial}{\partial x} \left(\frac{1}{\mathcal{D}_0} h(1-\theta) \partial_x g' \right) \quad (4.78)$$

and equation (4.77) can be expressed as

$$\dot{\Psi} = -\frac{\partial}{\partial x} \left(\frac{\theta \sigma h^3}{3} \partial_x^3 h \right) \quad (4.79)$$

4.2.2 Coupled gradient flow

Equations (4.78) and (4.79) are in a coupled gradient flow form in the sense that the gradient dynamics depends on both \dot{h} and $\dot{\Psi}$. This can be seen by first finding expressions for $\frac{\delta F}{\delta h}$ and $\frac{\delta F}{\delta \Psi}$, which are derived from the reduced free energy

$$F = \int_{x_-}^{x_+} \left(\frac{\sigma}{2} |\nabla h|^2 + hg \right) dx \quad (4.80)$$

where we have used $\int_0^h g(\theta(x, z, t)) dz \approx hg(\theta(x, t))$. We have also assumed that $\partial_x h \ll 1$ and Taylor expanded the free energy given in the dimensionless version of equation (4.16). We can write \dot{F} in the form

$$\dot{F} = \int_{\omega} \left(\frac{\delta F}{\delta h} \dot{h} + \frac{\delta F}{\delta \Psi} \dot{\Psi} \right) dx \quad (4.81)$$

which in our formulation, now expressed in three dimensions, requires that

$$\frac{\delta F}{\delta h} = -\sigma \Delta h + g - g' \frac{\Psi}{h} \quad (4.82)$$

where we have used $\theta = \frac{\Psi}{h}$. Similarly, we require

$$\frac{\delta F}{\delta \Psi} = g' \quad (4.83)$$

which means that we can derive the relation

$$\sigma \nabla \Delta h = -\nabla \frac{\delta F}{\delta h} - \frac{\Psi}{h} \nabla \frac{\delta F}{\delta \Psi} \quad (4.84)$$

In three dimensions, equations (4.78) and (4.79) become

$$\dot{h} = \nabla \cdot \left(\frac{1}{3D_0 \Psi} \left((D_0 h^3 \Psi + 3(h^2 - h\Psi)) \nabla \frac{\delta F}{\delta h} + (D_0 h^2 \Psi^2) \nabla \frac{\delta F}{\delta \Psi} \right) \right) \quad (4.85)$$

and

$$\dot{\Psi} = \nabla \cdot \left(\frac{1}{3D_0 \Psi} \left((D_0 h^2 \Psi^2) \nabla \frac{\delta F}{\delta h} + (D_0 h \Psi^3) \nabla \frac{\delta F}{\delta \Psi} \right) \right) \quad (4.86)$$

By defining the *mobility matrix*

$$M(h, \Psi) = \frac{1}{3D_0 \Psi} \begin{bmatrix} D_0 h^3 \Psi + 3(h^2 - h\Psi) & D_0 h^2 \Psi^2 \\ D_0 h^2 \Psi^2 & D_0 h \Psi^3 \end{bmatrix} \quad (4.87)$$

we can formulate the thin-film equations in the corresponding gradient flow form, given by

$$\begin{bmatrix} \dot{h} \\ \dot{\Psi} \end{bmatrix} = \nabla \cdot \left(M(h, \Psi) \nabla \begin{bmatrix} \delta F / \delta h \\ \delta F / \delta \Psi \end{bmatrix} \right) \quad (4.88)$$

We can also write the free energy in terms of the mobility matrix as

$$\dot{F} = \int_{\omega} \begin{bmatrix} \delta F / \delta h \\ \delta F / \delta \Psi \end{bmatrix} \cdot \begin{bmatrix} \dot{h} \\ \dot{\Psi} \end{bmatrix} d\mathbf{x} \quad (4.89)$$

$$= - \int_{\omega} \left(\nabla \begin{bmatrix} \delta F / \delta h \\ \delta F / \delta \Psi \end{bmatrix} \right) : \left(M \nabla \begin{bmatrix} \delta F / \delta h \\ \delta F / \delta \Psi \end{bmatrix} \right) d\mathbf{x} \quad (4.90)$$

Note that the reciprocal relation $M_{ij} = M_{ji}$ holds in accordance with Onsager's variational principle. In addition, M must be positive definite so that the free energy decreases along solutions [52].

4.3 Modelling the binary mixture evolution

4.3.1 Weak form of binary mixture thin-film equation

In three dimensions, the relevant dimensionless equations for the thin-film evolution for a binary mixture are

$$\begin{bmatrix} \dot{h} \\ \dot{\Psi} \end{bmatrix} = \nabla \cdot \left(M \nabla \begin{bmatrix} \delta F / \delta h \\ \delta F / \delta \Psi \end{bmatrix} \right) \quad (4.91)$$

and

$$F(h, \Psi) = \int_{\omega(t)} \left(\frac{1}{2} |\nabla h|^2 + hg + S \right) dx \quad (4.92)$$

where we have performed the same procedure to attain a reduced free energy as in section 3.3, except the mixing energy density term g has absorbed a factor of σ_{lg}^{-1} , i.e. $g \rightarrow g\sigma_{lg}$.

We now let the support be time-dependent, and aim to construct the weak form for this free boundary problem in the absence of gravity. Let us take the Gateaux derivative of the free energy at h and Ψ in the $\phi \in H^1(\omega)$ and $\varphi \in H^1(\omega)$ directions, respectively. Using Reynolds transport theorem, $\delta F(h, \Psi)[\phi, \varphi]$ becomes

$$\begin{aligned} \int_{\omega(t)} \left(\frac{\delta F}{\delta h} \phi + \frac{\delta F}{\delta \Psi} \varphi \right) dx &= \int_{\omega(t)} \left(\nabla h \cdot \nabla \phi + g\phi - \frac{\delta F}{\delta \Psi} \frac{\Psi}{h} \phi + \frac{\delta F}{\delta \Psi} \varphi \right) dx \\ &\quad + \int_{\partial\omega(t)} |\nabla h|^{-1} \left(\frac{1}{2} |\nabla h|^2 + S \right) \phi ds \end{aligned} \quad (4.93)$$

where we have used $\mathbf{v} \cdot \mathbf{n} = |\nabla h|^{-1} \dot{h}$ on the boundary. Let us use the notation $p_h = \frac{\delta F}{\delta h}$ for increased readability. Substituting $\frac{\delta F}{\delta \Psi} = g'$ and performing a semi-implicit time-discretization via $h \rightarrow h + \tau \dot{h}$, equation (4.93) becomes

$$\begin{aligned} \int_{\omega(t)} p_h \phi dx &= \int_{\omega(t)} \left(\nabla h \cdot \nabla \phi + \tau \nabla \dot{h} \cdot \nabla \phi + g\phi - g' \frac{\Psi}{h} \phi \right) dx \\ &\quad + \int_{\partial\omega(t)} |\nabla h|^{-1} \left(\frac{1}{2} |\nabla h|^2 + S \right) \phi ds \end{aligned} \quad (4.94)$$

We next multiply both sides of the vector equation (4.91) by a test function $\vartheta \in H^1(\omega)$ and integrate over the support, yielding

$$\int_{\omega(t)} \left(\begin{bmatrix} \dot{h} \\ \dot{\Psi} \end{bmatrix} \vartheta + M \nabla \begin{bmatrix} \delta F / \delta h \\ \delta F / \delta \Psi \end{bmatrix} \cdot \nabla \vartheta \right) dx = 0 \quad (4.95)$$

where we have also performed an integration by parts.

Let us now assume that the support $\omega(t)$ is one dimensional. Expanding M for a one dimensional support, equation (4.95) becomes

$$\begin{aligned} \int_{\omega(t)} \left(\dot{h} \vartheta + \partial_x p_h \partial_x \vartheta \left(\frac{1}{3} h^3 + \frac{1}{D_0 \Psi} (h^2 - h\Psi) \right) \right. \\ \left. + \partial_x g' \partial_x \vartheta \left(\frac{1}{3} h^2 \Psi \right) \right) dx = 0 \end{aligned} \quad (4.96)$$

and

$$\int_{\omega(t)} \left(\dot{\Psi} \vartheta + \partial_x p_h \partial_x \vartheta \left(\frac{1}{3} h^2 \Psi \right) + \partial_x g' \partial_x \vartheta \left(\frac{1}{3} h \Psi^2 \right) \right) dx = 0 \quad (4.97)$$

At this point, we are faced with solving the three equations (4.94), (4.96), and (4.97) for the three unknowns \dot{h} , $\dot{\Psi}$, and p_h . We shall approach this problem via finite element methods.

4.3.2 Finite element analysis of binary mixture model

We shall perform a finite element analysis to prepare the problem for numerical evaluation. The variables are decomposed in terms of basis functions $\phi \in H^1(\omega)$ as

$$\begin{aligned}\dot{h} &= \sum_{i=1}^N u_i \phi_i & h &= \sum_{i=1}^N h_i \phi_i & \dot{H} &= \sum_{i=1}^N U_i \phi_i & \Psi &= \sum_{i=1}^N \Psi_i \phi_i \\ p_h &= \sum_{i=1}^N p_{hi} \phi_i & \phi &= \sum_{i=1}^N v_i \phi_i & \dot{\Psi} &= \sum_{i=1}^N \varpi_i \phi_i\end{aligned}$$

In addition, let us define the matrices and vectors with entries

$$\begin{aligned}S_{ij} &= \int_{\omega(t)} \partial_x \phi_i \partial_x \phi_j dx & Z_{ij} &= \int_{\omega(t)} \phi_i \phi_j dx \\ \tilde{b}_j &= \int_{\partial\omega(t)} |\nabla h|^{-1} \left(\frac{1}{2} |\nabla h|^2 + S \right) \phi_j ds & \tilde{l}_j &= \int_{\omega(t)} \left(g - g' \frac{\Psi}{h} \right) \phi_j dx \\ \tilde{S}_{ij}^1 &= \int_{\omega(t)} \partial_x \phi_i \partial_x \phi_j M_{11} dx & \tilde{s}_j^1 &= \int_{\omega(t)} \partial_x g' \partial_x \phi_j M_{12} dx \\ \tilde{S}_{ij}^2 &= \int_{\omega(t)} \partial_x \phi_i \partial_x \phi_j M_{21} dx & \tilde{s}_j^2 &= \int_{\omega(t)} \partial_x g' \partial_x \phi_j M_{22} dx\end{aligned}$$

Upon expanding with the respective finite element decompositions, equation (4.94) becomes

$$Z_{ij} p_{hi} - \tau S_{ij} u_i = S_{ij} h_i + \tilde{l}_j + \tilde{b}_j \quad (4.98)$$

while equations (4.96) and (4.97) become

$$Z_{ij} u_i + \tilde{S}_{ij}^1 p_{hi} + \tilde{s}_j^1 = 0 \quad (4.99)$$

and

$$Z_{ij} \varpi_i + \tilde{S}_{ij}^2 p_{hi} + \tilde{s}_j^2 = 0 \quad (4.100)$$

respectively, where we have used Einstein notation.

Hereafter in this section, the notation $\mathbf{a} = (a_1, a_2, \dots, a_N)^T$ will be implied for vectors. Let us define the matrices

$$A = \begin{bmatrix} Z & 0 & \tilde{S}^2 \\ 0 & Z & \tilde{S}^1 \\ 0 & -\tau S & Z \end{bmatrix} \quad \boldsymbol{\chi} = \begin{bmatrix} \boldsymbol{\varpi} \\ \mathbf{u} \\ \mathbf{p}_h \end{bmatrix} \quad \mathbf{b} = \begin{bmatrix} -\tilde{s}^2 \\ -\tilde{s}^1 \\ Sh + \tilde{l} + \tilde{b} \end{bmatrix} \quad (4.101)$$

Finding the solution $(\boldsymbol{\varpi}, \mathbf{u}, \mathbf{p}_h)$ therefore amounts to solving $A\boldsymbol{\chi} = \mathbf{b}$ with respect to $\boldsymbol{\chi}$. One could incorporate this numerically alongside an update rule for the boundary via an ALE transformation. This will not be implemented in this text.

5

Discussion and conclusion

5.1 Final remarks

Asymmetric binary mixture bulk system

In section 4.1.1, a fully asymmetric bulk system was derived for binary mixtures. This was done by considering both phases as coexisting with a free interface between them and imposing relationships between the network, solvent, and interphase pressures. This is in fact equivalent to imposing conditions relating the free energy density of mixing g and chemical potential g' with the effective hydrostatic pressure. Therefore, we have shown that for a binary mixture composed of a Newtonian and inviscid fluid, we can always express the resulting bulk equations of motion in terms of an explicit asymmetric momentum-conservation system only by imposing conditions on the free energy density of mixing.

This is an interesting result, and implies that expressing the equations of motion in asymmetric form only depends on the free energy functional. It is expected that adding additional terms to the free energy functional such as ones which account for long-range van der Waals liquid-solid interactions [52] or gravity would allow one to impose similar conditions to attain an explicitly asymmetric system.

Viscous dissipation functional term

For the binary mixture bulk equations in section 4.1, replacing the no-slip condition (4.8) at the liquid-gas interface with a general slip condition, i.e.

$$\mathbf{v}_1 \cdot \mathbf{n}|_{z=h(x,t)} = \mathbf{v}_2 \cdot \mathbf{n}|_{z=h(x,t)} = \mathbf{v} \cdot \mathbf{n}|_{z=h(x,t)}$$

results in the tangential velocities corresponding to both phases at the free surface becoming independent, yet yields the same system of equations. This is a direct consequence of our choice of the viscous term of the dissipation functional, which only depends on the viscous stress tensor of the Newtonian fluid, and has no

dependence on the properties of the inviscid fluid. If we replace the inviscid fluid with another Newtonian fluid, the specific slip condition would become relevant, affecting the appearance of an extra term in equation (4.26). This is consistent with reality; inviscid fluids do not stick to interfaces to prevent slip [27].

In [52], Onsager's variational principle is applied to a thin-film binary mixture with an identical Rayleighian to the one used in section 4.2 except for the viscous term of the dissipation functional, for which they use the mean velocity \mathbf{v} instead of the velocity of the Newtonian fluid \mathbf{v}_2 . The thin-film equations derived in [52] and those derived in section 4.2.1 differ in the sense that the structural form of the conservation laws (4.78) and (4.79) are swapped.

The previous two remarks imply that the thin-film binary mixture evolution equations and their gradient structure are mainly dependent on the structure of the viscous part of the dissipation functional.

5.2 Conclusion and future work

In this work, we have applied Onsager's variational principle to derive the equations of motion for both a monofluid and binary mixture. In the binary mixture, we have established the connection between the resulting thin-film evolution equations and gradient flows, thereby ensuring thermodynamic consistency and stability of solutions for a general class of binary mixtures composed of Newtonian and inviscid fluid components. In addition, the bulk equations for the binary mixture were derived in a fully asymmetric form only by imposing constraints on the free energy density of mixing. We have also explored an ALE-based algorithm to numerically model the evolution of a monofluid droplet and laid the foundations for a similar approach in a binary mixture droplet.

It is expected that future progress in this field would involve further development of the analysis introduced in section 4.3 to numerically simulate a binary mixture droplet with a time-dependent support as a free boundary problem. This could yield interesting and unexpected dynamics which should be investigated further.

Understanding for which cases an asymmetric system for binary mixtures can be derived is a topic which requires further study. We have shown that this is possible when incorporating a free energy functional with mixing dependence, but have not yet verified this for other terms which appear in the free energy or dissipation functionals. Similar approaches could be used for van der Waals or gravitational potentials.

Appendix A

Mathematical Methods

Definition A.0.1 (Bounded bilinear form) *A bilinear form $a : V \times V \rightarrow \mathbb{R}$ is bounded if there exists some $0 < C \in \mathbb{R}$ such that*

$$|a(\phi, \theta)| \leq C\|\phi\|_V\|\theta\|_V \quad \forall \phi, \theta \in V$$

Definition A.0.2 (Coercive bilinear form) *A bilinear form $a : V \times V \rightarrow \mathbb{R}$ is coercive on $Q \subset V$ if there exists some $0 < \alpha \in \mathbb{R}$ such that*

$$a(\phi, \phi) \geq \alpha\|\phi\|_V^2 \quad \forall \phi \in Q$$

Definition A.0.3 (Gateaux derivative) *The Gateaux derivative of an arbitrary functional $J(f(x)) = \int j(x, f(x), \nabla f(x))dx$ in an arbitrary direction $\phi(x) \in C^1$ is*

$$\begin{aligned} \delta J(f)[\phi] &= \int dx \frac{\delta J}{\delta f} \phi \equiv \left(\frac{d}{d\epsilon} \int j(x, f + \epsilon\phi, \nabla f + \epsilon\nabla\phi)dx \right) \Big|_{\epsilon=0} \\ &= \int dx \left(\frac{\partial j}{\partial(\nabla f)} \cdot \nabla\phi + \frac{\partial j}{\partial f} \phi \right) \end{aligned}$$

Theorem A.0.1 (Reynold's Transport Theorem) *For a time-dependent function $\mathbf{g} = \mathbf{g}(\mathbf{x}, t)$ and domain $\Omega(t)$ with volume and surface area element dV and dA ,*

$$\frac{d}{dt} \int_{\Omega(t)} \mathbf{g} dV = \int_{\Omega(t)} \frac{\partial \mathbf{g}}{\partial t} dV + \int_{\Omega(t)} (\mathbf{v} \cdot \mathbf{n}) \mathbf{g} dA \quad (\text{A.1})$$

where $\mathbf{v} \cdot \mathbf{n}$ is the velocity of the area element in the outward-pointing normal direction to the volume. If dV is a material element, then \mathbf{v} is the flow velocity [4].

Appendix B

Simple application of Onsager's variational principle

Consider a viscous fluid rising in a capillary with cross-sectional area S filled with particles as shown in figure B.1. The height of the fluid at a given time is given by $h(t)$. The capillary volume will consist of either particles, fluid, or air. Assume that the particles are spherical with radius a and number density n . The fraction of volume ϕ taken up by the particles is

$$\phi = \left(\frac{4}{3} \pi a^3 \right) n \quad (\text{B.1})$$

The remaining fraction of volume taken up by fluid or air is $1 - \phi$.

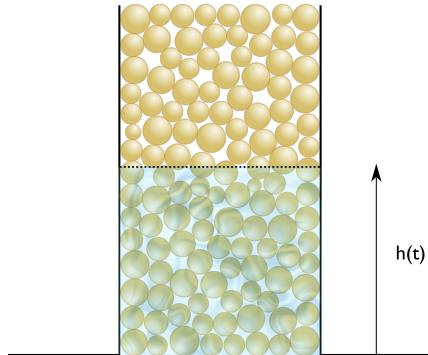


Figure B.1: Illustration of a fluid rising with height $h(t)$ in a capillary filled with particles.

The potential energy of the system arises partially due to the surface tension, inducing a surface energy U_γ . The surface energy arises due to a phenomenon called wetting, which occurs when a liquid droplet is placed on a solid substrate [45]. The surface energy of a liquid droplet with spreading coefficient γ_S covering

a solid surface area of A is

$$U_\gamma = -A\gamma_S \quad (\text{B.2})$$

If γ_S is positive, the surface energy will decrease as A increases, and so the liquid drop will spread over the entire solid surface. If γ_S is negative, the surface energy will increase as A increases, and so the liquid drop will only partially spread over the solid surface, eventually taking an equilibrium configuration.

In our example, the surface energy depends on the surface area of the particles that are covered by the fluid. To acquire the total surface area, we multiply the surface area of a single particle $4\pi a^2$ by the number of submerged particles, nhS . Therefore, the surface energy at a given time is

$$\begin{aligned} U_\gamma &= -(4\pi a^2 nhS)\gamma_S \\ &= -\frac{3}{a}\phi\gamma_S hS \end{aligned} \quad (\text{B.3})$$

There will also be energy stored in the gravitational potential energy U_g of the fluid. We will ignore the gravitational energy of the particles themselves, as this stationary energy will vanish when we take a time derivative later. A single infinitesimal volume of the capillary will have gravitational potential energy $dU_g = \rho g h dV$. We shall integrate over the volume of the submerged section of the capillary while excluding the volume of the particles to find the gravitational potential energy of the fluid at a given time. The gravitational potential energy of the fluid is given by,

$$\begin{aligned} U_g &= \int dx \int dy \int_0^{h(t)} dz \rho g z \\ &= \frac{1}{2}(1-\phi)\rho g h^2 S \end{aligned} \quad (\text{B.4})$$

Therefore, we attain \dot{U} by

$$\begin{aligned} \dot{U} &= \dot{U}_g + \dot{U}_\gamma \\ &= \left(-\frac{3}{a}\phi\gamma_S + (1-\phi)\rho g h \right) \dot{h} S \end{aligned} \quad (\text{B.5})$$

Our next goal is to compute the heat dissipation of the system per unit time D . According to Stokes's law, fluid travelling at a small velocity v relative to a particle experiences a drag force of the form

$$F_f = -\xi V v \quad (\text{B.6})$$

where V is the typical volume of the system and ξ is the friction coefficient per unit volume [45]. If F_f is the friction force acting on the fluid, the work done on

the fluid per unit time by a single particle is $\dot{W}_f = F_f \cdot v = -\xi V v^2$. However, we are interested in the overall heat dissipation of the system, and since all heat dissipation arises from friction,

$$D = |\dot{W}_f| = \xi V v^2 \quad (\text{B.7})$$

where $v = \dot{h}$ is the fluid velocity up the capillary. The volume in question is the submerged section of the capillary, so $V = hS$. Thus, the heat dissipated per unit time is

$$D = \xi(hS)\dot{h}^2 \quad (\text{B.8})$$

From which the energy dissipation function follows trivially as $\Phi = \frac{1}{2}D$.

The Rayleighian can now be written as

$$R(\dot{h}, h) = \frac{1}{2}\xi\dot{h}^2 hS + \left(-\frac{3}{a}\phi\gamma_S + (1-\phi)\rho gh\right)\dot{h}S \quad (\text{B.9})$$

We apply the condition $\nabla_{\dot{h}} R = 0$ to acquire the equation of motion for our system, given by

$$0 = \xi h\dot{h} - \frac{3}{a}\phi\gamma_S + (1-\phi)\rho gh \quad (\text{B.10})$$

which completes the approach.

Appendix C

Continuum mechanics

C.1 Stress

The *stress tensor* σ_{ij} is defined as the tensor which characterizes the infinitesimal force

$$dF_i = \sigma_{ij} n_j dS \quad (\text{C.1})$$

on some infinitesimally small surface dS . We can interpret σ_{ij} as the i th component of the force per unit area acting on the plane normal to j [45]. For a body at static equilibrium, the stress tensor is symmetric [15], i.e.

$$\sigma_{ij} = \sigma_{ji} \quad (\text{C.2})$$

A body experiencing equal pressure p on all sides is under what is known as hydrostatic compression. The stress tensor under only hydrostatic compression is

$$\sigma_{ij} = -p\delta_{ij} \quad (\text{C.3})$$

which is diagonal [15].

C.2 Deformation in highly viscous fluids

Suppose that at reference time $t = t_0$, a set of material points P are located in a reference domain $\Omega(t_0)$ at positions $\mathbf{r} = \mathbf{X} \in \Omega(t_0)$. At later times, the domain will have morphed into $\Omega(t)$ with material points P at positions $\mathbf{r} = \mathbf{x}(\mathbf{X}, t) \in \Omega(t)$. We can measure the deformation using the *deformation vector*, defined as

$$\mathbf{u}(\mathbf{X}, t) = \mathbf{x}(\mathbf{X}, t) - \mathbf{X} \quad (\text{C.4})$$

In elastic media, resistance forces arise from the deformation $\mathbf{u}(\mathbf{x}, t)$, while in viscous fluids they arise from the flow velocity $\mathbf{v}(\mathbf{x}, t)$ [27]. Therefore, discussions

on the deformation of elastic materials have an analogous application in the flow of viscous fluids.

For *Newtonian* fluids, the *strain rate* tensor is approximately

$$\dot{\epsilon}_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial X_j} + \frac{\partial v_j}{\partial X_i} \right) \quad (\text{C.5})$$

The general form of *Hooke's law* for highly viscous fluids is given by

$$\sigma_{ij} = A_{ijk\lambda} \dot{\epsilon}_{k\lambda} \quad (\text{C.6})$$

which postulates a linear relationship between the viscous stress and strain rate of a material. $A_{ijk\lambda}$ is the *viscosity tensor*, which has 21 independent parameters for a general anisotropic fluid [15]. Isotropic fluids have a viscosity tensor with only two independent parameters. Hooke's law can then be expressed in terms of the Lamé constants λ and μ [15] as

$$\sigma_{ij} = \lambda \delta_{ij} \dot{\epsilon}_{kk} + 2\mu \dot{\epsilon}_{ij} \quad (\text{C.7})$$

C.3 Stoke's flow

If we assume that a fluid flow has low Reynolds number $R_e \ll 1$, i.e. inertial forces are small compared to viscous forces, the Navier-Stokes equations reduce to the Stokes equation of motion, given by

$$\frac{\partial \sigma_{ij}}{\partial x_j} + f_{Vi} = 0 \quad (\text{C.8})$$

where f_{Vi} is a volume force term per unit volume, such as some gravitational force density [45].

Consider an incompressible, isotropic, Newtonian fluid that is negligibly affected by volume forces. In Einstein notation, the stress tensor including hydrostatic compression is given by

$$\sigma_{ij} = \lambda \delta_{ij} \dot{\epsilon}_{kk} + 2\mu \dot{\epsilon}_{ij} - p \delta_{ij} \quad (\text{C.9})$$

where λ and μ are the Lamé constants. This fluid obeys

$$\frac{\partial \sigma_{ij}}{\partial x_j} = \frac{\partial}{\partial x_j} (\lambda \delta_{ij} \dot{\epsilon}_{kk} + 2\mu \dot{\epsilon}_{ij} - p \delta_{ij}) = 0 \quad (\text{C.10})$$

Substituting for the strain rate tensor gives

$$\lambda \nabla (\nabla \cdot \mathbf{v}) + \mu (\nabla^2 \mathbf{v} + \nabla (\nabla \cdot \mathbf{v})) - \nabla p = 0 \quad (\text{C.11})$$

Applying the incompressibility constraint $\nabla \cdot \mathbf{v} = 0$ yields the Stoke's flow equation, given by

$$\mu \nabla^2 \mathbf{v} - \nabla p = 0 \quad (\text{C.12})$$

where μ is the dynamic viscosity coefficient in units of Pa · s.

C.4 Dissipation relations

A collection of particles will have a surface S that depends on the geometry of the configuration. The velocity of the surface will depend on this geometry as well as the position and velocity of each particle. The velocity of the surface at a point \mathbf{r} can be expressed as

$$\mathbf{v}_S(\mathbf{r}, x, \dot{x}) = G(\mathbf{r}, x) \cdot \dot{\mathbf{x}} \quad (\text{C.13})$$

where G is a tensor that depends on the particle geometry.

The work done by a fluid on a collection of particles whose surface travels at velocity \mathbf{v}_S through the fluid for time Δt is

$$W_f = - \int dF_i v_{Si} \Delta t = - \int f_i v_{Si} dS \Delta t \quad (\text{C.14})$$

in Einstein notation. The fluid only does work through surface forces, so volume forces can be ignored. Since F_i can only act on the surface, it must be a stress force. Therefore, the work becomes

$$W_f = - \int (\sigma_{ij} n_j G_{ik} dS) \dot{x}_k \Delta t \quad (\text{C.15})$$

We know that the work done by friction on each particle must be in the form $W_f = - \int F_{fi} \dot{x}_k \Delta t$. By comparing to equation (C.15), we can immediately identify the form of the friction force as

$$F_{fi} = \int_S \sigma_{jk} n_k G_{ji} dS \quad (\text{C.16})$$

In addition, we can write the friction force acting on the moving surface in Einstein notation as $F_{fi} = -\Gamma v_{Si} = -\Gamma G_{ij} \dot{x}_j = -\zeta_{ij} \dot{x}_j$, where ζ_{ij} is the friction coefficient.

Suppose two different particle configurations are prepared: one in which the particles have velocity $\dot{x}_i^{(A)}$ corresponding to friction force $F_{fi}^{(A)}$, and another in which the particles have velocity $\dot{x}_i^{(B)}$ corresponding to friction force $F_{fi}^{(B)}$. Let us compute the quantity

$$\mathcal{Q} = -F_{fi}^{(A)} \dot{x}_i^{(B)} = \zeta_{ij}^{(A)} \dot{x}_j^{(A)} \dot{x}_i^{(B)} \quad (\text{C.17})$$

which, for $A = B$, is the work done by the particles onto the fluid. By plugging in equation (C.16), this quantity becomes

$$\mathcal{Q} = - \int_S \sigma_{jk}^{(A)} n_k G_{ji} dS \dot{x}_i^{(B)} = - \int_S \sigma_{jk}^{(A)} v_j^{(B)} n_k dS \quad (\text{C.18})$$

where we have used $v_j^{(B)} = G_{ji} \dot{x}_i^{(B)}$ at the particle surface. By applying the divergence theorem such that n_k points from the particle surface to the fluid, we attain

$$\mathcal{Q} = \int_V \frac{\partial(\sigma_{jk}^{(A)} v_j^{(B)})}{\partial x_k} dV = \int_V \left(\frac{\partial \sigma_{jk}^{(A)}}{\partial x_k} v_j^{(B)} + \frac{\partial v_j^{(B)}}{\partial x_k} \sigma_{jk}^{(A)} \right) dV \quad (\text{C.19})$$

We assume that the fluid is incompressible, isotropic, Newtonian, and negligibly affected by volume forces. The stress tensor is written as

$$\sigma_{ij} = \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) - p \delta_{ij} \quad (\text{C.20})$$

where η is the viscosity coefficient. The $\dot{\epsilon}_{kk}$ term of the stress tensor is zero due to fluid incompressibility. Equation (C.8) for a Newtonian fluid can be invoked and the symmetry of the stress tensor can be exploited to write \mathcal{Q} as

$$\mathcal{Q} = \frac{\eta}{2} \int_V \left(\frac{\partial v_j^{(B)}}{\partial x_k} + \frac{\partial v_k^{(B)}}{\partial x_j} \right) \left(\frac{\partial v_i^{(A)}}{\partial x_j} + \frac{\partial v_j^{(A)}}{\partial x_i} \right) dV \quad (\text{C.21})$$

The term in the stress tensor arising from hydrostatic compression, $p \delta_{ij}$, vanished after applying the incompressibility constraint of the fluid.

Note that equation (C.21) is not affected by exchanging A and B . Therefore, $\zeta_{ij}^{(A)} \dot{x}_j^{(A)} \dot{x}_i^{(B)} = \zeta_{ij}^{(B)} \dot{x}_j^{(B)} \dot{x}_i^{(A)}$, which implies that

$$\zeta_{ij} = \zeta_{ji} \quad (\text{C.22})$$

This proves the reciprocal relation. Plugging in $\dot{x}_i^{(A)} = \dot{x}_i^{(B)} = \dot{x}_i$ to equation (C.17) yields

$$\mathcal{Q} = \frac{\eta}{2} \int_V \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)^2 dV \quad (\text{C.23})$$

which is always non-negative except for $\mathbf{v} = \mathbf{0}$. Consequently, the friction matrix ζ is positive-definite, i.e.

$$\sum_{i,j} \zeta_{ij} \dot{x}_i \dot{x}_j > 0 \quad \forall \dot{x}_i \neq 0 \quad (\text{C.24})$$

The dissipation functional for an incompressible, isotropic Newtonian fluid is then

$$\Phi = \int_V \frac{\eta}{4} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)^2 dV \quad (\text{C.25})$$

C.5 Computer code

```
import numpy as np
import scipy as sp
from scipy.linalg import solve
import matplotlib.pyplot as plt
from scipy import integrate

from matplotlib.ticker import FormatStrFormatter

##### With gravity: f = -g1*h*x + g2*h**2

#####
# build matrices for the finite element method
def build_FE_matrices(x, h, dt):

    npoint = x.shape[0]
    nelement = npoint - 1

    nd = np.zeros([nelement,2]) # element id storage: e.g. nd[31,0] = id of
    left node of 32nd mesh element.
    nd[:,0] = np.arange(0,npoint-1).astype(int) # id of left point of
    elements (array of integers including 1 to npoint-1).
    nd[:,1] = np.arange(1,npoint).astype(int) # id of right points of
    elements.
    # Note: np.arange() includes startpoint; does not include endpoint.
    nd = nd.astype(int)

    #mobility = np.zeros([nelement,1])
    jacobian = x[nd[:,1],0] - x[nd[:,0],0]
    print("x[nd[:,1],0]: "+str(x[nd[:,1],0]))
    print("x[nd[:,0],0]: "+str(x[nd[:,0],0]))
    print(jacobian)

    # Local matrices
    M_local = np.array([[1/3, 1/6],[1/6,1/3]]) # Local reference mass matrix
    in coordinates x=[0,1]
    S_local = np.array([[1, -1],[-1,1]])
    C_local = np.array([[-1/2, 1/2],[-1/2,1/2]])

    # Global matrices
    M_global = np.zeros([npoint,npoint])
    S_global = np.zeros([npoint,npoint])
```

```

C_global = np.zeros([npoint,npoint])
Sw_global = np.zeros([npoint,npoint])

# Assembly
for i in range(nelement):
    #Add to globals
    M_local_trans = M_local*jacobian[i]
    M_global[i:i+2,i:i+2] += M_local_trans

    S_local_trans = S_local/jacobian[i]
    S_global[i:i+2,i:i+2] += S_local_trans

    C_local_trans = C_local
    C_global[i:i+2,i:i+2] += C_local_trans

    hihj = np.einsum('i,j',h[i:i+2,0],h[i:i+2,0]) # Outer product <h,h>
--> generates (2 x 2) matrix
    mobility = np.einsum('ij,ij',M_local,hihj) # Matrix double inner
product
    Sw_global[i:i+2,i:i+2] += mobility*S_local

A = np.block([
    [M_global, Sw_global],
    [-dt*S_global, M_global]
])
return A, S_global, C_global, M_global


def weak_derivative(C,M,h):
    b = np.dot(C,h)
    g = solve(M,b)
    return g

def kinematic_construction(x,g,u):
    xi = (x-x[0,0])/(x[-1,0]-x[0,0])
    x_dot_plus = -(u[-1,0]/g[-1,0])
    x_dot_minus = -(u[0,0]/g[0,0])
    psi_dot = (x_dot_plus - x_dot_minus)*xi + x_dot_minus

```

```
    return psi_dot
#####
##### set model & computational parameters #####
L = 1.0 # initial domain size (0,L)
T = 10.0 # final time
SL = 1.0 # negative spreading coefficient at x=x-
SR = 1.0 # negative spreading coefficient at x=x+
g1 = 0.0 # tangential gravity
g2 = 0.0 # normal gravity
nt = 500 # number of time steps
npoint = 101 # number of vertices      # Needs to be odd for Simpson's rule
dt = T/nt # Time step size

num_red_plots = 5
#####

nelement = npoint-1 # number of elements
zero = np.zeros([npoint,1])

#####
# Initial data
x_0 = np.linspace(0, L, num=npoint).reshape((npoint,1)) # Initial support
distribution. This is an array of evenly spaced points ("num" of them) from
0 to L (including endpoints).
x = x_0

h_0 = L/2-abs(L/2-x) # Initial height
h_0 = np.where(h_0 < 1.0, h_0,1.0)
h = h_0

t = 0 # Initial time

#####
## Integration for volume conservation test
h_list = h.reshape(101).tolist()
x_list = x.reshape(101).tolist()
```

```
Masses = []
Masses.append(integrate.simps(h_list, x_list))
#####

##### Droplet figures preparation
fig = plt.figure()
ax = fig.add_subplot(111)

plt.ylabel("Height", fontsize=12)
plt.xlabel("Position", fontsize=12)

plt.plot(x_0,h_0,color='black',linestyle=':', linewidth=1, label='t = 0') #
Initial droplet
#####

num_inter_plots = 0

for i in range(nt):

    # Intermediary plotting
    if (i % int(nt/num_red_plots) == 0) and (i != 0):
        #if (i % 50 == 0) and (i != 0) and (num_inter_plots <= num_red_plots):
            plt.plot(x,h,color='red',linestyle='--', linewidth=0.5, label='t =
%.1e' % (i*dt)) # Intermediary droplet
            num_inter_plots += 1

    A, S, C, M = build_FE_matrices(x, h, dt)
    g = weak_derivative(C,M,h)

    b_tilde = np.zeros([npoint,1])
    b_tilde[0,0] = (SL + (1./2.)*np.abs(g[0,0]**2.0))/np.abs(g[0,0])
    b_tilde[-1,0] = (SR + (1./2.)*np.abs(g[-1,0]**2.0))/np.abs(g[-1,0])

    print("b_tilde: "+str(b_tilde))

    gravity = 2*g2*h - g1*x

    rhs = np.block([
        [zero],
        [np.dot(S,h) + np.dot(M,gravity) + b_tilde]]
```

```
] )

u = solve(A,rhs)[:npoint]

print("g: "+str(g))
print("u: "+str(u))
print("u[0]: "+str(u[0]))
print("u[-1]: "+str(u[-1]))

psi_dot = kinematic_construction(x,g,u)

print("psi_dot: "+str(psi_dot))

U = u + g*psi_dot

print("U: "+str(U))

x = x + dt*psi_dot
h = h + dt*U

print("x: "+str(x))
print("h: "+str(h))

## Mass conservation test
Masses.append(integrate.simps(h.reshape(101).tolist(),
x.reshape(101).tolist()))
##

### Stationary solution (g1=g2=0, SL=SR=1, L=1)
# Calculating
a = np.sqrt(np.sqrt(18)/16)
x_stat = np.linspace(L/2 - a, L/2 + a, num=npoint).reshape((npoint,1))
eta = (x_stat - 1./2.)/a
h_stat = a*(1 - eta**2.)/np.sqrt(2)

# Plotting
plt.scatter(x_stat,h_stat, facecolors='none', edgecolors='r', s=4.0,
label='Stationary solution')
###
```

```
mass_fraction_remaining = Masses[-1]/Masses[0]
print("Total mass fraction remaining: {}".format(mass_fraction_remaining))
print("Total mass fraction lost: {}".format(1.0 - mass_fraction_remaining))
print("Masses: {}".format(Masses))

plt.plot(x,h,color='blue',linestyle='-',linewidth=1, label='t =
{}'.format(T)) # Final droplet

plt.axhline(0,color='black',linestyle='-',linewidth=0.5) # x-axis
plt.axvline(0,color='black',linestyle='-',linewidth=0.5) # y-axis

plt.legend(loc='upper right',fontsize = 'x-small')

plt.show()

##### Mass loss
time_steps = np.linspace(0,T,num=(nt+1)).tolist()
norm_Masses = [n / Masses[0] for n in Masses]
norm_Masses_scientific = [("%e" % n) for n in norm_Masses]
mass_error = [(1 - n) for n in norm_Masses]
mass_error_scientific = [("{:.4e}".format(n)) for n in mass_error]
print("norm_Masses: {}".format(norm_Masses))
print("norm_Masses_scientific: {}".format(norm_Masses_scientific))

fig, ax = plt.subplots()

ax.yaxis.set_major_formatter(FormatStrFormatter('%.1e'))
ax.set_yticklabels([]) # Removes y-axis ticks
#ax.set_xticklabels([]) # Removes x-axis ticks

ax.set_xlim([-0.1,5.0])
ax.set_ylim([norm_Masses[-1] - 0.000004,norm_Masses[0] + 0.000004])
plt.ylabel("Volume", fontsize=12)
plt.xlabel("Time", fontsize=12)
plt.plot(time_steps,norm_Masses,color='black',linestyle='-',linewidth=1.0) # Mass loss

plt.axhline(norm_Masses[0],color='red',linestyle='--',
            linewidth=2.0,label='Initial volume') # maximum mass
plt.axhline(norm_Masses[-1],color='red',linestyle='--',
            linewidth=2.0,label='Final volume') # minimum mass

plt.legend(loc='center right',fontsize = 'x-large')
```

mass_loss.py

file:///mass_loss_4.html

```
plt.show()  
#####
```

Bibliography

1. J. T. A. C.E., *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **10**, 330–333 (1855).
2. H. v. Helmholtz, *Wiss. Abh* **1**, 223–230 (1868).
3. O. Reynolds, *Philosophical Transactions of the Royal Society of London* **177**, 157–234 (1886).
4. O. Reynolds, *Papers on mechanical and physical subjects* (Cambridge University Press, 1903).
5. L. Onsager, *Phys. Rev.* **37**, 405–426 (4 1931).
6. L. Onsager, *Phys. Rev.* **38**, 2265–2279 (12 1931).
7. H. K. Moffatt, *Journal of Fluid Mechanics* **18**, 1–18 (1964).
8. C. Huh, L. Scriven, *Journal of Colloid and Interface Science* **35**, 85–101, ISSN: 0021-9797 (1971).
9. F. Brezzi, en, *ESAIM: Mathematical Modelling and Numerical Analysis - Modélisation Mathématique et Analyse Numérique* **8**, 129–151 (1974).
10. P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827–863 (3 1985).
11. D. Dimitrov, D. Zhflev, R. Jain, *Journal of Theoretical Biology* **113**, 353–377, ISSN: 0022-5193 (1985).
12. A. Sharma, E. Ruckenstein, *Journal of Colloid and Interface Science* **106**, 12–27, ISSN: 0021-9797 (1985).
13. M. Dembo, F. Harlow, *Biophysical Journal* **50**, 109–121 (1986).
14. D. Gallez, W. Coakley, *Progress in Biophysics and Molecular Biology* **48**, 155–199, ISSN: 0079-6107 (1986).
15. E. Lifshitz, A. Kosevich, L. Pitaevskii, in *Theory of Elasticity (Third Edition)*, ed. by E. LIFSHITZ, A. KOSEVICH, L. PITAEVSKII (Butterworth-Heinemann, Oxford, Third Edition, 1986), pp. 1–37, ISBN: 978-0-08-057069-3, DOI: <https://doi.org/10.1016/B978-0-08-057069-3.50008-5>, (<http://www.sciencedirect.com/science/article/pii/B9780080570693500085>).
16. A. Sharma, E. Ruckenstein, *Journal of Colloid and Interface Science* **113**, 456–479, ISSN: 0021-9797 (1986).
17. S. Boatto, L. P. Kadanoff, P. Olla, *Phys. Rev. E* **48**, 4423–4431 (6 1993).
18. R. L. Fusaro, “Lubrication of Space Systems”, tech. rep. (Lewis Research Center, 1994).

19. J. B. Grotberg, *Annual Review of Fluid Mechanics* **26**, 529–571 (1994).
20. W. Alt, A. Deutsch, G. Dunn, *Dynamics of Cell and Tissue Motion* (Birkhauser, 1997), ISBN: 9783764357818, (<https://books.google.co.uk/books?id=4PMZaAtJ7ZcC>).
21. S. D. Howison, J. A. Moriarty, J. R. Ockendon, E. L. Terrill, S. K. Wilson, *Journal of Engineering Mathematics* **32**, 377–394, ISSN: 1573-2703 (1997).
22. A. Oron, S. H. Davis, S. G. Bankoff, *Rev. Mod. Phys.* **69**, 931–980 (3 1997).
23. A. L. Bertozzi, *The Mathematics of Moving Contact Lines in Thin Liquid Films*, 1998.
24. T. Kerle, J. Klein, R. Yerushalmi-Rozen, *Physics World* **11**, 24–24 (1998).
25. W. Alt, M. Dembo, *Mathematical Biosciences* **156**, 207–228, ISSN: 0025-5564 (1999).
26. A. Sharma, R. Khanna, G. Reiter, *Colloids and Surfaces B: Biointerfaces* **14**, 223–235, ISSN: 0927-7765 (1999).
27. G. K. Batchelor, *An Introduction to Fluid Dynamics* (Cambridge University Press, 2000), DOI: [10.1017/CBO9780511800955](https://doi.org/10.1017/CBO9780511800955).
28. R. W. Griffiths, *Annual Review of Fluid Mechanics* **32**, 477–518 (2000).
29. H. Khalil, *Nonlinear Systems* (Prentice Hall, 2002), ISBN: 9780130673893, (https://books.google.co.uk/books?id=t%5C_d1QgAACAAJ).
30. J. Donea, A. Huerta, J.-P. Ponthot, A. Rodríguez-Ferran, in *Encyclopedia of Computational Mechanics* (American Cancer Society, 2004), chap. 14, ISBN: 9780470091357, DOI: [10.1002/0470091355.ecm009](https://doi.org/10.1002/0470091355.ecm009), eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/0470091355.ecm009>, (<https://onlinelibrary.wiley.com/doi/abs/10.1002/0470091355.ecm009>).
31. J. Eggers, *Physics of Fluids* **16**, 3491–3494 (2004).
32. N. Clarke, *Macromolecules* **38**, 6775–6778 (2005).
33. J. Eijkel, A. van den Berg, *Microfluidics and nanofluidics* **1**, 249–267, ISSN: 1613-4982 (2005).
34. S. Kim, S. Karrila, *Microhydrodynamics: Principles and Selected Applications* (Dover Publications, 2005), ISBN: 9780486442198, (https://books.google.co.uk/books?id=%5C_81lnUUGo0wC).
35. J. R. King, J. M. Oliver, *European Journal of Applied Mathematics* **16**, 519–553 (2005).
36. J. M. Oliver *et al.*, *Mathematical Medicine and Biology: A Journal of the IMA* **22**, 53–98, ISSN: 1477-8599 (2005).
37. P. Flores, J. Ambrósio, J. Claro, H. Lankarani, C. Koshy, *Mechanism and Machine Theory* **41**, 247–261, ISSN: 0094-114X (2006).
38. J. D. Hunter, *Computing in Science Engineering* **9**, 90–95, ISSN: 1521-9615 (2007).

39. J. Ralston, M. Popescu, R. Serein, *Annual Review of Materials Research* **38**, 23–43 (2008).
40. H. Sun, C. Liu, *Discrete and Continuous Dynamical Systems - DISCRETE CONTINUOUS DYN SYST* **23**, DOI: 10.3934/dcds.2009.23.455 (Sept. 2008).
41. D. Bonn, J. Eggers, J. Indekeu, J. Meunier, E. Rolley, *Rev. Mod. Phys.* **81**, 739–805 (2 2009).
42. R. V. Craster, O. K. Matar, *Rev. Mod. Phys.* **81**, 1131–1198 (3 2009).
43. L. Evans, *Partial differential equations (Graduate Studies in Mathematics)* (American Mathematical Society, 2010).
44. N. Giordano, H. Nakanishi, *Computational Physics: 2nd edition* (Dorling Kindersley, 2012), ISBN: 9788131766279, (https://books.google.co.uk/books?id=RCCVN2A%5C_1tQC).
45. M. Doi, *Soft matter physics* (Oxford University Press, 2013).
46. M. G. Hennessy, A. Munch, English, *SIAM Journal on Applied Mathematics* **73**, Copyright - © 2013, Society for Industrial and Applied Mathematics; Last updated - 2013-04-27, 974–1001 (2013).
47. J. R. King, R. M. Taranets, *Journal of Mathematical Analysis and Applications* **404**, 399–419, ISSN: 0022-247X (2013).
48. M. C. Marchetti *et al.*, *Rev. Mod. Phys.* **85**, 1143–1189 (3 2013).
49. U. Thiele, D. V. Todorova, H. Lopez, *Physical Review Letters* **111**, 117801 (2013).
50. M. A. Peletier, *arXiv e-prints*, arXiv:1402.1990 (2014).
51. D. Peschka, *Journal of Computational Physics* **295**, 770–778, ISSN: 0021-9991 (2015).
52. X. Xu, U. Thiele, T. Qian, *Journal of Physics: Condensed Matter* **27**, 085005 (2015).
53. A. Münch, *Lecture Notes: Topics in Fluids*, URL: https://courses.maths.ox.ac.uk/node/view_material/442., 2016.
54. B. E. Rapp, in *Microfluidics: Modelling, Mechanics and Mathematics*, ed. by B. E. Rapp (Elsevier, Oxford, 2017), pp. 243–263, ISBN: 978-1-4557-3141-1, DOI: <https://doi.org/10.1016/B978-1-4557-3141-1.50009-5>, (<http://www.sciencedirect.com/science/article/pii/B9781455731411500095>).
55. X. Xu, T. Qian, *Procedia IUTAM* **20**, 24th International Congress of Theoretical and Applied Mechanics, 144–151, ISSN: 2210-9838 (2017).
56. G. Kitavtsev, A. Münch, B. Wagner, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **474**, 20170828 (2018).
57. R. Sarma, P. K. Mondal, *Phys. Rev. E* **97**, 043105 (4 2018).
58. E. P. Farrell, *Lecture Notes: Finite Element Methods for PDEs*, URL: https://courses.maths.ox.ac.uk/node/view_material/4915., 2019.

59. R. V. Krechetnikov, *Doklady Physics* **64**, 27–29, ISSN: 1562-6903 (2019).
60. E. Jones, T. Oliphant, P. Peterson, *et al.*, *SciPy: Open source scientific tools for Python*, 2001–, (<http://www.scipy.org/>).
61. T. Oliphant, *NumPy: A guide to NumPy*, USA: Trelgol Publishing, 2006–, (<http://www.numpy.org/>).
62. In, *The Finite Element Method for Elliptic Problems*, pp. 36–109, DOI: 10.1137/1.9780898719208.ch2, eprint: <https://pubs.siam.org/doi/pdf/10.1137/1.9780898719208.ch2>, (<https://pubs.siam.org/doi/abs/10.1137/1.9780898719208.ch2>).
63. Python Software Foundation, *Python*, version 3.7.1, (<http://www.python.org>).