




2018

Spherulitic Growth and Thermodynamic Equilibrium in Multicomponent Elastic Films Under Solvent-vapor Annealing

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Digital Object Identifier: <https://doi.org/10.13023/etd.2018.256>

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Recommended Citation

Zhao, Ding, "Spherulitic Growth and Thermodynamic Equilibrium in Multicomponent Elastic Films Under Solvent-vapor Annealing" (2018). *Theses and Dissertations--Mathematics*. 56.
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Spherulitic Growth and Thermodynamic Equilibrium in Multicomponent Elastic
Films Under Solvent-vapor Annealing

DISSERTATION

A dissertation submitted in partial
fulfillment of the requirements for
the degree of Doctor of Philosophy
in the College of Arts and Sciences
at the University of Kentucky

By
Ding Zhao
Lexington, Kentucky

Director: Dr. Chi-Sing Man, Professor of Mathematics
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2018

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ABSTRACT OF DISSERTATION

Spherulitic Growth and Thermodynamic Equilibrium in Multicomponent Elastic Films Under Solvent-vapor Annealing

In this dissertation, we will study solvent-vapor induced spherulitic growth in multicomponent thin films modeled as prestressed elastic solids. The interface between the crystalline phase and the amorphous phase will be treated as an evolving thermodynamic system and no diffusion of any component will be considered.

The dissertation is divided into three parts. In Part I we will determine necessary conditions of thermodynamic equilibrium between the two solid phases, the interface, and the vapor. In Part II we will derive the thermodynamic driving force for solvent-vapor induced spherulitic growth in multicomponent elastic thin films. In Part III we will investigate the effect of prestress on the directional dependence of the growth. There a formula that delineates how the prestress affects the shape of the spherulite will be proposed.

KEYWORDS: solvent-vapor induced spherulitic growth, elastic solid with prestress, directional dependence on prestress, phase transition

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Date: _____ July 12, 2018

Spherulitic Growth and Thermodynamic Equilibrium in Multicomponent Elastic
Films Under Solvent-vapor Annealing

By
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Dedicated to my parents

ACKNOWLEDGMENTS

First, I would like to express my most sincere gratitude and appreciation to my advisor Dr. Chi-Sing Man for his patience, support, and guidance during my graduate study. His immense knowledge and professionalism will always inspire me throughout my career.

I thank Dr. Michel Jabbour for all the mechanics courses he offered and the discussion that we had. I thank Dr. Zhong Tan for encouraging me to pursue my education in the United States.

My gratitude extends to the other members of my committee : Dr. Joseph Brill, Dr. Russell Brown, Dr. Peter Hislop, and Dr. Fuqian Yang for their suggestions and help.

Special thanks goes to Ms. Sheri Rhine for her kindness and warmth.

I would like to thank Ms. Anqi Guo for being in my life and help me through my toughest time.

Last but not least, I want to thank my parents for their love. I could not have gone this far without their unconditional support.

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Chapter 1 Introduction

1 Background

Organic small-molecule semiconductors have attractive features for applications in organic photovoltaics (OPVs), organic thin-film transistors (OTFTs), and organic light-emitting diodes (OLEDs) [1]. They have been actively studied as the host-guest pair in OTFTs and as the donor-acceptor pair in bulk heterojunction OPVs [2].

Solvent-vapor annealing is known to have positive effect on device performance which is measured by the power conversion efficiency of OPVs and field-effect mobility of OTFTs. For thin-film blends of small-molecule semi-conductors which are formed by spin coating and are largely amorphous in the as-spun state, film restructuring upon exposition to solvent vapor often proceeds by crystallization through heterogeneous nucleation and spherulitic growth [1].

In experiments reported in [2] and [3], TES ADT (triethylsilylethynyl anthradithiophene) was dissolved in toluene and the solution was subsequently spin coated onto substrates to form 100-nm thick uniform films. The substrates were thermally annealed to drive off residual toluene and then exposed to DCE (1,2-dichloroethane) solvent vapor during which the originally amorphous film crystallized through nucleation and growth of spherulites; see Figure 1.1. We assume that the film no longer contains any toluene after thermal annealing and, after exposure of the film to DCE vapor, the solvent DCE dissolves in the film.

As was pointed out in a 2012 paper by Hedge *et al.* [4], the thermodynamic driving force behind the solvent-vapor induced crystallization was not hitherto addressed explicitly. Clarifying the physics of the spherulitic growth is therefore of crucial importance for further development of the subject.

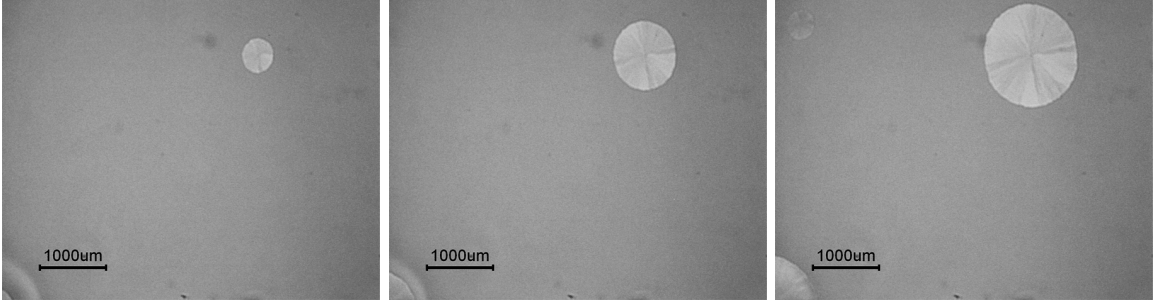


Figure 1.1: Growth of spherulites; courtesy of Y.-L. Loo and S.S. Lee (Princeton)

Jabbour, Man and Paroni [1] proposed an interface-driven, thermodynamically consistent, macroscopic theory to predict the growth rate of spherulites by identifying the thermodynamic driving force in question. By imposing the assumptions that, among others, the stress tensor in both amorphous and crystalline phase be spherical, the motion be smooth and the interface be massless, it is shown that the growth rate, measured by the normal velocity of the phase interface, was constant.

2 Main results and outline

In this dissertation, we will develop for the same process a theory parallel to and more general than that in [1] by relaxing the assumptions mentioned above. Specifically, instead of assuming the motion to be smooth, we assume that the motion be continuous and satisfies Hadamard's compatibility condition. The assumption that the stress tensor in both phases be spherical will be dropped and we will treat the interface as a thermodynamical system in itself by endowing it with excess quantities.

Our main results include a derivation of the thermodynamic driving force for isothermal crystallization of an isolated spherulite under solvent-vapor annealing and a formula that delineates the effect of prestress on the shape of the spherulites.

We will first review in chapter 2 some basic concepts in continuum mechanics, evolving curves and thermodynamics that are important to our discussion.

In chapter 3, thermodynamic equilibrium conditions, which will shed light on the

driving force formula, will be obtained for the system consisting of two solid phases, an interface and vapor when it is immersed in a heat bath of constant temperature. To this end, unlike the usual practice of minimizing the Helmholtz free energy, we will use the Duhem's principle of minimum ballistic free energy, which was reintroduced in the 1960s by Ericksen [5].

In chapter 4, balance of mass and momentum as well as the first two laws of thermodynamics will be discussed. By combining the energy balance and entropy imbalance, we will get for isothermal systems and processes the free energy imbalance which will deliver the dissipation inequalities for both bulk phases and the interface upon localization. The dissipation inequalities will restrict the constitutive relations adopted for the system, as per in essence the Coleman-Noll procedure [6]. The driving force behind the crystallization will be identified as the quantity conjugate to the normal velocity in the dissipation inequality on the interface. The main difference between the present theory and the existing ones on the similar topics, such as [7, 8, 9, 10, 11], among others, is that we treat the interface as a thermodynamic system in itself by endowing it with excess quantities as well as a well defined interface velocity. The product of the interface velocity and the interfacial stress will give the power expended by the interface. We will end chapter 4 by a comparison between the driving force we get and the counterpart in [1], which will deliver some insight on the role of the phase interface.

In chapter 5, we will specialize our theory and investigate the effect of the prestress on the shape of the spherulite by deriving a formula of the normal velocity as a function of the direction of the outward normal and an estimate of the shape of the spherulite. The formula is, to the best of our knowledge, new.

Chapter 2 Preliminaries

In this chapter, we will recall some results and definitions in continuum mechanics, evolving curves and thermodynamics of elastic solids that will be instrumental for our discussion. The readers are referred to [8, 9, 12, 13, 14, 15, 16] for more details on these topics.

Note that the thin film will be modeled as a plane and therefore we will restrict our theory to two space dimensions. Summation over repeated indices is implied throughout this dissertation unless otherwise specified.

1 Continuum mechanics

We start by presenting some important concepts in continuum mechanics.

Bodies and configurations

In continuum mechanics, a *body* \mathcal{B} is a collection of *particles* p which can be put into one-to-one correspondence with a region in a Euclidean space \mathbb{E} . Such a correspondence is called a *placement* of the body \mathcal{B} , i.e. the one-to-one mapping χ from \mathcal{B} into \mathbb{E} such that

$$\mathbf{x} = \chi(p) \quad \text{where } p \in \mathcal{B}, \quad \mathbf{x} \in \mathbb{E}. \quad (2.1)$$

is a *placement* of the body \mathcal{B} and \mathbf{x} is the position occupied by particle p under the placement χ . The image of the mapping $\mathcal{B}_\chi = \{\mathbf{x} \mid \mathbf{x} = \chi(p), p \in \mathcal{B}\}$ is called the *configuration* under the placement χ . Bodies are only available to us in their configurations.

It is usually convenient to choose a particular configuration, say \mathcal{B}_κ , as reference and use the position $\mathbf{X} = \kappa(p)$ to label the particles and to describe the change in geometrical quantities from the configuration \mathcal{B}_κ to some other configuration. We

will call \mathcal{B}_κ the (chosen) *reference configuration*. Note that the choice of the reference configuration is arbitrary and usually chosen for reasons of convenience.

Let \mathcal{B}_κ be a reference configuration, \mathcal{B}_χ be any other configuration of the body \mathcal{B} . The mapping $\chi_\kappa : \mathcal{B}_\kappa \rightarrow \mathcal{B}_\chi$

$$\mathbf{x} = \chi_\kappa(\mathbf{X}) = \chi(\kappa^{-1}(\mathbf{X})) \quad (2.2)$$

defines a *deformation* from placement κ to placement χ ; see Figure 2.1.

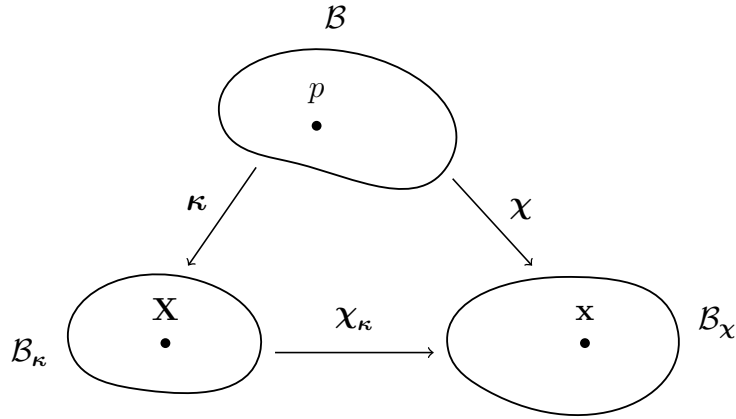


Figure 2.1: Placements and deformation

When we work with one fixed reference configuration, we may identify the body \mathcal{B} with the reference configuration \mathcal{B}_κ in question, drop the subscript κ in equation (2.2)₁ and write $\mathbf{x} = \chi(\mathbf{X})$ for simplicity.

In addition, we require that $J = \det \mathbf{F}(\mathbf{X}) > 0$ where $\mathbf{F} = \text{grad } \chi$ is called the deformation gradient.

A *motion* of \mathcal{B} is a one-parameter family of placements where the parameter is time t , i.e. we call

$$\chi = \{\chi_t, t \in [0, \infty) \mid \chi_t : \mathcal{B} \rightarrow \mathbb{E}\} \quad (2.3)$$

a motion of \mathcal{B} . The configuration of the body at time t will be denoted by \mathcal{B}_t . A motion can be written as

$$\chi : \mathcal{B} \times [0, \infty) \rightarrow \mathbb{E}, \quad \mathbf{x} = \chi(\mathbf{X}, t) = \chi_t(\mathbf{X}). \quad (2.4)$$

Similarly, we require that $\det \mathbf{F}(\mathbf{X}, t) > 0$ for all t . When we investigate a body, \mathcal{B}_t is the region actually observed during the motion, \mathcal{B} serves only to label the particles.

Referential and spatial description of fields

Consider a motion χ of a body \mathcal{B} . Let φ be a scalar, vector or tensor field defined over $\mathcal{B} \times [0, \infty)$ with its value in some space W , i.e.

$$\varphi : \mathcal{B} \times [0, \infty) \rightarrow W. \quad (2.5)$$

Since $\mathbf{x} = \chi(\mathbf{X}, t)$ is invertible in \mathbf{X} for fixed t , it has an inverse $\mathbf{X} = \chi^{-1}(\mathbf{x}, t)$. Then the field can also be defined on the region that currently occupied by the body

$$\phi(\cdot, t) : \mathcal{B}_t \rightarrow W \quad (2.6)$$

by

$$\phi(\mathbf{x}, t) = \varphi(\chi^{-1}(\mathbf{x}, t), t) = \varphi(\mathbf{X}, t). \quad (2.7)$$

The left hand side of the above equation is called the *spatial description* of the field and the the right hand side the *referential description* of the field.

In continuum mechanics, we usually use the same symbol for both referential and spatial description of the field, i.e. we write,

$$\varphi = \varphi(\mathbf{X}, t) = \varphi(\mathbf{x}, t) \quad (2.8)$$

For instance, as we shall see in the next subsection, we will use the same symbol \mathbf{T} to express the *Cauchy stress tensor* both spatially $\mathbf{T}(\mathbf{x}, t)$ and referentially $\mathbf{T}(\mathbf{X}, t)$.

Cauchy stress and Piola-Kirchhoff stress

Central to the discussion of continuum mechanics are Cauchy's hypothesis and Cauchy's theorem which state, in two dimensional case, as follows:

Cauchy's Hypothesis *Given any oriented curve \mathcal{C} in the current configuration with unit normal vector $\hat{\mathbf{m}}$, $\mathbf{s}(\hat{\mathbf{m}}, \mathbf{x}, t)$ represents the force, per unit length, exerted across \mathcal{C} upon the material on the negative side of $\hat{\mathbf{m}}$ by the material on the positive side.*

Theorem 1 (Cauchy's Theorem). [12] *A consequence of balance of forces is that there exists a spatial tensor field \mathbf{T} called the **Cauchy stress tensor**, such that*

$$\mathbf{s}(\hat{\mathbf{m}}) = \mathbf{T}\hat{\mathbf{m}} \quad (2.9)$$

Therefore the term

$$\int_{\mathcal{C}} \mathbf{T}(\mathbf{x})\hat{\mathbf{m}}(\mathbf{x}) ds(\mathbf{x}) \quad (2.10)$$

represents the contact force exerted across the curve \mathcal{C} in the current configuration.

Assume \mathcal{S} is a curve in the reference configuration such that $\mathcal{C} = \chi(\mathcal{S})$ and \mathbf{m} is the unit normal to \mathcal{S} , then [12, Section 24.1]

$$\int_{\mathcal{S}} J(\mathbf{X})\mathbf{T}(\mathbf{X})\mathbf{F}^{-\top}(\mathbf{X})\mathbf{m}(\mathbf{X}) ds(\mathbf{X}) = \int_{\mathcal{C}} \mathbf{T}(\mathbf{x})\hat{\mathbf{m}}(\mathbf{x}) ds(\mathbf{x}). \quad (2.11)$$

We call the second-order tensor

$$\mathbf{S} = J\mathbf{T}\mathbf{F}^{-\top} \quad (2.12)$$

the *first Piola-Kirchhoff stress tensor* and the tensor

$$\mathbf{P} = \mathbf{F}^{-1}\mathbf{S} \quad (2.13)$$

the *second Piola-Kirchhoff stress tensor*. Note that the second Piola-Kirchhoff stress is symmetric.

2 Evolving curves

In this section, we shall discuss some facts on evolving curves which we will use to model the motion of phase interfaces in a thin film.

Definitions

An *evolving curve* is a family of curves $\Sigma(t)$ together with a smooth mapping $(p, t) \mapsto \mathbf{r}(p, t)$ where $\{(p, t) \in [P(t), Q(t)] \times [0, T)\}$ with $P, Q : [0, T) \rightarrow \mathbb{R}$ ($P < Q$) being

smooth functions. For each t , $\mathbf{r}(\cdot, t)$ is a parametrization of $\Sigma(t)$ and $\|\mathbf{r}_p\|$ never vanish where the subscript p denotes the partial derivative with respect to p . We choose the parametrization to be such that the region enclosed by the curve falls to the right of the direction of increasing p .

Let $(p, t) \mapsto s(p, t)$ be the arc-length map defined by

$$s(p, t) = \int_{P(t)}^p \|\mathbf{r}_p(\lambda, t)\| d\lambda \quad (2.14)$$

where $p \in [P(t), Q(t)]$. Since $\|\mathbf{r}_p\|$ never vanish, $s = s(p, t)$ is invertible with respect to p . Any function $\varphi(p, t)$ may be considered a function $\varphi(s, t)$ and vice versa.

Let $\mathbf{t}(s, t)$ be the unit tangent vector of the evolving curve at time t , and $\mathbf{m}(s, t)$ be the unit normal pointing away from the enclosed region and falls to the left of the unit tangent vector. The curvature κ of the evolving curve at time t is given by the Frenet relation

$$\frac{\partial \mathbf{t}}{\partial s} = \kappa \mathbf{m}. \quad (2.15)$$

Under this choice of \mathbf{t} and \mathbf{m} , $\kappa \leq 0$ on $\Sigma(t)$ whenever the enclosed region is convex.

Normal velocity and normal time-derivative

Let $\Sigma(t)$ be an evolving curve and $\mathbf{r}(p, t)$ be its parametrization. We refer to

$$V = \frac{\partial \mathbf{r}}{\partial t} \cdot \mathbf{m} \quad (2.16)$$

as the *scalar normal velocity* of the evolving curve and $\boldsymbol{\nu} = V\mathbf{m}$ as the *vector normal velocity*.

Let \mathbf{X}_0 be a point on $\Sigma(t_0)$, the curve at time t_0 . The *normal trajectory* through \mathbf{X}_0 at time t_0 is a curve $\mathbb{X}(t)$ which is the solution to the initial value problem

$$\frac{d\mathbb{X}(t)}{dt} = \boldsymbol{\nu}(\mathbb{X}(t), t), \quad \mathbb{X}(t_0) = \mathbf{X}_0. \quad (2.17)$$

Then given a scalar, vector or tensor field $\varphi(\mathbf{X}, t)$ for $\mathbf{X} \in \Sigma(t)$, the *normal time-derivative* of φ following $\Sigma(t)$ is defined by

$$\dot{\varphi}(\mathbf{X}, t) = \left. \frac{d\varphi(\mathbb{X}(t), t)}{dt} \right|_{t=t_0} \quad (2.18)$$

which represents the rate of change of φ following the normal trajectory $\mathbb{X}(t)$.

Hadamard's compatibility condition

A coherent phase transition is manifested by the propagation of the phase interface $\Sigma(t)$ in the reference configuration \mathcal{B} during which the motion $\boldsymbol{\chi}(\mathbf{X}, t)$ is continuous while the velocity $\dot{\boldsymbol{\chi}}$ and deformation gradient $\mathbf{F} = \text{grad } \boldsymbol{\chi}$ suffer a jump discontinuity across $\Sigma(t)$. The overhead dot denotes the partial derivative with respect to time t .

Let φ be a scalar, vector or tensor field that is smooth up to the phase interface $\Sigma(t)$. For each $\mathbf{X} \in \Sigma(t)$, let $\varphi^-(\mathbf{X}, t)$ and $\varphi^+(\mathbf{X}, t)$ denote the values of φ when \mathbf{X} is a limit point from the region enclosed by $\Sigma(t)$ and from outside of $\Sigma(t)$, respectively. We use

$$[[\varphi]](\mathbf{X}, t) = \varphi^+(\mathbf{X}, t) - \varphi^-(\mathbf{X}, t) \quad (2.19)$$

to denote the jump of the field φ across $\Sigma(t)$.

We introduce Hadamard's compatibility condition [12]

$$[[\dot{\boldsymbol{\chi}}]] = -[[\mathbf{F}]]\mathbf{m}V \quad \text{and} \quad [[\mathbf{F}]]\mathbf{t} = \mathbf{0} \quad (2.20)$$

where \mathbf{F} is the deformation gradient and \mathbf{m} is the unit normal vector pointing away from the enclosed region. In fact, if we let $\mathcal{C}(t) = \boldsymbol{\chi}(\Sigma(t), t)$ be the deformed curve in the deformed body and $\mathbf{r}(s, t)$ be the arc-length parametrization of $\Sigma(t)$, then $\hat{\mathbf{x}}(s, t) = \boldsymbol{\chi}(\mathbf{r}(s, t), t)$ is the parametrization of $\mathcal{C}(t)$.

Note that

$$\frac{\partial \hat{\mathbf{x}}(s, t)}{\partial s} = \mathbf{F}^\pm \mathbf{t}. \quad (2.21)$$

Therefore we have $\llbracket \mathbf{F} \rrbracket \mathbf{t} = \mathbf{0}$.

On the other hand, we have, by the chain rule

$$\frac{\partial \hat{\mathbf{x}}(s, t)}{\partial t} = \dot{\boldsymbol{\chi}}^\pm + \mathbf{F}^\pm \frac{\partial \mathbf{r}(s, t)}{\partial t}. \quad (2.22)$$

Together with (2.20)₂, we have (2.20)₁.

Note that the normal time derivative of the motion is, by the chain rule,

$$\begin{aligned} \dot{\boldsymbol{\chi}} &= \frac{d}{dt} \boldsymbol{\chi}(\mathbb{X}(t), t) \\ &= \dot{\boldsymbol{\chi}}^\pm + \mathbf{F}^\pm \mathbf{m} V \\ &= \langle\langle \dot{\boldsymbol{\chi}} \rangle\rangle + \langle\langle \mathbf{F} \rangle\rangle \mathbf{m} \end{aligned} \quad (2.23)$$

where $\langle\langle f \rangle\rangle = \frac{1}{2}(f^+ + f^-)$ for any scalar, vector or tensor field that is smooth up to the interface.

Transport identities

Let $\mathcal{S}(t)$ be an evolving subcurve of $\Sigma(t)$ and $\mathbb{X}_a(t)$, $\mathbb{X}_b(t)$ be the endpoints of $\mathcal{S}(t)$. For any scalar or vector interfacial field φ , we write $\varphi_a(t) = \varphi(\mathbb{X}_a(t), t)$ and $\varphi_b(t) = \varphi(\mathbb{X}_b(t), t)$. We have the following transport theorem for line integrals.

Theorem 2 (Transport Theorem for Line Integrals). *[8] For $\mathcal{S}(t)$ a smoothly evolving subcurve of $\Sigma(t)$ and φ a smooth interfacial field,*

$$\frac{d}{dt} \int_{\mathcal{S}(t)} \varphi ds = \int_{\mathcal{S}(t)} (\dot{\varphi} - \varphi \kappa V) ds + \int_{\partial \mathcal{S}(t)} \varphi W \quad (2.24)$$

where

$$\int_{\partial \mathcal{S}(t)} \varphi W = \varphi_b W_b - \varphi_a W_a \quad (2.25)$$

and $W = \frac{d\mathbb{X}}{dt} \cdot \mathbf{t}$ denotes the tangential component of the velocity of the endpoints of $\mathcal{S}(t)$.

We also introduce the transport relation in the bulk with singular curve:

Theorem 3 (Transport Theorem with Singular Curve). [12] *Let \mathcal{R} be any fixed region in \mathcal{B} and $\Sigma(t) \subset \mathcal{B}$ be a curve such that a scalar, vector or tensor field φ is smooth up to $\Sigma(t)$, then we have*

$$\frac{d}{dt} \int_{\mathcal{R}} \varphi da = \int_{\mathcal{R}} \frac{\partial \varphi}{\partial t} da - \int_{\mathcal{R} \cap \Sigma(t)} [[\varphi]] V ds \quad (2.26)$$

where V is the normal velocity of $\Sigma(t)$.

3 Gibbs dividing interface and excess quantities

In this section, we briefly introduce the notion of the Gibbs dividing interface.

A phase interface, in reality, is not a sharp interface. Instead, it is a transition layer with certain thickness where quantities, for instance the mass density, can have a drastic but smooth change. Different models had been proposed to describe the phase interface. In this dissertation, we shall adopt the model proposed by Gibbs, namely the Gibbs dividing interface.

The Gibbs dividing interface, which we shall just call the interface for simplicity, is an imaginary interface that separate the thin film into two parts with area A^α and A^β , such that

$$A = A^\alpha + A^\beta \quad (2.27)$$

where A is the area of the entire film. All other extensive quantities can be written as a sum of three terms: one for bulk phase α , one for bulk phase β and one for the interfacial region Σ . For example

$$\begin{aligned} U &= U^\alpha + U^\beta + U^\Sigma \\ S &= S^\alpha + S^\beta + S^\Sigma \\ M &= M^\alpha + M^\beta + M^\Sigma \end{aligned} \quad (2.28)$$

where U , S and M represent the internal energy, entropy and mass, respectively. If we assume that the bulk phases are homogeneous and ρ^α and ρ^β are the mass

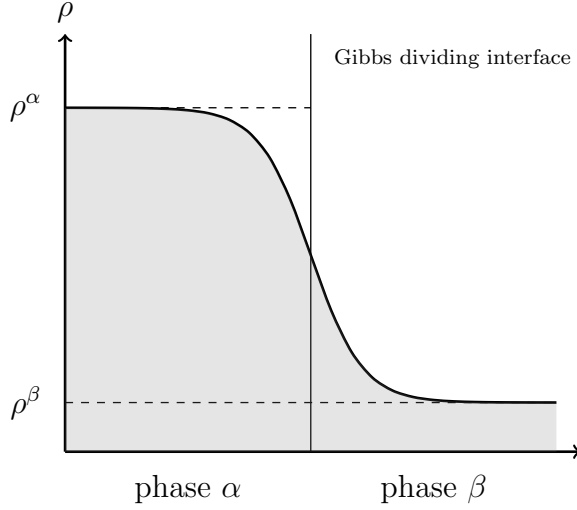


Figure 2.2: A sketch of the Gibbs dividing interface

densities of the two phases, then

$$M^\Sigma = M - \rho^\alpha A^\alpha - \rho^\beta A^\beta, \quad (2.29)$$

which we will call the mass excess on the interface. We will define the *mass excess density*:

$$\Gamma = \frac{M^\Sigma}{L} \quad (2.30)$$

where L is the length of Σ . Similarly one can define the excess internal energy density $\varepsilon = \frac{U^\Sigma}{L}$, excess entropy density $\varsigma = \frac{S^\Sigma}{L}$, etc.

4 Thermodynamics of elastic solids with interface

In this section, we will derive a thermodynamic relation for the phase interface of a planar two phase system.

The work form

Consider an elastic film that consists of two phases, α and β , and a sharp phase interface. Let \mathcal{B} be the reference configuration of the elastic film and $\mathcal{B}^\alpha, \mathcal{B}^\beta \subset \mathcal{B}$ denotes region occupied by the respective phases. The phase interface is denoted by

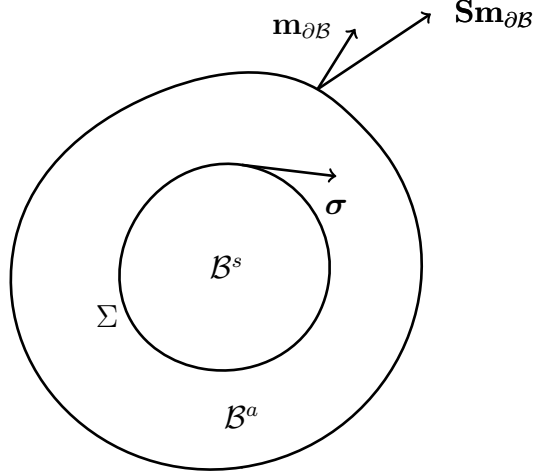


Figure 2.3: A sketch of a body with two phases and a sharp interface

$\Sigma = \partial\mathcal{B}^\alpha \cap \partial\mathcal{B}^\beta$ in the reference configuration. We assume that the interface Σ is closed and the region \mathcal{B}^α is enclosed by Σ ; see Figure 2.3.

Consider a process that the thin film undergoes in the time interval $[a, b]$, during which the body is acted upon by contact force. The work done on \mathcal{B} , i.e. W , by the environment during the process is given by

$$-W = \int_a^b \left(\int_{\partial\mathcal{B}} \mathbf{S}\mathbf{m}_{\partial\mathcal{B}} \cdot \dot{\boldsymbol{\chi}} ds \right) dt \quad (2.31)$$

where \mathbf{S} denotes the first Piola-Kirchhoff stress defined by (2.12) and $\mathbf{m}_{\partial\mathcal{B}}$ denotes the outward unit normal of $\partial\mathcal{B}$.

In order to further exploit equation (2.31), we introduce the interfacial stress tensor $\boldsymbol{\sigma}(\mathbf{X}, t)$; see Figure 2.3. The vector $\boldsymbol{\sigma}(\mathbf{X}, t)$ represents the force exerted across \mathbf{X} by the material that \mathbf{t} points to on the material that \mathbf{t} points from. It will be shown in (4.23) that the interfacial stress vector $\boldsymbol{\sigma}$ is tangential to the phase interface in the current configuration. The relationship between the interfacial stress vector and the excess free energy density will be discussed later in this chapter.

By the principle of balance of linear momentum, we have (as special cases of (4.16))

and (4.17) respectively, where $\mathcal{F}_i = 0$, $\mathbf{f}_i = 0$ and $V = 0$)

$$\rho \ddot{\boldsymbol{\chi}} = \operatorname{div} \mathbf{S} \quad (2.32)$$

in both \mathcal{B}^α and \mathcal{B}^β where ρ is the mass density and

$$\Gamma \ddot{\boldsymbol{\chi}} = \llbracket \mathbf{S} \rrbracket \mathbf{m} + \frac{\partial \boldsymbol{\sigma}}{\partial s} \quad (2.33)$$

where \mathbf{m} denotes the outward unit normal of Σ , $\boldsymbol{\sigma}$ denotes the interfacial stress and Γ is the excess mass density defined in section 3.

From the divergence theorem with the presence of a singular surface, we have for a closed interface $\Sigma(t)$,

$$\begin{aligned} \int_{\partial \mathcal{B}} \mathbf{S} \mathbf{m}_{\partial \mathcal{B}} \cdot \dot{\boldsymbol{\chi}} \, ds &= \sum_{j=\alpha, \beta} \left(\int_{\mathcal{B}^j} \operatorname{div} \mathbf{S} \cdot \dot{\boldsymbol{\chi}} \, da + \int_{\mathcal{B}^j} \mathbf{S} : \dot{\mathbf{F}} \, da \right) + \int_{\Sigma} \llbracket \mathbf{S} \rrbracket \mathbf{m} \cdot \dot{\boldsymbol{\chi}} \, ds \\ &= \sum_{j=\alpha, \beta} \left(\frac{d}{dt} \int_{\mathcal{B}^j} \frac{1}{2} \rho \dot{\boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} \, da \right) + \frac{d}{dt} \int_{\Sigma} \frac{1}{2} \Gamma \dot{\boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} \, ds \\ &\quad + \sum_{j=\alpha, \beta} \left(\int_{\mathcal{B}^j} \mathbf{S} : \dot{\mathbf{F}} \, da \right) + \int_{\Sigma} \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} \, ds, \end{aligned} \quad (2.34)$$

where

$$\mathbf{F} = \operatorname{grad} \boldsymbol{\chi}, \quad \mathbf{e} = \frac{\partial \boldsymbol{\chi}}{\partial s}, \quad (2.35)$$

and for any second-order tensor \mathbf{A} and \mathbf{B} , $\mathbf{A} : \mathbf{B} = \operatorname{tr}(\mathbf{A}\mathbf{B}^\top)$ denotes the inner product of the two tensors. If one chooses an orthonormal basis $\{\mathbf{e}_1, \mathbf{e}_2\}$ and assume that A_{ij} , B_{ij} for $i = 1, 2$ are the components of \mathbf{A} and \mathbf{B} under the given basis, then $\mathbf{A} : \mathbf{B} = A_{ij}B_{ij}$. It then follows that

$$-W = K(b) - K(a) + \int_a^b \left(\sum_{j=\alpha, \beta} \left(\int_{\mathcal{B}^j} \mathbf{S} : \dot{\mathbf{F}} \, da \right) + \int_{\Sigma} \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} \, ds \right) dt \quad (2.36)$$

where $K(\cdot)$ denotes the kinetic energy of the body at any given time. For a process that $K(a) = K(b)$ and $\mathbf{S} : \dot{\mathbf{F}}$, $\boldsymbol{\sigma} \cdot \dot{\mathbf{e}}$ being homogeneous for each t , we have

$$-W = \int_a^b \left(\sum_{j=\alpha, \beta} \mathbf{S} : \dot{\mathbf{F}} A^j + \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} L \right) dt \quad (2.37)$$

where A^j and L denote the area of the j -th phase and the length of the interface, respectively. We can write

$$\begin{aligned} -W^\alpha &= A^\alpha \int_a^b \mathbf{S} : \dot{\mathbf{F}} dt \\ -W^\beta &= A^\beta \int_a^b \mathbf{S} : \dot{\mathbf{F}} dt \\ -W^\Sigma &= L \int_a^b \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} dt \end{aligned} \tag{2.38}$$

where W^j (for $j = \alpha, \beta, \Sigma$) stands for the work done on the respective part of the body by the environment.

Remark 1. The vector \mathbf{e} in (2.35) describes the deformation of the interface. By the compatibility relation (2.20)₂,

$$\mathbf{e} = \frac{\partial \boldsymbol{\chi}}{\partial s} = \mathbf{F} \mathbf{t}. \tag{2.39}$$

Therefore it is parallel to the tangent vector of the interface in the current configuration. The magnitude of \mathbf{e} , i.e. $j = \|\mathbf{e}\|$, is called the interfacial stretch ratio.

Thermodynamical relations

Assume further that the elastic film consists of N components and consider a homogeneous deformation $\boldsymbol{\chi}$ of the film.

By (2.38), one can write down the work form for each part of the body,

$$\begin{aligned} w^\alpha &= -A^\alpha \mathbf{S} : d\mathbf{F} - \mu_i^\alpha dM_i^\alpha \\ w^\beta &= -A^\beta \mathbf{S} : d\mathbf{F} - \mu_i^\beta dM_i^\beta \\ w^\Sigma &= -L \boldsymbol{\sigma} \cdot d\mathbf{e} - \mu_i^\Sigma dM_i^\Sigma \end{aligned} \tag{2.40}$$

where M_i^j and μ_i^j for $j = \alpha, \beta$ are the total mass and chemical potential of the i -th component in the respective phases. The quantity M_i^Σ is the mass excess of the i -th component on the interface. The second term in equations (2.40) represent the chemical work [17, p. 32].

Recall equation (2.28), let $U = U^\alpha + U^\beta + U^\Sigma$ and $S = S^\alpha + S^\beta + S^\Sigma$ be the total internal energy and entropy of the system. Then by the first two laws of thermodynamics, we have for a reversible system,

$$dU = q - w, \quad TdS = q \quad (2.41)$$

For the purpose of the discussion that follows, we are particularly interested in an isothermal case and hence consider the Helmholtz free energy $F = F^\alpha + F^\beta + F^\Sigma$ where $F^{\alpha,\beta,\Sigma} = U^{\alpha,\beta,\Sigma} - TS^{\alpha,\beta,\Sigma}$ and

$$dF = d(U - TS) = dU - TdS = -(w^\alpha + w^\beta + w^\Sigma). \quad (2.42)$$

It follows that

$$dF^j = A^j \mathbf{S}^j : d\mathbf{F} + \mu_i^j dM_i^j \quad \text{for } j = \alpha, \beta \quad (2.43)$$

$$dF^\Sigma = L\boldsymbol{\sigma} \cdot d\mathbf{e} + \mu_i^\Sigma dM_i^\Sigma \quad (2.44)$$

In terms of Helmholtz free energy density $\Psi^j = F^j/A^j$ for $j = \alpha, \beta$, the excess Helmholtz free energy per unit length $\psi = F^\Sigma/L$, (2.43) and (2.44) can be recast as

$$d\Psi^j = \mathbf{S}^j : d\mathbf{F} + \mu_i^j d\rho_i \quad \text{for } j = \alpha, \beta \quad (2.45)$$

$$d\psi = \boldsymbol{\sigma} \cdot d\mathbf{e} + \mu_i^\Sigma d\Gamma_i \quad (2.46)$$

where ρ_i and Γ_i are the mass density of the i -th component and the excess mass density of the interface, respectively.

Note that by (2.44), we have

$$F^\Sigma = F^\Sigma(L\mathbf{e}, \vec{M}^\Sigma) \quad (2.47)$$

where $\vec{M}^\Sigma = \langle M_1^\Sigma, \dots, M_N^\Sigma \rangle$. Assume that F^Σ is a homogeneous function of degree 1, we have, with the help of (2.44)

$$F^\Sigma = \frac{\partial F^\Sigma}{\partial(L\mathbf{e})} \cdot (L\mathbf{e}) + \frac{\partial F^\Sigma}{\partial M_i^\Sigma} M_i^\Sigma \quad (2.48)$$

$$= \boldsymbol{\sigma} \cdot (L\mathbf{e}) + \mu_i^\Sigma M_i^\Sigma \quad (2.49)$$

and therefore

$$\psi = \boldsymbol{\sigma} \cdot \mathbf{e} + \mu_i^\Sigma \Gamma_i \quad (2.50)$$

Remark 2. Note that as mentioned before, the vector $\boldsymbol{\sigma}$ is tangential to the interface in the current configuration, i.e.

$$\boldsymbol{\sigma} = \sigma \hat{\mathbf{t}}, \quad (2.51)$$

where $\hat{\mathbf{t}}$ denotes the unit tangent in the current configuration and σ is the surface tension. Hence equation (2.50) can be recast as

$$\psi = \sigma j + \mu_i^\Sigma \Gamma_i \quad (2.52)$$

Therefore the excess free energy per unit length in the current configuration is

$$\hat{\psi} = \sigma + \mu_i^\Sigma \hat{\Gamma}_i \quad (2.53)$$

where $\hat{\Gamma}_i = \Gamma_i/j$; see [18]. □

As noted in [19], different conjugate pairs of stress and strain can be utilized in the work form (2.40). Let $\mathbf{E} = \frac{1}{2} (\mathbf{F}^\top \mathbf{F} - \mathbf{1})$ denotes the Lagrange strain tensor and \mathbf{P} denote the second Piola-Kirchhoff stress tensor defined by (2.13), we then have the relation

$$\begin{aligned} \mathbf{P} : \dot{\mathbf{E}} &= \mathbf{F}^{-1} \mathbf{S} : \frac{1}{2} (\dot{\mathbf{F}}^\top \mathbf{F} + \mathbf{F}^\top \dot{\mathbf{F}}) \\ &= \frac{1}{2} \mathbf{S} : \mathbf{F}^{-T} (\dot{\mathbf{F}}^\top \mathbf{F} + \mathbf{F}^\top \dot{\mathbf{F}}) \\ &= \frac{1}{2} (\mathbf{S} : \mathbf{F}^{-T} \dot{\mathbf{F}}^\top \mathbf{F} + \mathbf{S} : \dot{\mathbf{F}}) \\ &= \frac{1}{2} \text{tr} (\mathbf{S} \mathbf{F}^\top \dot{\mathbf{F}} \mathbf{F}^{-1}) + \frac{1}{2} \mathbf{S} : \dot{\mathbf{F}} \\ &= \frac{1}{2} \text{tr} (\mathbf{S}^\top \dot{\mathbf{F}}) + \frac{1}{2} \mathbf{S} : \dot{\mathbf{F}} \\ &= \mathbf{S} : \dot{\mathbf{F}}. \end{aligned}$$

It follows that (2.45) can be recast as

$$d\Psi^j = \mathbf{P}^j : d\mathbf{E} + \mu_i^j d\rho_i \quad \text{for } j = \alpha, \beta \quad (2.54)$$

In this dissertation, we will use both (2.45) and (2.54) as well as (2.46) when discussing the constitutive relation.

Chapter 3 Equilibrium of a Two-Phase Thermoelastic Solid

In this chapter, we will investigate the conditions of thermodynamic equilibrium between the two solid phases, the interface and the vapor when the system is immersed in a heat bath of constant temperature T_b . The equilibrium conditions will serve as a check on the driving force that we will derive in the next chapter. Specifically, one would expect that the driving force vanishes when equilibrium conditions are satisfied.

Similar topic has been studied by, among others, Šilhavý [20], Johnson and Alexander [21], Leo and Sekerka [22]. As was pointed out in [22], the result of Johnson and Alexander was incomplete.

In what follows, we will use the principle of minimum ballistic energy, which could be traced back to Duhem and was reintroduced in the 1960's by Ericksen [5], to determine the equilibrium conditions. We will incorporate the thermodynamical relation (2.50) in our derivation. It should be pointed out that Ericksen [23] showed working with the Helmholtz free energy at fixed temperature $F(\cdot, T_b)$ is not equivalent to working with the ballistic free energy $E - T_b S$.

1 Equilibrium conditions

We will focus on an isolated spherulite in a thin-film, modeled as a planar object, which undergoes isothermal crystallization while exposed to the vapor of its own constituents.

Assume that the thin film consists of N components and two coexistent phases, the amorphous phases, denoted by (a) and the crystalline phase, denoted by (s) . The thin film is placed in a chamber filled with vapor of its own species. The whole system is immersed in a heat bath at fixed temperature T_b . We further assume that the gas

chamber wall is rigid and the boundary of the thin film is fixed so that the system is mechanically isolated.

The ballistic free energy B is defined by [5],

$$B = E - T_b S \quad (3.1)$$

where E and S are the internal energy and the entropy of the system, respectively, and T_b is the absolute temperature of the heat bath the system is in contact with. We have the following minimizing principle [5]:

For the equilibrium of any mechanically isolated system, in contact with a heat bath at constant temperature, it is necessary and sufficient that in all possible variations of the system the variation of its ballistic free energy shall either vanish or be positive

Now, let Ω denote the region that the thin film occupies. We use \mathcal{B} to denote the reference configuration of the film and we will use referential description in the discussion that follows.

The given equilibrium configuration of the film in Ω is described by a one-to-one mapping $\chi_0 : \mathcal{B} \rightarrow \Omega$. Let $\Sigma \subset \mathcal{B}$ be the simple closed curve that represents the phase interface in the equilibrium configuration. The interface Σ divides \mathcal{B} into two regions \mathcal{B}^s and \mathcal{B}^a . The points in \mathcal{B}^s are in crystalline phase and the points in \mathcal{B}^a are in amorphous phase. We assume that χ_0 is continuous in \mathcal{B} while the deformation gradient $\mathbf{F}_0 = \text{grad} \chi_0$ can have a jump discontinuity across Σ . We also assume that the crystalline phase (s) is enclosed by the curve Σ .

Let \mathcal{E}^s and \mathcal{E}^a be the internal energy density of the respective phase and ε be the excess internal energy per unit length of the interface.

The total ballistic free energy of the film at the given equilibrium configuration is given by

$$B_0^f = \int_{\mathcal{B}^a} \mathcal{E}^a(\eta_0) - T_b \eta_0 \, da + \int_{\mathcal{B}^s} \mathcal{E}^s(\eta_0) - T_b \eta_0 \, da + \int_{\Sigma} \varepsilon(s_0) - T_b s_0 \, ds \quad (3.2)$$

where $\mathcal{E}^{a,s}$, η_0 , ε , ς_0 represent the internal energy density of the respective phases, entropy density, excess internal energy, and excess entropy density, respectively. The subscript “0” means the value of the functions when the system is at equilibrium. Note that η_0 and ς_0 are functions of \mathbf{X} and, because we shall consider only variations in η and ς as a first step, we have suppressed the dependence of $\mathcal{E}^{a,s}$ and ε on variables other than η and ς for simplicity.

The total ballistic energy of the system is then

$$B_0 = B_0^f + \int_{\mathcal{V}} \mathcal{E}^v(\eta_0^v) - T_b \eta_0^v dv \quad (3.3)$$

where \mathcal{E}^v , η^v denote the internal energy density and entropy density of the vapor, respectively, and \mathcal{V} stands for the region that the vapor occupies.

First, consider a variation in the entropy, i.e. $\eta(\mathbf{X}, \epsilon)$, $\eta^v(\mathbf{X}, \epsilon)$ and $\varsigma(\mathbf{X}, \epsilon)$ which satisfy

$$\eta(\mathbf{X}, 0) = \eta_0, \quad \eta^v(\mathbf{X}, 0) = \eta_0^v, \quad \varsigma(\mathbf{X}, 0) = \varsigma_0 \quad (3.4)$$

We treat ϵ as if it were virtual time and we shall use the the language in standard continuum mechanics in what follows.

The ballistic free energy after the variation is then

$$B_\epsilon = B_\epsilon^f + \int_{\mathcal{V}} \mathcal{E}^v(\eta^v(\mathbf{X}, \epsilon)) - T_b \eta^v(\mathbf{X}, \epsilon) dv \quad (3.5)$$

where B_ϵ^f denotes the ballistic free energy of the film at virtual time ϵ .

The minimizing principle dictates that

$$B_0 \leq B_\epsilon \quad \text{for each } \epsilon. \quad (3.6)$$

Therefore a necessary condition for (3.6) is

$$\left. \frac{dB_\epsilon}{d\epsilon} \right|_{\epsilon=0} = 0. \quad (3.7)$$

Substituting (3.5) into (3.7), we obtain

$$\left(\sum_{\alpha=a,s} \int_{\mathcal{B}^\alpha} \left(\frac{\partial \mathcal{E}^\alpha}{\partial \eta} - T_b \right) \frac{\partial \eta}{\partial \epsilon} da + \int_{\Sigma} \left(\frac{\partial \varepsilon}{\partial \zeta} - T_b \right) \frac{\partial \zeta}{\partial \epsilon} ds + \int_{\mathcal{V}} \left(\frac{\partial \mathcal{E}^v}{\partial \eta^v} - T_b \right) \frac{\partial \eta^v}{\partial \epsilon} dv \right) \Big|_{\epsilon=0} = 0. \quad (3.8)$$

We deduce, by the arbitrariness of the variations in the entropy densities, that

$$T^{a,s}|_{\epsilon=0} = T^\Sigma|_{\epsilon=0} = T^v|_{\epsilon=0} = T_b, \quad (3.9)$$

where we have invoked the thermodynamic relations

$$\frac{\partial \mathcal{E}^{a,s}}{\partial \eta} = T^{a,s}, \quad \frac{\partial \varepsilon}{\partial \zeta} = T^\Sigma, \quad \frac{\partial \mathcal{E}^v}{\partial \eta^v} = T^v, \quad (3.10)$$

i.e., the temperature distribution is homogeneous across the entire system when it is in equilibrium.

Note that the ballistic free energy and the Helmholtz free energy coincide when the temperature of the system is the same as that of the heat bath. Henceforth, we will assume that the system is isothermal with the absolute temperature being the same as the heat bath and drop the explicit dependence on temperature. Instead of writing $\Psi(\mathbf{F}, \vec{\rho}, T_b)$, we will simply write $\Psi(\mathbf{F}, \vec{\rho})$. Substituting (3.9) into (3.3), we obtain

$$F_0 = F_0^f + \int_{\mathcal{V}} \Psi^v(\vec{\rho}_0^v) dv, \quad (3.11)$$

where Ψ^v is the Helmholtz free energy density of the vapor, $\vec{\rho}_0^v = \langle \rho_{1_0}^v, \dots, \rho_{N_0}^v \rangle$ denotes the list of corresponding variables, and

$$F_0^f = \int_{\mathcal{B}^s} \Psi^s(\mathbf{F}_0, \vec{\rho}_0) da + \int_{\mathcal{B}^a} \Psi^a(\mathbf{F}_0, \vec{\rho}_0) da + \int_{\Sigma} \psi(\mathbf{e}_0, \vec{\Gamma}_0) ds, \quad (3.12)$$

with $\Psi^{a,s}$ being the Helmholtz free energy density of the respective phases and ψ being the excess free energy density of the interface.

Now we consider the following set of virtual changes of the system:

$$\{\chi(\mathbf{X}, \epsilon), \Sigma_\epsilon, \vec{\rho}(\mathbf{X}, \epsilon), \vec{\rho}^v(\mathbf{X}, \epsilon), \vec{\Gamma}(\mathbf{X}, \epsilon)\} \quad (3.13)$$

The one-parameter families $\chi(\mathbf{X}, \epsilon)$ and Σ_ϵ represent the perturbation caused by deformation and phase transition, respectively. The rest of the set describe the perturbation caused by condensation and/or evaporation. The one-parameter family of curve Σ_ϵ divides \mathcal{B} into \mathcal{B}_ϵ^s and \mathcal{B}_ϵ^a . The points in \mathcal{B}_ϵ^s are in crystalline phase and the points in \mathcal{B}_ϵ^a are in amorphous phase.

The perturbation of the system satisfies the following conditions:

$$\begin{aligned}
\chi(\mathbf{X}, \epsilon) &= \chi_0(\mathbf{X}) \text{ for } \mathbf{X} \in \partial\mathcal{B} \\
\chi(\mathbf{X}, 0) &= \chi_0(\mathbf{X}) \text{ for } \mathbf{X} \in \mathcal{B} \\
\vec{\rho}(\mathbf{X}, 0) &= \vec{\rho}_0(\mathbf{X}) \text{ for } \mathbf{X} \in \mathcal{B} \\
\vec{\Gamma}(\mathbf{X}, 0) &= \vec{\Gamma}_0(\mathbf{X}) \text{ for } \mathbf{X} \in \Sigma \\
\vec{\rho}^v(\mathbf{X}, 0) &= \vec{\rho}_0^v(\mathbf{X}) \text{ for } \mathbf{X} \in \mathcal{V} \\
\Sigma_0 &= \Sigma.
\end{aligned} \tag{3.14}$$

Note that since we allow the mass density to change, we shall impose an additional constraint on the change of the system, i.e., the total mass should be conserved for each component provided that there is no chemical reaction.

The total free energy of the system, at each virtual ‘time’, is given by

$$F_\epsilon = F_\epsilon^f + \int_{\mathcal{V}} \Psi^v(\vec{\rho}^v) dv \tag{3.15}$$

where

$$F_\epsilon^f = \int_{\mathcal{B}_\epsilon^a} \Psi^a(\mathbf{F}, \vec{\rho}(\mathbf{X}, \epsilon)) da + \int_{\mathcal{B}_\epsilon^s} \Psi^s(\mathbf{F}, \vec{\rho}(\mathbf{X}, \epsilon)) da + \int_{\Sigma_\epsilon} \psi(\mathbf{e}, \vec{\Gamma}(\mathbf{X}, \epsilon)) ds. \tag{3.16}$$

and

$$\mathbf{F} = \text{grad} \chi(\mathbf{X}, \epsilon), \quad \mathbf{e} = \frac{\partial \chi(\mathbf{X}, \epsilon)}{\partial s}. \tag{3.17}$$

The total mass of the i -th component is

$$M_{i_\epsilon} = \int_{\mathcal{B}_\epsilon^a \cup \mathcal{B}_\epsilon^s} \rho_i(\mathbf{X}, \epsilon) da + \int_{\Sigma_\epsilon} \Gamma_i(\mathbf{X}, \epsilon) ds + \int_{\mathcal{V}} \rho_i^v(\mathbf{X}, \epsilon) dv. \tag{3.18}$$

The minimizing principle should now be interpreted as

$$F_0 \leq F_\epsilon \quad \text{for each } \epsilon, \quad (3.19)$$

under the constraint that

$$M_{i_\epsilon} = M_{i_0}, \quad (3.20)$$

where M_{i_0} are constants for all i .

By the method of Lagrange multipliers, each minimizer of the constrained problem:

$$\begin{aligned} & \text{minimize } F_\epsilon \\ & \text{subject to } M_{i_\epsilon} = M_{i_0} \end{aligned} \quad (3.21)$$

for all $i = 1, \dots, N$ with M_{i_0} being constants, is necessarily a stationary point of the following functional

$$F_\epsilon - \lambda_i M_{i_\epsilon} \quad (3.22)$$

without constraint, where $\lambda_i \in \mathbb{R}$, $i = 1, \dots, N$ are the Lagrange multipliers.

Therefore, we have

$$\left(\frac{dF_\epsilon}{d\epsilon} - \lambda_i \frac{dM_{i_\epsilon}}{d\epsilon} \right) \Big|_{\epsilon=0} = 0. \quad (3.23)$$

Substituting (3.15), (3.16) and (3.18) into the preceding equation, we compute, by using the transport identities (2.24) and (2.26) to obtain

$$\begin{aligned} \frac{dF_\epsilon}{d\epsilon} = & \int_{\mathcal{B}_\epsilon^s} \mathbf{S}^s : \frac{\partial \mathbf{F}}{\partial \epsilon} da + \int_{\mathcal{B}_\epsilon^s} \mu_i^s \frac{\partial \rho_i}{\partial \epsilon} da + \int_{\mathcal{B}_\epsilon^a} \mathbf{S}^a : \frac{\partial \mathbf{F}}{\partial \epsilon} da + \int_{\mathcal{B}_\epsilon^a} \mu_i^a \frac{\partial \rho_i}{\partial \epsilon} da + \\ & \int_{\mathcal{V}} \mu_i^v \frac{\partial \rho_i^v}{\partial \epsilon} dv - \int_{\Sigma_\epsilon} \llbracket \Psi \rrbracket V ds + \int_{\Sigma_\epsilon} \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} + \mu_i^\Sigma \dot{\Gamma}_i - \psi \kappa V ds. \end{aligned} \quad (3.24)$$

In the equation above, we have used the relations (2.45) and (2.46) for each phases, as well as

$$\frac{\partial \Psi^v}{\partial \rho_i^v} = \mu_i^v. \quad (3.25)$$

Similarly, by using the transport identities, we have

$$\frac{dM_{i\epsilon}}{d\epsilon} = \int_{\mathcal{B}_\epsilon^s \cup \mathcal{B}_\epsilon^a} \frac{\partial \rho_i}{\partial \epsilon} da - \int_{\Sigma_\epsilon} \llbracket \rho_i \rrbracket V ds + \int_{\mathcal{V}} \frac{\partial \rho_i^v}{\partial \epsilon} dv + \int_{\Sigma_\epsilon} \dot{\Gamma}_i - \Gamma_i \kappa V ds \quad (3.26)$$

With (3.24) and (3.26), (3.23) can be recast as

$$\begin{aligned} & \left(\int_{\mathcal{B}_\epsilon^s} (\mu_i^s - \lambda_i) \frac{\partial \rho_i}{\partial \epsilon} da + \int_{\mathcal{B}_\epsilon^a} (\mu_i^a - \lambda_i) \frac{\partial \rho_i}{\partial \epsilon} da \right. \\ & + \int_{\mathcal{V}} (\mu_i^v - \lambda_i) \frac{\partial \rho_i^v}{\partial \epsilon} dv + \int_{\Sigma_\epsilon} (\mu_i^\Sigma - \lambda_i) \dot{\Gamma}_i ds + \int_{\mathcal{B}_\epsilon^s} \mathbf{S}^s : \frac{\partial \mathbf{F}}{\partial \epsilon} da + \int_{\mathcal{B}_\epsilon^a} \mathbf{S}^a : \frac{\partial \mathbf{F}}{\partial \epsilon} da \\ & \left. + \int_{\Sigma_\epsilon} \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} ds - \int_{\Sigma_\epsilon} \llbracket \Psi - \lambda_i \rho_i \rrbracket V ds - \int_{\Sigma_\epsilon} (\psi - \lambda_i \Gamma_i) \kappa V ds \right) \Big|_{\epsilon=0} = 0. \quad (3.27) \end{aligned}$$

Note that equation (3.27) is valid for any virtual change satisfying (3.14). We first consider the virtual change where

$$\boldsymbol{\chi}(\mathbf{X}, \epsilon) = \boldsymbol{\chi}_0(\mathbf{X}), \quad \Sigma_\epsilon = \Sigma \quad (3.28)$$

for all ϵ , i.e. only virtual condensation and evaporation take place. In this case, the normal time-derivative $\dot{\Gamma}_i$ reduces to standard partial derivative with respect to the virtual time ϵ , and only the first four terms of the sum in parentheses in (3.27) remain. Thus we have

$$\begin{aligned} & \left(\int_{\mathcal{B}_\epsilon^s} (\mu_i^s - \lambda_i) \frac{\partial \rho_i}{\partial \epsilon} da + \int_{\mathcal{B}_\epsilon^a} (\mu_i^a - \lambda_i) \frac{\partial \rho_i}{\partial \epsilon} da \right. \\ & \left. + \int_{\mathcal{V}} (\mu_i^v - \lambda_i) \frac{\partial \rho_i^v}{\partial \epsilon} dv + \int_{\Sigma_\epsilon} (\mu_i^\Sigma - \lambda_i) \frac{\partial \Gamma_i}{\partial \epsilon} ds \right) \Big|_{\epsilon=0} = 0 \quad (3.29) \end{aligned}$$

By the arbitrariness of the variations in ρ_i , ρ_i^v and Γ_i , we observe that

$$\mu_i^s|_{\epsilon=0} = \mu_i^a|_{\epsilon=0} = \mu_i^v|_{\epsilon=0} = \mu_i^\Sigma|_{\epsilon=0} = \lambda_i \quad (3.30)$$

for all i throughout the film and the vapor.

Substituting (3.30) into (3.27), we have

$$\begin{aligned} & \left(\int_{\mathcal{B}_\epsilon^s} \mathbf{S}^s : \frac{\partial \mathbf{F}}{\partial \epsilon} da + \int_{\mathcal{B}_\epsilon^a} \mathbf{S}^a : \frac{\partial \mathbf{F}}{\partial \epsilon} da \right. \\ & \left. + \int_{\Sigma_\epsilon} \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} ds - \int_{\Sigma_\epsilon} \llbracket \Psi - \mu_i^\Sigma \rho_i \rrbracket V ds - \int_{\Sigma_\epsilon} (\psi - \mu_i^\Sigma \Gamma_i) \kappa V ds \right) \Big|_{\epsilon=0} = 0. \quad (3.31) \end{aligned}$$

By integration by parts with boundary condition (3.14)₁ and the divergence theorem, the preceding equation can be rewritten as

$$\left(- \int_{\mathcal{B}_\epsilon^s} \operatorname{div} \mathbf{S}^s \cdot \dot{\boldsymbol{\chi}} \, da - \int_{\mathcal{B}_\epsilon^a} \operatorname{div} \mathbf{S}^a \cdot \dot{\boldsymbol{\chi}} \, da - \int_{\Sigma_\epsilon} \llbracket \mathbf{S} \mathbf{m} \cdot \dot{\boldsymbol{\chi}} \rrbracket \, ds + \int_{\Sigma_\epsilon} \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} \, ds - \int_{\Sigma_\epsilon} \llbracket \Psi - \mu_i^\Sigma \rho_i \rrbracket V \, ds - \int_{\Sigma_\epsilon} (\psi - \mu_i^\Sigma \Gamma_i) \kappa V \, ds \right) \Big|_{\epsilon=0} = 0, \quad (3.32)$$

where $\dot{\boldsymbol{\chi}}$ denote the partial derivative with respect to the virtual time ϵ .

Consider a subclass of virtual changes where only virtual deformation can occur, i.e. $V = 0$. In this case, the normal time-derivative $\dot{\mathbf{e}}$ reduces to the ordinary time derivative and the compatibility condition (2.20) dictates that $\llbracket \dot{\boldsymbol{\chi}} \rrbracket = \mathbf{0}$. By the fact that Σ is closed, we have

$$- \int_{\mathcal{B}^s} \operatorname{div} \mathbf{S}^s \cdot \mathbf{v} \, da - \int_{\mathcal{B}^a} \operatorname{div} \mathbf{S}^a \cdot \mathbf{v} \, da - \int_{\Sigma} \left(\llbracket \mathbf{S} \rrbracket \mathbf{m} + \frac{\partial \boldsymbol{\sigma}}{\partial s} \right) \cdot \mathbf{v} \, ds = 0, \quad (3.33)$$

where

$$\mathbf{v} = \frac{\partial \boldsymbol{\chi}}{\partial \epsilon}(\mathbf{X}, \epsilon) \Big|_{\epsilon=0} \quad (3.34)$$

Since \mathbf{v} can be arbitrarily assigned, we have

$$\operatorname{div} \mathbf{S} = \mathbf{0} \quad (3.35)$$

in both of the bulk phases \mathcal{B}^s and \mathcal{B}^a , and

$$\llbracket \mathbf{S} \rrbracket \mathbf{m} + \frac{\partial \boldsymbol{\sigma}}{\partial s} = \mathbf{0} \quad (3.36)$$

on the interface Σ .

Substituting (3.35) into (3.32), we have, at $\epsilon = 0$

$$- \int_{\Sigma} \llbracket \mathbf{S} \mathbf{m} \cdot \mathbf{v} \rrbracket \, ds + \int_{\Sigma} \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} \, ds - \int_{\Sigma} \llbracket \Psi - \mu_i^\Sigma \rho_i \rrbracket V \, ds - \int_{\Sigma} (\psi - \mu_i^\Sigma \Gamma_i) \kappa V \, ds = 0. \quad (3.37)$$

Note that by the commutator relation [8, equation (14.15)], for any scalar, vector or tensor field φ , one has

$$\frac{\partial \dot{\varphi}}{\partial s} = \overline{\left(\frac{\partial \varphi}{\partial s} \right)} - \kappa V \frac{\partial \varphi}{\partial s}. \quad (3.38)$$

Therefore by replacing φ with $\boldsymbol{\chi}$, we have

$$\dot{\mathbf{e}} = \frac{\partial \dot{\boldsymbol{\chi}}}{\partial s} + \mathbf{e}\kappa V. \quad (3.39)$$

Then by the fact that Σ is closed, we have, through integration by parts

$$\int_{\Sigma} \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} \, ds = - \int_{\Sigma} \frac{\partial \boldsymbol{\sigma}}{\partial s} \cdot \dot{\boldsymbol{\chi}} \, ds + \int_{\Sigma} \boldsymbol{\sigma} \cdot \mathbf{e}\kappa V \, ds. \quad (3.40)$$

By (2.20), (2.23), (3.36) and the relation

$$\llbracket f_1 f_2 \rrbracket = \llbracket f_1 \rrbracket \langle\langle f_2 \rangle\rangle + \langle\langle f_1 \rangle\rangle \llbracket f_2 \rrbracket, \quad (3.41)$$

where f_1 and f_2 are any scalar, vector or tensor field that is smooth up to the interface, we calculate

$$- \llbracket \mathbf{S}\mathbf{m} \cdot \mathbf{v} \rrbracket - \frac{\partial \boldsymbol{\sigma}}{\partial s} \cdot \dot{\boldsymbol{\chi}} = - \langle\langle \mathbf{S}\mathbf{m} \rangle\rangle \cdot \llbracket \mathbf{v} \rrbracket - \frac{\partial \boldsymbol{\sigma}}{\partial s} \cdot \langle\langle \mathbf{F}\mathbf{m} \rangle\rangle V = \llbracket \mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m} \rrbracket V. \quad (3.42)$$

Eventually, we have

$$- \int_{\Sigma} (\llbracket \Psi - \mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m} - \mu_i^{\Sigma} \rho_i \rrbracket + (\psi - \boldsymbol{\sigma} \cdot \mathbf{e} - \mu_i^{\Sigma} \Gamma_i) \kappa) V \, ds = 0. \quad (3.43)$$

By invoking the thermodynamical relation (2.50) and (3.30) as well as the arbitrariness of V , we conclude that

$$\llbracket \omega - \mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m} \rrbracket = 0 \quad (3.44)$$

on the interface Σ where

$$\omega = \Psi - \mu_i \rho_i \quad (3.45)$$

is the grand canonical potential in the reference configuration.

Consider the special case where the Cauchy stress is spherical, i.e. $\mathbf{T} = -p\mathbf{1}$. Equation (3.44) reduces to

$$\llbracket \omega + Jp \rrbracket = \llbracket J(\hat{\omega} + p) \rrbracket = 0, \quad (3.46)$$

where $J = \det \mathbf{F}$ and $\hat{\omega}$ denotes the grand canonical potential in the current configuration. By the fact that $\hat{\omega} = -p$, equation (3.44) does not deliver new information in this case. The set of equilibrium conditions are given by (3.9), (3.30), and (3.36).

Let $\hat{\mathbf{m}}$ denote the unit normal of the interface in the current configuration that points to the amorphous phase. Note that \mathbf{m} and $\hat{\mathbf{m}}$ are related through

$$\hat{\mathbf{m}} = \frac{\mathbf{F}^{\pm-\top} \mathbf{m}}{\|\mathbf{F}^{\pm-\top} \mathbf{m}\|}. \quad (3.47)$$

Together with the definition of the first Piola-Kirchhoff stress (2.12) and the relation [12, (8.14)]

$$j = J^{\pm} \|\mathbf{F}^{\pm-\top} \mathbf{m}\|, \quad (3.48)$$

we have

$$\llbracket \mathbf{S} \rrbracket \mathbf{m} + \frac{\partial \sigma}{\partial s} = j \left(-\llbracket p \rrbracket \hat{\mathbf{m}} + \frac{\partial \sigma}{\partial \hat{s}} \right), \quad (3.49)$$

where \hat{s} is the arc length in the current configuration. Therefore (3.36) can be recast as

$$-\llbracket p \rrbracket \hat{\mathbf{m}} + \frac{\partial \sigma}{\partial \hat{s}} = \mathbf{0} \quad (3.50)$$

If we assume that the surface tension σ is constant, then by the Frenet relation, we have

$$-\llbracket p \rrbracket + \sigma \kappa = 0. \quad (3.51)$$

If the interface is a circle, then (3.51) reduces to the two-dimensional version of the classical Young-Laplace equation

$$-\llbracket p \rrbracket + \frac{\sigma}{r} = 0, \quad (3.52)$$

where r is the radius.

Chapter 4 Driving Force for Spherulitic Growth

This chapter will be devoted to the derivation of the thermodynamic driving force for spherulitic crystallization.

Continuum theories of phase transitions in solids have been studied extensively in the past few decades. Abeyaratne and Knowles [7] investigated the surface of strain discontinuity in a continuum media and no interfacial structure was considered. The driving traction was identified to be the quantity conjugate to the normal velocity and the product of the two gave the entropy production on the interface. Gurtin and Struthers [11], Gurtin [9, 10], Fried and Gurtin [8] studied phase interfaces of different kinds, including solid-vapor interface with adatom density; massless solid-solid interface, with the notion of configurational force balance. Jabbour, Man and Paroni [1] considered a special case where the phase transition was induced by solvent vapor. The proposed driving force had explicit dependence on the chemical potential of the vapor and delivered a constant growth rate of the crystalline phase.

In what follows, we will make the same assumptions as in the last chapter on the system under consideration. Specifically, we consider a thin-film, modeled as a planar object, which at all times consists of N components and of two phases, namely the crystalline phase and the amorphous phase. The region occupied by the crystalline phase is assumed to be bounded and simply connected while that of the amorphous phase can be either bounded or unbounded. The film is placed in a chamber filled with vapor of the same components and each of the components can undergo evaporation and condensation. The vapor is modeled as a mixture of ideal gases. It is assumed that there is no diffusion of any species occurring in the process and the entire system is at all times isothermal at absolute temperature T_b . Moreover, configurational forces will not be considered in this discussion.

We will proceed by writing down the equations of balance of mass, balance of linear and angular momentum, the first two laws of thermodynamics and eventually the imbalance of free energy, which will deliver the dissipation inequality upon localization. The driving force will be identified as the term that is conjugate to the normal velocity in the dissipation inequality.

Note that by the compatibility condition (2.20), the velocity field of the thin film generally suffers a jump discontinuity across the interface. So before diving into the derivation of the driving force, we first introduce the notion of the interface velocity and the Lagrangian description of the interface [24].

1 Interface velocity

Let \mathcal{B} be the reference configuration of the film and $\Sigma(t) \subset \mathcal{B}$ be the one-parameter family of smooth closed simple curves that represent the phase interface at each time t . The curves $\Sigma(t)$ separates \mathcal{B} into two parts, \mathcal{B}_t^s and \mathcal{B}_t^a . For each t , \mathcal{B}_t^s represents the region in the crystalline phase in the reference configuration and \mathcal{B}_t^a the amorphous phase. We use the same convention as described in the paragraph containing equation (2.15) for \mathbf{t} , \mathbf{m} and κ which denotes the unit tangent, unit normal and curvature of $\Sigma(t)$, respectively.

Let $\chi : \mathcal{B} \times [0, d] \rightarrow \mathbb{E}$ be the motion of the film in the time interval $[0, d]$, where \mathbb{E} is the two-dimensional Euclidean space. We assume that the motion χ satisfies the following conditions:

- χ is continuous on $\mathcal{B} \times [0, d]$,
- χ is smooth in $\overline{\mathcal{B}_t^s}$, (i.e. the closure of \mathcal{B}_t^s), and $\overline{\mathcal{B}_t^a}$,
- χ satisfies the compatibility condition (2.20).

We further assume that for different instants t_1 and t_2 , $\Sigma(t_1) \cap \Sigma(t_2) = \emptyset$, i.e., the interface sweeps through different material points of the film as it evolves. Fix

a point P_0 on $\Sigma(0)$ and take it as the starting point for measuring arc length. If $\hat{\mathbf{X}}(s)$ is the arc-length parametrization of the initial curve $\Sigma(0)$, then a generic point $\hat{\mathbf{X}}(s_0)$ in $\Sigma(0)$ is specified by a number s_0 , which is its distance from P_0 as measured along $\Sigma(0)$. The parametrization of the normal trajectory \mathcal{N}_{s_0} through $\hat{\mathbf{X}}(s_0)$ is the solution of the initial value problem:

$$\frac{d\mathbb{X}(t)}{dt} = V\mathbf{m}, \quad \mathbb{X}(0) = \hat{\mathbf{X}}(s_0); \quad (4.1)$$

see (2.17). We can use the same name s_0 to specify the points in $\Sigma(t)$. Indeed we can plot the normal trajectory \mathcal{N}_{s_0} that starts from a given point s_0 in $\Sigma(0)$ and use the same name “ s_0 ” for the point in $\Sigma(t)$ where \mathcal{N}_{s_0} meets $\Sigma(t)$; see Figure 4.1.

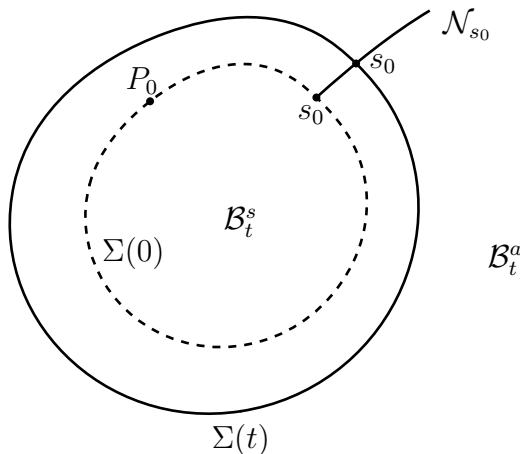


Figure 4.1: The initial curve $\Sigma(0)$ serving as a “reference”

Therefore we will use the name “ s_0 ” to label the particles of $\Sigma(t)$. The location of the particle labeled by s_0 at some time t is none other than the point in $\Sigma(t)$ with the same label.

Recall the normal time derivative of the motion in section 2. If $\mathbb{X}(t)$ in (4.1) is a parametrization of the normal trajectory \mathcal{N}_{s_0} , then $\dot{\mathbf{x}}$ in (2.23) gives the velocity in physical space of the interfacial particle labeled by s_0 . Hence we will call the quantity $\dot{\mathbf{x}}$ the interface velocity.

What we describe above can be taken as a Lagrangian description of the evolution of the interface: $\Sigma(0)$ is the “reference configuration” of the interface in the reference configuration of the body and $\dot{\chi}$ is the “material velocity” of the particle named s_0 .

Remark 3. It should be noted that it is not our intention to use $\Sigma(0)$ as the reference for the constitutive relation of the interface which we will discuss later in this chapter. It is solely for the introduction of the notion of interface velocity. \square

2 Balance of mass

For the i -th component, let ρ_i , Γ_i , \mathcal{F}_i and \mathfrak{f}_i be the bulk mass density, the excess mass density on the interface, the molecule flux from the vapor into the bulk and into the interface, respectively, measured per unit reference area or length. Thus $\mathcal{F}_i > 0$, $\mathfrak{f}_i > 0$ ($\mathcal{F}_i < 0$, $\mathfrak{f}_i < 0$) during condensation (evaporation). Let \mathcal{R} be a fixed region in \mathcal{B} , and $\mathcal{S}(t) = \mathcal{R} \cap \Sigma(t)$. We let the region \mathcal{R} be such that the tangential component of the velocity of the endpoints of $\mathcal{S}(t)$ is 0, i.e. $W = 0$ in (2.24), but otherwise arbitrary. We make the above choice because we find the tangential component W irrelevant to our discussion when configurational forces are not considered. For simplicity, we will drop the argument and write \mathcal{S} for the part of the interface that lies in \mathcal{R} ; see Figure 4.2.

The balance of mass requires that, for each component,

$$\frac{d}{dt} \left(\int_{\mathcal{R}} \rho_i da + \int_{\mathcal{S}} \Gamma_i ds \right) = \int_{\mathcal{R}} \mathcal{F}_i da + \int_{\mathcal{S}} \mathfrak{f}_i ds. \quad (4.2)$$

By applying (2.24) with $W = 0$ and (2.26), (4.2) becomes

$$\int_{\mathcal{R}} \dot{\rho}_i da - \int_{\mathcal{S}} \llbracket \rho_i \rrbracket V ds + \int_{\mathcal{S}} (\dot{\Gamma}_i - \Gamma_i \kappa V) ds = \int_{\mathcal{R}} \mathcal{F}_i da + \int_{\mathcal{S}} \mathfrak{f}_i ds, \quad (4.3)$$

where the overhead dot represents the partial derivative with respect to time t .

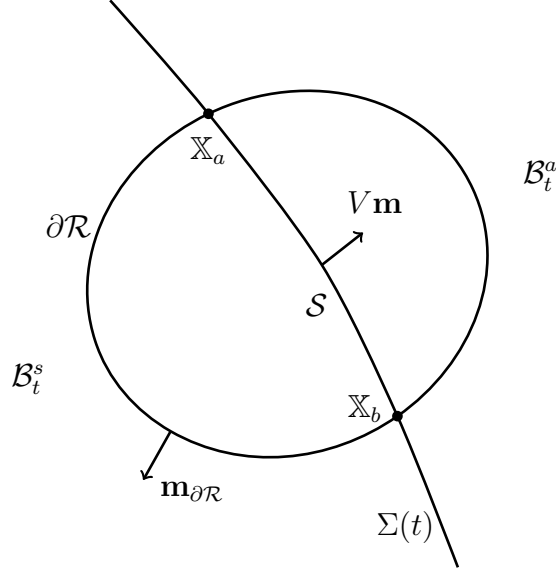


Figure 4.2: A sketch of the region \mathcal{R}

We first consider the case where \mathcal{R} lies entirely in \mathcal{B}_t^s or \mathcal{B}_t^a , i.e. $\mathcal{R} \cap \Sigma = \emptyset$. In this case, (4.3) reduces to

$$\int_{\mathcal{R}} (\dot{\rho}_i - \mathcal{F}_i) da = 0. \quad (4.4)$$

By the arbitrariness of \mathcal{R} , we conclude that

$$\dot{\rho}_i = \mathcal{F}_i \quad (4.5)$$

in both of the crystalline phase \mathcal{B}_t^s and the amorphous phase \mathcal{B}_t^a .

Next [13] we take the limit of (4.3) by shrinking $\partial\mathcal{R}$ down to \mathcal{S} in such a way that the area of \mathcal{R} tends to 0 while the length of \mathcal{S} remains unchanged. The area integrals will vanish in such a process, which leads to

$$-\int_{\mathcal{S}} \llbracket \rho_i \rrbracket V ds + \int_{\mathcal{S}} (\mathring{\Gamma}_i - \Gamma_i \kappa V) ds = \int_{\mathcal{S}} \mathfrak{f}_i ds \quad (4.6)$$

and therefore,

$$\mathring{\Gamma}_i - \Gamma_i \kappa V - \llbracket \rho_i \rrbracket V = \mathfrak{f}_i \quad (4.7)$$

on the interface $\Sigma(t)$ for each component.

Let

$$\rho = \sum_{i=1}^N \rho_i, \quad \Gamma = \sum_{i=1}^N \Gamma_i, \quad \mathcal{F} = \sum_{i=1}^N \mathcal{F}_i, \quad \mathfrak{f} = \sum_{i=1}^N \mathfrak{f}_i \quad (4.8)$$

denote the total mass density in the bulk, the total excess density on the interface, the net mass flux in the bulk, the net mass flux on the interface, respectively, and sum over all components in (4.5) as well as in (4.7), we then have the mass balance relation

$$\dot{\rho} = \mathcal{F} \quad (4.9)$$

in both \mathcal{B}_t^s and \mathcal{B}_t^a and

$$\dot{\Gamma} - \Gamma \kappa V - \llbracket \rho \rrbracket V = \mathfrak{f} \quad (4.10)$$

on the interface $\Sigma(t)$.

3 Balance of linear and angular momentum

Balance of linear momentum

We endowed the interface with non-zero excess mass density; therefore the interface carries momentum with it. By our notion of interface velocity introduced in section 1, the linear momentum associated with the interface is then

$$\int_{\Sigma} \Gamma \dot{\chi} ds.$$

In discussing the momentum balance and the first law of thermodynamics, we shall consider the following force system:

- S** first Piola-Kirchoff stress
 - σ** interfacial stress
 - B** body force in the bulk phases
 - b** body force on the interface.
- (4.11)

The first Piola-Kirchhoff stress **S** is defined in (2.12) and the interfacial stress **σ** represents the traction exerted on \mathcal{S} by the rest of the interface; see Fig 2.3 and the

discussion that follows equation (2.31). As opposed to contact forces such as \mathbf{S} and $\boldsymbol{\sigma}$, the body forces \mathbf{B} and \mathbf{b} represent forces that exerted on the interior points of a body by the environment. Specifically, \mathbf{B} and \mathbf{b} denote the force exerted on the points in the bulk phases $\mathcal{B}_t^s \cup \mathcal{B}_t^a$ and Σ , measured per unit area and per unit length, respectively. We will regard \mathbf{B} and \mathbf{b} as assignable¹.

Let \mathbf{u}_i denotes the velocity of the molecules of i -th component that are condensing or evaporating. Then

$$\mathbf{u}_i = \begin{cases} \mathbf{v}^v & \text{during condensation} \\ \dot{\boldsymbol{\chi}} & \text{during evaporation from interface} \\ \dot{\boldsymbol{\chi}} & \text{during evaporation from bulk phases} \end{cases}, \quad (4.12)$$

where \mathbf{v}^v is the velocity of the vapor flow. The balance of linear momentum requires that

$$\begin{aligned} \frac{d}{dt} \left(\int_{\mathcal{R}} \rho \dot{\boldsymbol{\chi}} da + \int_{\mathcal{S}} \Gamma \dot{\boldsymbol{\chi}} ds \right) = \\ \int_{\partial \mathcal{R}} \mathbf{S} \mathbf{m}_{\partial \mathcal{R}} ds + \int_{\partial \mathcal{S}} \boldsymbol{\sigma} + \int_{\mathcal{R}} \mathcal{F}_i \mathbf{u}_i da + \int_{\mathcal{S}} \mathbf{f}_i \mathbf{u}_i ds + \int_{\mathcal{R}} \mathbf{B} da + \int_{\mathcal{S}} \mathbf{b} ds, \end{aligned} \quad (4.13)$$

where $\mathbf{m}_{\partial \mathcal{R}}$ is the outward unit normal of $\partial \mathcal{R}$. In the above equation

$$\int_{\partial \mathcal{S}} \boldsymbol{\sigma} = \boldsymbol{\sigma}(\mathbb{X}_b, t) - \boldsymbol{\sigma}(\mathbb{X}_a, t)$$

where \mathbb{X}_a and \mathbb{X}_b are the endpoints of \mathcal{S} ; see Figure 4.2.

By applying the transport identities (2.24), (2.26), the divergence theorem with the presence of a discontinuity as well as invoking the mass balance relations (4.9) on (4.13), we obtain

$$\begin{aligned} \int_{\mathcal{R}} \mathcal{F} \dot{\boldsymbol{\chi}} + \rho \ddot{\boldsymbol{\chi}} da - \int_{\mathcal{S}} [[\rho \dot{\boldsymbol{\chi}}]] V ds + \int_{\mathcal{S}} \overset{\circ}{\Gamma} \dot{\boldsymbol{\chi}} - \Gamma \dot{\boldsymbol{\chi}} \kappa V ds = \\ \int_{\mathcal{R}} \operatorname{div} \mathbf{S} da + \int_{\mathcal{S}} [[\mathbf{S}]] \mathbf{m} ds + \int_{\mathcal{S}} \frac{\partial \boldsymbol{\sigma}}{\partial s} ds + \\ \int_{\mathcal{R}} \mathcal{F}_i \mathbf{u}_i da + \int_{\mathcal{S}} \mathbf{f}_i \mathbf{u}_i ds + \int_{\mathcal{R}} \mathbf{B} da + \int_{\mathcal{S}} \mathbf{b} ds. \end{aligned} \quad (4.14)$$

¹More discussion on the presence of body forces can be found in [6] and [25, Chapter 4]

In the case where \mathcal{R} lies entirely in the bulk phases, i.e. $\mathcal{R} \cap \Sigma = \emptyset$, (4.14) reduces to

$$\int_{\mathcal{R}} (\mathcal{F}\dot{\boldsymbol{\chi}} + \rho\ddot{\boldsymbol{\chi}} - \operatorname{div} \mathbf{S} - \mathcal{F}_i \mathbf{u}_i - \mathbf{B}) da = 0 \quad (4.15)$$

which leads to

$$\rho\ddot{\boldsymbol{\chi}} = \operatorname{div} \mathbf{S} + \sum_{i=1}^N \mathcal{F}_i (\mathbf{u}_i - \dot{\boldsymbol{\chi}}) + \mathbf{B} \quad (4.16)$$

upon localization.

Then by shrinking $\partial\mathcal{R}$ down to \mathcal{S} while keeping the length of \mathcal{S} unchanged, one can get the balance of linear momentum on the interface, i.e.

$$\overset{\circ}{\Gamma}\dot{\boldsymbol{\chi}} - \Gamma\dot{\boldsymbol{\chi}}\kappa V = [[\rho\dot{\boldsymbol{\chi}}]]V + [[\mathbf{S}]]\mathbf{m} + \frac{\partial\boldsymbol{\sigma}}{\partial s} + \mathbf{u}_i \mathbf{f}_i + \mathbf{b}. \quad (4.17)$$

Balance of angular momentum

Balance of angular momentum requires that

$$\begin{aligned} \frac{d}{dt} \left(\int_{\mathcal{R}} \boldsymbol{\chi} \times \rho\dot{\boldsymbol{\chi}} da + \int_{\mathcal{S}} \boldsymbol{\chi} \times \Gamma\dot{\boldsymbol{\chi}} ds \right) = \\ \int_{\partial\mathcal{R}} \boldsymbol{\chi} \times \mathbf{S}\mathbf{m}_{\partial\mathcal{R}} ds + \int_{\partial\mathcal{S}} \boldsymbol{\chi} \times \boldsymbol{\sigma} + \int_{\mathcal{R}} \boldsymbol{\chi} \times \mathcal{F}_i \mathbf{u}_i da + \int_{\mathcal{S}} \boldsymbol{\chi} \times \mathbf{f}_i \mathbf{u}_i ds + \\ \int_{\mathcal{R}} \boldsymbol{\chi} \times \mathbf{B} da + \int_{\mathcal{S}} \boldsymbol{\chi} \times \mathbf{b} ds. \end{aligned} \quad (4.18)$$

If we choose an orthonormal basis $\{\mathbf{e}_1, \mathbf{e}_2\}$, then $\mathbf{X} = X_i \mathbf{e}_i$, $\boldsymbol{\chi} = \chi_i \mathbf{e}_i$, $\mathbf{S} = S_{ij} \mathbf{e}_i \otimes \mathbf{e}_j$ and $\mathbf{m} = m_i \mathbf{e}_i$, where X_i , χ_i , S_{ij} and m_i are scalars. By introducing the alternating symbol ϵ_{ijk} which is defined by

$$\epsilon_{ijk} = \begin{cases} 1, & \text{if } \{i, j, k\} \text{ is an even permutation of } \{1, 2, 3\} \\ -1, & \text{if } \{i, j, k\} \text{ is an odd permutation of } \{1, 2, 3\} \\ 0, & \text{if an index is repeated} \end{cases}, \quad (4.19)$$

then for any vector $\mathbf{a} = a_i \mathbf{e}_i$ and $\mathbf{b} = b_i \mathbf{e}_i$, we let the cross product of two vectors \mathbf{a} and \mathbf{b} be

$$\mathbf{a} \times \mathbf{b} = \epsilon_{3jk} a_j b_k = a_1 b_2 - a_2 b_1.$$

Together with the divergence theorem, we have

$$\begin{aligned}
\int_{\partial\mathcal{R}} \boldsymbol{\chi} \times \mathbf{S}\mathbf{m} \, ds &= \int_{\partial\mathcal{R}} \chi_j S_{kl} m_l \epsilon_{3jk} \, ds \\
&= \int_{\mathcal{R}} \frac{\partial(S_{kl}\chi_j)}{\partial X_l} \epsilon_{3jk} \, da + \int_{\mathcal{S}} \boldsymbol{\chi} \times \llbracket \mathbf{S} \rrbracket \mathbf{m} \, ds \\
&= \int_{\mathcal{R}} \epsilon_{3jk} \frac{\partial S_{kl}}{\partial X_l} \chi_j \, da + \int_{\mathcal{R}} \epsilon_{3jk} S_{kl} \frac{\partial \chi_j}{\partial X_l} \, da + \int_{\mathcal{S}} \boldsymbol{\chi} \times \llbracket \mathbf{S} \rrbracket \mathbf{m} \, ds \\
&= \int_{\mathcal{R}} \boldsymbol{\chi} \times \operatorname{div} \mathbf{S} \, da + \int_{\mathcal{R}} \epsilon_{3jk} S_{kl} \frac{\partial \chi_j}{\partial X_l} \, da + \int_{\mathcal{S}} \boldsymbol{\chi} \times \llbracket \mathbf{S} \rrbracket \mathbf{m} \, ds.
\end{aligned} \tag{4.20}$$

Therefore by invoking the transport identities and the balance of mass relation (4.9), (4.18) can be rewritten as

$$\begin{aligned}
&\int_{\mathcal{R}} \boldsymbol{\chi} \times \mathcal{F}\dot{\boldsymbol{\chi}} + \boldsymbol{\chi} \times \rho\ddot{\boldsymbol{\chi}} \, da - \int_{\mathcal{S}} \boldsymbol{\chi} \times \llbracket \rho\dot{\boldsymbol{\chi}} \rrbracket V \, ds + \int_{\mathcal{S}} \boldsymbol{\chi} \times \overset{\circ}{\Gamma}\dot{\boldsymbol{\chi}} - \boldsymbol{\chi} \times \Gamma\dot{\boldsymbol{\chi}}\kappa V \, ds = \\
&\int_{\mathcal{R}} \boldsymbol{\chi} \times \operatorname{div} \mathbf{S} + \epsilon_{ijk} S_{kl} \frac{\partial \chi_j}{\partial X_l} \mathbf{e}_i \, da + \int_{\mathcal{S}} \frac{\partial \boldsymbol{\chi}}{\partial s} \times \boldsymbol{\sigma} + \boldsymbol{\chi} \times \llbracket \mathbf{S} \rrbracket \mathbf{m} + \boldsymbol{\chi} \times \frac{\partial \boldsymbol{\sigma}}{\partial s} \, ds + \\
&\int_{\mathcal{R}} \boldsymbol{\chi} \times \mathcal{F}_i \mathbf{u}_i \, da + \int_{\mathcal{S}} \boldsymbol{\chi} \times \mathbf{f}_i \mathbf{u}_i \, ds + \int_{\mathcal{R}} \boldsymbol{\chi} \times \mathbf{B} \, da + \int_{\mathcal{S}} \boldsymbol{\chi} \times \mathbf{b} \, ds.
\end{aligned} \tag{4.21}$$

With the help of balance of linear momentum (4.16), we conclude that away from the interface,

$$\epsilon_{3jk} S_{kl} \frac{\partial \chi_j}{\partial X_l} = 0,$$

which implies

$$\mathbf{S}\mathbf{F}^\top = \mathbf{F}\mathbf{S}^\top \tag{4.22}$$

in the bulk phases where \mathbf{F}^\top denotes the transpose of \mathbf{F} . By shrinking $\partial\mathcal{R}$ to \mathcal{S} and invoking the balance of linear momentum on the interface (4.17), we obtain

$$\frac{\partial \boldsymbol{\chi}}{\partial s} \times \boldsymbol{\sigma} = 0 \tag{4.23}$$

on the phase interface. Note that by (2.39), the interfacial stress vector is parallel to phase interface in the current configuration.

4 The first two laws of thermodynamics and the free energy imbalance

The first two laws of thermodynamics

Let \mathcal{E} and ε be the internal energy density in the bulk and on the interface, respectively. By the thermodynamical analysis in [1] and the first law of thermodynamics, we have

$$\begin{aligned}
 \frac{d}{dt} \left(\int_{\mathcal{R}} \left(\mathcal{E} + \frac{1}{2} \rho |\dot{\boldsymbol{\chi}}|^2 \right) da + \int_{\mathcal{S}} \left(\varepsilon + \frac{1}{2} \Gamma |\dot{\boldsymbol{\chi}}|^2 \right) ds \right) = \\
 \underbrace{\int_{\partial\mathcal{R}} \mathbf{S} \mathbf{m}_{\partial\mathcal{R}} \cdot \dot{\boldsymbol{\chi}} ds + \int_{\partial\mathcal{S}} \boldsymbol{\sigma} \cdot \dot{\boldsymbol{\chi}} + \sum_{i=1}^N \left(\int_{\mathcal{R}} \frac{p_i^v}{\rho_i^v} \mathcal{F}_i da + \int_{\mathcal{S}} \frac{p_i^v}{\rho_i^v} \mathbf{f}_i ds \right)}_{I_1} + \\
 \underbrace{\int_{\mathcal{R}} \mathbf{B} \cdot \dot{\boldsymbol{\chi}} da + \int_{\mathcal{S}} \mathbf{b} \cdot \dot{\boldsymbol{\chi}} ds}_{I_2} + \\
 \underbrace{\int_{\mathcal{R}} \mathcal{E}_i^v \mathcal{F}_i + \frac{1}{2} \mathcal{F}_i |\mathbf{u}_i|^2 da + \int_{\mathcal{S}} \mathcal{E}_i^v \mathbf{f}_i + \frac{1}{2} \mathbf{f}_i |\mathbf{u}_i|^2 ds}_{II} + \\
 \underbrace{\int_{\mathcal{R}} R da + \int_{\mathcal{S}} r ds}_{III}, \quad (4.24)
 \end{aligned}$$

where p_i^v , ρ_i^v and \mathcal{E}_i^v denote the partial pressure, mass density, and internal energy density of the i -th component in the vapor, respectively. The term $I_1 + I_2$ represents the power expended on the thin film. As noted in the paragraph above (4.11), the second term in I represents the power of the interfacial stress $\boldsymbol{\sigma}$. The energy flow from the vapor to the film is expressed by term II and the term III describes the heat supply to the film where R and r denote the heat supply densities into the bulk phases and the interface, respectively.

The second law asserts that the rate at which the entropy is increasing is not smaller than the entropy inflow. Therefore if we let η denote the entropy density in the bulk and ς denote the excess entropy density on the interface, then we have

$$\frac{d}{dt} \left(\int_{\mathcal{R}} \eta da + \int_{\mathcal{S}} \varsigma ds \right) \geq \int_{\mathcal{R}} \frac{R}{T_b} da + \int_{\mathcal{S}} \frac{r}{T_b} ds + \int_{\mathcal{R}} \eta_i^v \mathcal{F}_i da + \int_{\mathcal{S}} \eta_i^v \mathbf{f}_i ds, \quad (4.25)$$

where η_i^v is the entropy density of the vapor of the i -th component.

Free energy imbalance and constitutive relations

By combining (4.24), (4.25), we have the free energy inequality

$$\begin{aligned} \frac{d}{dt} \left(\int_{\mathcal{R}} \Psi + \frac{1}{2} \rho |\dot{\boldsymbol{\chi}}|^2 da + \int_S \psi + \frac{1}{2} \Gamma |\dot{\boldsymbol{\chi}}|^2 ds \right) \leq \\ \int_{\partial \mathcal{R}} \mathbf{S} \mathbf{m}_{\partial \mathcal{R}} \cdot \dot{\boldsymbol{\chi}} ds + \int_{\partial S} \boldsymbol{\sigma} \cdot \dot{\boldsymbol{\chi}} + \int_{\mathcal{R}} \mathbf{B} \cdot \dot{\boldsymbol{\chi}} da + \int_S \mathbf{b} \cdot \dot{\boldsymbol{\chi}} ds + \\ \int_{\mathcal{R}} \frac{1}{2} |\mathbf{u}_i|^2 \mathcal{F}_i da + \int_S \frac{1}{2} |\mathbf{u}_i|^2 \mathfrak{f}_i ds + \int_{\mathcal{R}} \mu_i^v \mathcal{F}_i da + \int_S \mu_i^v \mathfrak{f}_i ds, \end{aligned} \quad (4.26)$$

where $\Psi = \mathcal{E} - T_b \eta$ and $\psi = \varepsilon - T_b \varsigma$ are the Helmholtz free energy density in the bulk phases and the excess free energy density on the interface, respectively, and

$$\mu_i^v = \mathcal{E}_i^v - \eta_i^v T_b + \frac{p_i^v}{\rho_i^v} \quad (4.27)$$

is the chemical potential of the i -th component in the vapor.

In view of the mass balance relation (4.5), the balance of linear momentum relations (4.16), (4.17), we obtain the dissipation inequalities

$$\dot{\Psi} - \mathbf{S} : \dot{\mathbf{F}} - \mu_i^v \mathcal{F}_i - \sum_i \frac{1}{2} |\dot{\boldsymbol{\chi}} - \mathbf{u}_i|^2 \mathcal{F}_i \leq 0 \quad (4.28)$$

in both the crystalline phase and the amorphous phase and

$$\begin{aligned} - \llbracket \Psi \rrbracket V - \frac{1}{2} \llbracket \rho |\dot{\boldsymbol{\chi}}|^2 \rrbracket V + \dot{\psi} - \psi \kappa V + \frac{1}{2} \Gamma |\dot{\boldsymbol{\chi}}|^2 - \frac{1}{2} \Gamma |\dot{\boldsymbol{\chi}}|^2 \kappa V - \\ \llbracket \mathbf{S} \mathbf{m} \cdot \dot{\boldsymbol{\chi}} \rrbracket - \frac{\partial \boldsymbol{\sigma}}{\partial s} \cdot \dot{\boldsymbol{\chi}} - \boldsymbol{\sigma} \cdot \frac{\partial \dot{\boldsymbol{\chi}}}{\partial s} - \frac{1}{2} |\mathbf{u}_i|^2 \mathfrak{f}_i - \mu_i^v \mathfrak{f}_i - \mathbf{b} \cdot \dot{\boldsymbol{\chi}} \leq 0 \end{aligned} \quad (4.29)$$

on the interface upon localization of the free energy imbalance (4.26).

Next, we simplify the inequality (4.29) to convert it to a more informative form.

By the relation (2.23),

$$\begin{aligned} & - \llbracket \mathbf{S} \mathbf{m} \cdot \dot{\boldsymbol{\chi}} \rrbracket - \frac{\partial \boldsymbol{\sigma}}{\partial s} \cdot \dot{\boldsymbol{\chi}} \\ & = - \llbracket \mathbf{S} \mathbf{m} \rrbracket \cdot (\dot{\boldsymbol{\chi}} - \langle \mathbf{F} \mathbf{m} \rangle V) - \langle \mathbf{S} \mathbf{m} \rangle \cdot \llbracket \dot{\boldsymbol{\chi}} \rrbracket - \frac{\partial \boldsymbol{\sigma}}{\partial s} \cdot \dot{\boldsymbol{\chi}} \\ & = \llbracket \mathbf{S} \mathbf{m} \cdot \mathbf{F} \mathbf{m} \rrbracket V - \left(\Gamma \dot{\boldsymbol{\chi}} \cdot \sum_{i=1}^N \mathfrak{f}_i (\mathbf{u}_i - \dot{\boldsymbol{\chi}}) - \langle \rho \rangle \llbracket \dot{\boldsymbol{\chi}} \rrbracket V + \llbracket \rho \rrbracket \langle \mathbf{F} \mathbf{m} \rangle V^2 - \mathbf{b} \right) \cdot \dot{\boldsymbol{\chi}}. \end{aligned} \quad (4.30)$$

By (2.20), (3.41) as well as the relation

$$\langle\langle f_1 f_2 \rangle\rangle = \langle\langle f_1 \rangle\rangle \langle\langle f_2 \rangle\rangle + \frac{1}{4} \llbracket f_1 \rrbracket \llbracket f_2 \rrbracket$$

for f_1, f_2 being any scalar, vector or tensor fields, we have

$$\begin{aligned} & -\frac{1}{2} \llbracket \rho |\dot{\boldsymbol{\chi}}|^2 \rrbracket V + \langle\langle \rho \rangle\rangle \llbracket \dot{\boldsymbol{\chi}} \rrbracket \cdot \dot{\boldsymbol{\chi}} V - \llbracket \rho \rangle\rangle \langle\langle \mathbf{Fm} \rangle\rangle \cdot \dot{\boldsymbol{\chi}} V^2 \\ = & -\frac{1}{2} \langle\langle \rho \rangle\rangle \llbracket \mathbf{Fm} \cdot \mathbf{Fm} \rrbracket V^3 - \frac{1}{2} \llbracket \rho \rangle\rangle \langle\langle \dot{\boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} \rangle\rangle V - \llbracket \rho \rangle\rangle \langle\langle \mathbf{Fm} \rangle\rangle \cdot \langle\langle \dot{\boldsymbol{\chi}} \rangle\rangle V^2 - \llbracket \rho \rangle\rangle \langle\langle \mathbf{Fm} \rangle\rangle \cdot \langle\langle \mathbf{Fm} \rangle\rangle V^3 \\ = & -\frac{1}{2} \llbracket \rho \rangle\rangle \dot{\boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} V - \frac{1}{2} \llbracket \rho \mathbf{Fm} \cdot \mathbf{Fm} \rrbracket V^3. \end{aligned} \quad (4.31)$$

By invoking the mass balance on the interface (4.7), we have

$$-\Gamma \ddot{\boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} - \frac{1}{2} \llbracket \rho \rangle\rangle \dot{\boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} V + \frac{\overset{\circ}{}}{2} \Gamma |\dot{\boldsymbol{\chi}}|^2 - \frac{1}{2} \Gamma |\dot{\boldsymbol{\chi}}|^2 \kappa V = \frac{1}{2} \mathbf{f} \dot{\boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} \quad (4.32)$$

and

$$\frac{1}{2} \mathbf{f} \dot{\boldsymbol{\chi}} \cdot \dot{\boldsymbol{\chi}} + \sum_{i=1}^N \mathbf{f}_i (\mathbf{u}_i - \dot{\boldsymbol{\chi}}) \cdot \dot{\boldsymbol{\chi}} - \frac{1}{2} |\mathbf{u}_i|^2 \mathbf{f}_i = -\frac{1}{2} \sum_{i=1}^N |\mathbf{u}_i - \dot{\boldsymbol{\chi}}|^2 \mathbf{f}_i. \quad (4.33)$$

The last term on the right hand side of (4.31) can be recast as

$$\frac{1}{2} \llbracket \rho \mathbf{Fm} \cdot \mathbf{Fm} \rrbracket V^3 = \frac{1}{2} \llbracket \rho |\dot{\boldsymbol{\chi}} - \dot{\boldsymbol{\chi}}|^2 \rrbracket V, \quad (4.34)$$

which represent the jump in the relative kinetic energy [10].

With (4.30)–(4.34), (4.29) can be rewritten as

$$\begin{aligned} & - \left(\llbracket \Psi + \frac{1}{2} \rho |\dot{\boldsymbol{\chi}} - \dot{\boldsymbol{\chi}}|^2 \rrbracket - \llbracket \mathbf{Sm} \cdot \mathbf{Fm} \rrbracket \right) V - \frac{1}{2} \sum_{i=1}^N |\mathbf{u}_i - \dot{\boldsymbol{\chi}}|^2 \mathbf{f}_i \\ & \quad + \overset{\circ}{\psi} - \psi \kappa V - \boldsymbol{\sigma} \cdot \frac{\partial \overset{\circ}{\boldsymbol{\chi}}}{\partial s} - \mu_i^v \mathbf{f}_i \leq 0. \end{aligned} \quad (4.35)$$

Constitutive relations

We will take as basic hypothesis the requirement that all constitutive processes be consistent with the dissipation inequalities [12]. A constitutive process \mathbb{P} of the isothermal thermodynamic system in question is defined by

- $\boldsymbol{\chi} : \mathcal{B} \times [0, d] \rightarrow \mathbb{E}$, which satisfies the three conditions laid out at the beginning of Section 1 and specifies also the evolution of the interface $\Sigma(t)$, $t \in [0, d]$,
- $\rho_i(\mathbf{X}, t)$, where $\mathbf{X} \in \mathcal{B} \setminus \Sigma(t)$ for each t ,
- $\Gamma_i(\mathbf{X}, t)$, where $\mathbf{X} \in \Sigma(t)$ for each t ,
- the fields \mathbf{B} , \mathbf{b} , \mathcal{F}_i , \mathbf{f}_i , and \mathbf{v}^v ,

which for each time $t \in [0, d]$ satisfy the balance equations (4.5), (4.7), (4.16), and (4.17). Besides \mathbf{B} and \mathbf{b} , we also assume that \mathcal{F}_i , \mathbf{f}_i and \mathbf{v}^v are assignable.

We are focusing on spherulitic growth under isothermal condition at constant absolute temperature T_b . Therefore we will drop the explicit dependence on temperature in all the constitutive relations. We shall consider the relation

$$\Psi = \Psi(\mathbf{F}, \vec{\rho}) \quad (4.36)$$

that gives the free energy density in the reference configuration in both of the bulk phases where $\mathbf{F} = \text{grad } \boldsymbol{\chi}$ and $\vec{\rho} = \langle \rho_1, \dots, \rho_N \rangle$ denotes the list of mass densities.

By invoking the mass balance (4.5) and the constitutive relation (2.45), equation (4.28) reduces to

$$(\mu_i - \mu_i^v) \mathcal{F}_i - \sum_{i=1}^N \frac{1}{2} |\dot{\boldsymbol{\chi}} - \mathbf{u}_i|^2 \mathcal{F}_i \leq 0. \quad (4.37)$$

The reduced dissipation inequality (4.37) will put restrictions on the constitutive processes \mathbb{P} that the system may undergo.

Note that when the i -th component is evaporating, i.e. $\mathcal{F}_i < 0$ and $\mathbf{u}_i = \dot{\boldsymbol{\chi}}$ by (4.12), we have

$$-\frac{1}{2} |\dot{\boldsymbol{\chi}} - \mathbf{u}_i|^2 \mathcal{F}_i = 0 \quad (4.38)$$

for each admissible process \mathbb{P} . When the component is condensing, i.e., $\mathcal{F}_i > 0$ and $\mathbf{u}_i = \mathbf{v}^v$, the same term will be non-positive, i.e.,

$$-\frac{1}{2} |\dot{\boldsymbol{\chi}} - \mathbf{u}_i|^2 \mathcal{F}_i \leq 0. \quad (4.39)$$

Hence a sufficient condition for the bulk dissipation inequality (4.37) to be observed is that the inequality

$$(\mu_i - \mu_i^v)\mathcal{F}_i \leq 0 \quad (4.40)$$

holds for all admissible processes.

We proceed to prove that condition (4.40) is also necessary [26]. Indeed, suppose there is an admissible process \mathbb{P} for which

$$(\mu_i(\mathbf{X}_o, t_o) - \mu_i^v(\mathbf{X}_o, t_o))\mathcal{F}_i(\mathbf{X}_o, t_o) > 0 \quad (4.41)$$

for some $\mathbf{X}_o \in \mathcal{B} \setminus \Sigma(t)$ and $t_o \in [0, d]$. Let us construct a new admissible process $\tilde{\mathbb{P}}$ as follows: Replace the field \mathbf{v}^v (that pertains to the process \mathbb{P}) by the constant velocity field

$$\tilde{\mathbf{v}}^v = \mathbf{v}^v(\mathbf{X}_o, t_o). \quad (4.42)$$

Let $\tilde{\mathbf{u}}_i$ be the modified \mathbf{u}_i with \mathbf{v}^v replaced by $\tilde{\mathbf{v}}^v$. Let

$$\tilde{\mathbf{B}} = \mathbf{B} + \mathcal{F}_i \mathbf{u}_i - \mathcal{F}_i \tilde{\mathbf{u}}_i, \quad (4.43)$$

$$\tilde{\mathbf{b}} = \mathbf{b} + \mathfrak{f}_i \mathbf{u}_i - \mathfrak{f}_i \tilde{\mathbf{u}}_i. \quad (4.44)$$

We make no change on \mathcal{F}_i and \mathfrak{f}_i . Then the motion $\boldsymbol{\chi}$ and the fields ρ_i, Γ_i that pertain to process \mathbb{P} will satisfy the balance equations for the process $\tilde{\mathbb{P}}$, i.e., (4.5), (4.7), and

$$\rho \ddot{\boldsymbol{\chi}} = \text{div } \mathbf{S} + \sum_i^N \mathcal{F}_i (\tilde{\mathbf{u}}_i - \dot{\boldsymbol{\chi}}) + \tilde{\mathbf{B}}, \quad (4.45)$$

$$\bar{\Gamma} \overset{\circ}{\boldsymbol{\chi}} - \Gamma \overset{\circ}{\boldsymbol{\chi}} \kappa V = \llbracket \rho \dot{\boldsymbol{\chi}} \rrbracket V + \llbracket \mathbf{S} \rrbracket \mathbf{m} + \frac{\partial \boldsymbol{\sigma}}{\partial s} + \tilde{\mathbf{u}}_i \mathfrak{f}_i + \tilde{\mathbf{b}}. \quad (4.46)$$

Note that except for the assignable $\mathbf{B}, \mathbf{b}, \mathbf{v}^v$, and \mathbf{u}_i , which is none other than \mathbf{v}^v as far as condensing solvent molecules are concerned, all fields of the process $\tilde{\mathbb{P}}$ remain the same as their respective counterpart that pertains to \mathbb{P} . For the process $\tilde{\mathbb{P}}$, however, we have

$$(\mu_i(\mathbf{X}_o, t_o) - \mu_i^v(\mathbf{X}_o, t_o))\mathcal{F}_i(\mathbf{X}_o, t_o) > 0, \quad (4.47)$$

$$\frac{1}{2} |\dot{\boldsymbol{\chi}}(\mathbf{X}_o, t_o) - \tilde{\mathbf{u}}_i(\mathbf{X}_o, t_o)|^2 \mathcal{F}_i(\mathbf{X}_o, t_o) = 0. \quad (4.48)$$

Thus the constitutive process $\tilde{\mathbb{P}}$ violates the bulk dissipation inequality. Hence a necessary condition for the bulk dissipation inequality to hold is:

$$(\mu_i - \mu_i^v)\mathcal{F}_i \leq 0 \quad (4.49)$$

for all constitutive processes \mathbb{P} .

Therefore a sufficient and necessary condition for (4.37) to hold is that

$$(\mu_i - \mu_i^v)\mathcal{F}_i \leq 0 \quad (4.50)$$

In the product $(\mu_i - \mu_i^v)\mathcal{F}_i$ (no sum), $(\mu_i - \mu_i^v)$ is the thermodynamic driving force for the evaporation or condensation conjugate to the flux \mathcal{F}_i . If we further assume that the molecule flux of the i -th component \mathcal{F}_i is a smooth function of $\mu_i - \mu_i^v$ and other parameters which are suppressed for simplicity, i.e.

$$\mathcal{F}_i = \hat{\mathcal{F}}_i(\mu_i - \mu_i^v), \quad (4.51)$$

such that $\hat{\mathcal{F}}_i(0) = 0$, then linearization of (4.51) will lead to

$$\mathcal{F}_i = -K_i(\mu_i - \mu_i^v) \quad (\text{no sum}), \quad (4.52)$$

where $K_i \geq 0$ when the driving force is small. The preceding constitutive relation has the same theoretical status as Fourier's law of heat conduction and Fick's law of diffusion. It should be emphasized that (4.52) is a special case of the more general statement presented in the paragraph that follows equation (4.50). One has to appeal to experimental approaches to single out the constitutive relation for a specific material.

On the phase interface $\Sigma(t)$, we shall assume that

$$\psi = \psi_{\Sigma(t)}(\mathbf{e}, \vec{\Gamma}) \quad (4.53)$$

which represents the excess free energy per unit length in the reference configuration, where

$$\mathbf{e} = \frac{\partial \boldsymbol{\chi}}{\partial s}, \quad \vec{\Gamma} = \langle \Gamma_1, \dots, \Gamma_N \rangle. \quad (4.54)$$

Remark 4. The subscript $\Sigma(t)$ in (4.53) indicates that the reference of the the arguments of the function is $\Sigma(t)$ instead of $\Sigma(0)$, i.e. it is changing with time.

Gathering (2.46), (2.50) and the interfacial mass balance (4.7), we obtain

$$\begin{aligned}
\dot{\psi} - \psi\kappa V - \boldsymbol{\sigma} \cdot \frac{\partial \dot{\boldsymbol{\chi}}}{\partial s} - \mu_i^v \mathbf{f}_i &= \boldsymbol{\sigma} \cdot \dot{\mathbf{e}} + \mu_i^\Sigma \dot{\Gamma}_i - \psi\kappa V - \boldsymbol{\sigma} \cdot (\dot{\mathbf{e}} - \kappa V \mathbf{e}) - \mu_i^v \mathbf{f}_i \\
&= \mu_i^\Sigma (\mathbf{f}_i + \kappa V \Gamma_i + \llbracket \rho_i \rrbracket V) - (\psi - \boldsymbol{\sigma} \cdot \mathbf{e}) \kappa V - \mu_i^v \mathbf{f}_i \\
&= (\mu_i^\Sigma - \mu_i^v) \mathbf{f}_i - (\psi - \boldsymbol{\sigma} \cdot \mathbf{e} - \mu_i^\Sigma \Gamma_i) \kappa V + \mu_i^\Sigma \llbracket \rho_i \rrbracket V \\
&= (\mu_i^\Sigma - \mu_i^v) \mathbf{f}_i + \mu_i^\Sigma \llbracket \rho_i \rrbracket V.
\end{aligned}$$

Therefore, (4.35) can be rewritten as

$$-\left(\llbracket \Psi + \frac{1}{2} \rho |\dot{\boldsymbol{\chi}} - \dot{\boldsymbol{\chi}}|^2 \rrbracket - \llbracket \mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m} \rrbracket - \mu_i^\Sigma \llbracket \rho_i \rrbracket \right) V + (\mu_i^\Sigma - \mu_i^v) \mathbf{f}_i - \frac{1}{2} \sum_{i=1}^N |\mathbf{u}_i - \dot{\boldsymbol{\chi}}|^2 \mathbf{f}_i \leq 0. \quad (4.55)$$

In the experiments reported in [2] and [3], the measured values of V for the thin films studied were less than 3×10^{-5} m/s. By (4.34) the jump in relative kinetic energy is given by

$$\frac{1}{2} \llbracket \rho |\dot{\boldsymbol{\chi}} - \dot{\boldsymbol{\chi}}|^2 \rrbracket = \frac{1}{2} \llbracket \rho \mathbf{F}\mathbf{m} \cdot \mathbf{F}\mathbf{m} \rrbracket V^2 = \frac{1}{2} \llbracket \rho \rrbracket V^2 + \llbracket \rho \mathbf{m} \cdot \mathbf{E}\mathbf{m} \rrbracket V^2, \quad (4.56)$$

where \mathbf{E} is the Lagrangian strain. Hence this term would be very small with the measured values of V , which is consistent with the fact that motion in both bulk phases was unnoticed in those experiments. If motion in both bulk phases is negligible, then so is the jump in relative kinetic energy, which we shall neglect in our further discussions. In the discussion that follows, we will consider the dissipation inequality of the form

$$-\left(\llbracket \Psi \rrbracket - \llbracket \mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m} \rrbracket - \mu_i^\Sigma \llbracket \rho_i \rrbracket \right) V + (\mu_i^\Sigma - \mu_i^v) \mathbf{f}_i - \frac{1}{2} \sum_{i=1}^N |\mathbf{u}_i - \dot{\boldsymbol{\chi}}|^2 \mathbf{f}_i \leq 0. \quad (4.57)$$

By an argument similar to that which we use to prove (4.50) as a necessary and sufficient condition for the reduced bulk dissipation inequality (4.37) to hold for all

constitutive processes, it is easy to show that a necessary and sufficient condition for the reduced interfacial dissipation inequality (4.57) to be observed in all constitutive processes is that the inequality

$$-([\Psi] - [\mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m}] - \mu_i^\Sigma [\rho_i]) V + (\mu_i^\Sigma - \mu_i^v) \mathfrak{f}_i \leq 0 \quad (4.58)$$

holds for all constitutive processes.

Let us assume the

$$-([\Psi] - [\mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m}] - \mu_i^\Sigma [\rho_i]) V \leq 0 \quad (4.59)$$

and

$$(\mu_i^\Sigma - \mu_i^v) \mathfrak{f}_i \leq 0 \quad (4.60)$$

hold and let

$$f = [\Psi] - [\mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m}] - \mu_i^\Sigma [\rho_i] \quad (4.61)$$

be the driving force of the spherulitic growth. Then we have

$$\begin{aligned} fV > 0 & \quad \text{if } f \neq 0 \text{ and } V \neq 0, \\ \mathfrak{f}_i(\mu_i^\Sigma - \mu_i^v) < 0 & \quad \text{if } \mathfrak{f}_i \neq 0 \text{ and } \mu_i^\Sigma - \mu_i^v \neq 0. \end{aligned} \quad (4.62)$$

If we further assume that V and \mathfrak{f}_i are smooth functions for f and $\mu_i^\Sigma - \mu_i^v$, i.e.

$$V = \mathcal{V}(f), \quad \mathfrak{f}_i = \hat{\mathfrak{f}}_i(\mu_i^\Sigma - \mu_i^v) \quad (\text{no sum}), \quad (4.63)$$

and that $\mathcal{V}(0) = 0$ and $\hat{\mathfrak{f}}_i(0) = 0$, then with small driving forces f and $\mu_i^\Sigma - \mu_i^v$, we have

$$V = \frac{f}{\beta} \quad (4.64)$$

and

$$\mathfrak{f}_i = -k_i(\mu_i^\Sigma - \mu_i^v) \quad (\text{no sum}) \quad (4.65)$$

by linearization where $\beta = 1/\mathcal{V}'(0)$ is referred to as the kinetic coefficient.

When the equilibrium conditions (3.30) and (3.44) are satisfied, it is clear that f will vanish.

If we consider the special case where the Cauchy stress is hydrostatic, i.e. $\mathbf{T} = -p\mathbf{I}$, then $\mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m} = -Jp$ where $J = \det \mathbf{F}$. We further assume that the normal velocity V is small, then by (4.34), the relative kinetic energy is of higher order term of V and thus ignored. Thus

$$\begin{aligned} f &= \llbracket \Psi + Jp - \mu_i^\Sigma \rho_i \rrbracket \\ &= \llbracket (\mu_i - \mu_i^\Sigma) \rho_i \rrbracket. \end{aligned} \quad (4.66)$$

One can compare (4.66) with the driving force

$$\hat{f} = \llbracket (\mu_i - \mu_i^v) \rho_i \rrbracket \quad (4.67)$$

derived in [1] where the interface was assumed to be massless.

Other than the obvious mathematical cause of the difference between the two driving forces, i.e. assumption that the interface is massless or not, one can look at it in a more physics point of view [26].

In fact, \hat{f} can be seen as a special case of f when the evaporation/condensation happens reversibly. Let us consider a simple example to illustrate the difference.

Assume that the amorphous phase of a certain one-component B involatile solid film can form a solution with molecules of solvent A , while the crystallized phase rejects all molecules of A . Consider the growth of a spherulite in a film where the amorphous phase initially carries “dissolved” A at concentration ρ_0 . Since there is no diffusion, the molecules of A are rejected into the interface and then evaporate. Indeed, after an initial buildup, the density of the A will come to a steady state, i.e. $\overset{\circ}{\Gamma}_A$ is practically 0. If we assume that the curvature κ is small enough that the term $\Gamma_A \kappa V$ can be neglected, then by (4.7), we have $0 > -\rho_0 V \approx \mathbf{f}_A$ which implies $\mu_A^\Sigma > \mu_A^v$. Therefore

$$-\mu_A^\Sigma \rho_0 < -\mu_A^v \rho_0. \quad (4.68)$$

If we assume all other quantities are the same, then f will deliver a smaller driving force than \hat{f}

Chapter 5 Effects of Prestress on Directional Dependence of Growth Rate

In this chapter, we will derive a formula for the normal velocity V of the phase interface as a function of the direction of its outward unit normal and get an estimate on the shape of the spherulite under V to investigate the effect of prestress.

Consider a homogeneous amorphous thin film modeled as a two dimensional planar object. It is kept at a fixed temperature T_b and is subjected to boundary traction so that the film initially carries a homogeneous Cauchy stress \mathbf{T}^a . We will assume that the amorphous film is isotropic¹ and linearly elastic.

The following assumptions are crucial to our discussion:

- the amorphous film possesses a stress-free natural configuration;
- the natural configuration will be taken as reference, denoted by \mathcal{B} , for each material point in the thin-film at all time (before and after crystallization);
- after spherulitic crystallization of the material point, the chosen reference configuration carries an initial stress;
- the amorphous phase can be taken at all time as in a state of a fixed homogeneous Cauchy stress \mathbf{T}^a ;
- the crystalline phase is also isotropic.

In the experiments, the ternary thin film is composed of chemical components, say A, B and S , among which A, B can be taken as involatile and S be of minuscule amount. Since no diffusion of any species is considered, the density of A and B are

¹We take the definition given in [25], i.e. a material is *isotropic* if there is a reference placement κ such that the peer group $\mathcal{G}_\kappa \supset O(2)$. If we let $\mathbf{S} = \hat{\mathbf{S}}(\mathbf{E})$, then $\mathbf{Q}\hat{\mathbf{S}}(\mathbf{E})\mathbf{Q}^\top = \hat{\mathbf{S}}(\mathbf{Q}\mathbf{E}\mathbf{Q}^\top)$ for any $\mathbf{Q} \in O(2)$

constants in each phase, as is suggested by (4.5) with $\mathcal{F}_i = 0$ for $i = A, B$. Note that since components A and B are involatile and non-diffusive, there is no mechanism in our model that may cause the density to change in the reference configuration before and after the phase transition, i.e. $[[\rho_i]] = 0$ for $i = A, B$. Furthermore, since the amount of component S is very small, for the sake of simplicity, we will also assume that $[[\rho_S]] = 0$. Therefore by (4.61) and (4.64), we have

$$\beta V = [[\Psi - \mathbf{S}\mathbf{m} \cdot \mathbf{F}\mathbf{m}]], \quad (5.1)$$

where $\beta > 0$ is referred to as the kinetic coefficient. In the discussion that follows, we will also ignore the effect of inertia which is usually a reasonable assumption to make when dealing with phase-transition phenomena in deformable solids [12, footnote 116].

1 Stress tensors and Helmholtz free energy

In this section, we will discuss the stress tensors and derive the expression for the Helmholtz free energy for later use. The following discussion is based on a private communication [26].

Consider a material point with 3 components A, B and S at the reference configuration. The discussion that follows can be extended to any number of components easily. Henceforth we shall use a superposed \star to specify the quantities pertaining to the material point at the reference configuration. Suppose that the constitutive equations of a material point depend also on a list of microstructural variables $\vec{\xi} = (\xi_1^\star, \dots, \xi_k^\star)$.

With the assumption that the component S be of very small amount, the effect of the change in density of S can be ignored and thus, the film can be treated as a closed system, i.e. $\rho_i = \rho_i^\star$ for $i = A, B, S$.

Let $\mathbf{E} = \frac{1}{2}(\mathbf{H} + \mathbf{H}^\top)$ be the infinitesimal strain tensor where $\mathbf{H} = \mathbf{F} - \mathbf{1}$ is the displacement gradient. The relationship between the infinitesimal strain tensor and the (finite) Lagrange strain tensor is

$$\mathbf{E} = \frac{1}{2}(\mathbf{F}^\top \mathbf{F} - \mathbf{1}) = \frac{1}{2}(\mathbf{H} + \mathbf{H}^\top + \mathbf{H}^\top \mathbf{H}) = \mathbf{E} + o(\|\mathbf{H}\|). \quad (5.2)$$

For a closed system with fixed temperature, i.e. constant T , if the second Piola-Kirchhoff stress $\mathbf{P}(\cdot; \vec{\xi})$ is a smooth function of $(T, \mathbf{E}, \rho_A, \rho_B, \rho_S)$, We have [27, 28]

$$\mathbf{P}(T, \mathbf{E}, \rho_A, \rho_B, \rho_S; \vec{\xi}) = \overset{\star}{\mathbf{T}} + \mathbb{L}(T, \mathbf{0}, \overset{\star}{\rho}_A, \overset{\star}{\rho}_B, \overset{\star}{\rho}_S; \vec{\xi})[\mathbf{E}], \quad (5.3)$$

where

$$\overset{\star}{\mathbf{T}} = \mathbf{P}(T, \mathbf{0}, \overset{\star}{\rho}_A, \overset{\star}{\rho}_B, \overset{\star}{\rho}_S; \vec{\xi}) \quad (5.4)$$

denotes the initial stress and

$$\mathbb{L}(T, \mathbf{0}, \overset{\star}{\rho}_A, \overset{\star}{\rho}_B, \overset{\star}{\rho}_S; \vec{\xi}) = D_2 \mathbf{P}(T, \mathbf{0}, \overset{\star}{\rho}_A, \overset{\star}{\rho}_B, \overset{\star}{\rho}_S; \vec{\xi}). \quad (5.5)$$

In (5.3), the $o(\|\mathbf{E}\|)$ terms are dropped. For notational simplicity, we will suppress the dependence of \mathbb{L} on $T, \overset{\star}{\rho}_i$ (for $i = A, B, S$) and $\vec{\xi}$. Note that with fixed $T, \overset{\star}{\rho}_i$ and $\vec{\xi}$, \mathbb{L} is a constant fourth-order tensor with major and minor symmetries.

In what follows we derive, for the amorphous and for the crystalline phase, respectively, an expression that delineates the dependence of the free energy density on \mathbf{E} when all the other independent variables remain fixed. The empirical Harting's Law [29] suggests that for many materials the initial stress $\overset{\star}{\mathbf{T}}$ should be treated as a microstructural variable, and that \mathbb{L} can be taken as [27, 30]

$$\mathbb{L}[\mathbf{E}] = \mathbb{C}[\mathbf{E}] + \mathbb{D}[\overset{\star}{\mathbf{T}}, \mathbf{E}]. \quad (5.6)$$

where \mathbb{C} is a fourth-order tensor and \mathbb{D} is a sixth-order tensor which will vanish when $\overset{\star}{\mathbf{T}} = \mathbf{0}$.

By integrating (2.54) with constant T and ρ_i , we have

$$\Psi = \overset{\star}{\Psi} + \overset{\star}{\mathbf{T}} : \mathbf{E} + \frac{1}{2} \mathbb{L}[\mathbf{E}] : \mathbf{E}, \quad (5.7)$$

where $\star\Psi$ is the free energy density pertaining to the reference configuration.

Now for our application, prior to crystallization the reference configuration \mathcal{B} is natural, i.e. $\star\mathbf{T}^a = \mathbf{0}$. Then by (5.3) and (5.6)

$$\mathbf{P}^a = \mathbb{C}^a[\mathbf{E}^a]. \quad (5.8)$$

It follows from (2.12) and (2.13) that

$$\mathbf{P}^a(\mathbf{E}^a) = (\mathbf{I} - \mathbf{H}^a) \mathbb{C}^a[\mathbf{E}^a] = \mathbf{S}^a \quad (5.9)$$

and

$$\mathbf{T}^a = (1 + \text{tr} \mathbf{H}^a) \mathbb{C}^a[\mathbf{E}^a] (\mathbf{I} + \mathbf{H}^{a\top}) = \mathbf{S}^a, \quad (5.10)$$

i.e. the Cauchy stress, the first and second Piola-Kirchhoff stress coincide up to $o(\|\mathbf{H}^a\|)$ when there is no initial stress. The free energy in the amorphous phase is then, by letting $\star\mathbf{T} = \mathbf{0}$ in (5.7)

$$\Psi^a = \star\Psi^a + \frac{1}{2} \mathbb{C}^a[\mathbf{E}^a] : \mathbf{E}^a. \quad (5.11)$$

After spherulitic crystallization, the material points in the crystalline phase will carry an initial stress $\star\mathbf{T}^s$. Then it follows from (5.3) and (5.6) that

$$\mathbf{P}^s(\mathbf{E}^s) = \star\mathbf{T}^s + \mathbb{C}^s[\mathbf{E}^s] + \mathbb{D}[\star\mathbf{T}^s, \mathbf{E}^s]. \quad (5.12)$$

By the relation between the first and second Piola-Kirchhoff stress, we have

$$\begin{aligned} \mathbf{S}^s &= \mathbf{F}^s \mathbf{P}^s \\ &= (\mathbf{I} + \mathbf{H}^s)(\star\mathbf{T}^s + \mathbb{L}[\mathbf{E}^s]) \\ &= \star\mathbf{T}^s + \mathbf{H}^s \star\mathbf{T}^s + \mathbb{L}[\mathbf{E}^s]. \end{aligned} \quad (5.13)$$

The free energy density in the crystalline phase is then

$$\Psi^s = \star\Psi^s + \star\mathbf{T}^s : \mathbf{E}^s + \frac{1}{2} \mathbb{L}^s[\mathbf{E}^s] : \mathbf{E}^s. \quad (5.14)$$

A comparison of (5.7) with the integrated fundamental equation [31, cf. (54.15), where the case with a natural reference configuration is considered]

$$\Psi = \mathbf{P} : \mathbf{E} + \rho_i \mu_i \quad (5.15)$$

may raise the question that whether the two formulas are compatible. The answer is affirmative. In fact by (2.54) and (5.15), we can get, for constant temperature T , the Gibbs-Duhem equation

$$\mathbf{E} : d\mathbf{P} + \rho_i d\mu_i = 0. \quad (5.16)$$

Since the incremental tensor \mathbb{L} is a constant fourth-order tensor,

$$\mathbf{E} : d\mathbf{P} = \mathbf{E} : d(\mathbf{T} + \mathbb{L}[\mathbf{E}]) = \mathbb{L}[\mathbf{E}] : d\mathbf{E}. \quad (5.17)$$

By integrating (5.16) from state $(T, \mathbf{0}, \rho_A^*, \rho_B^*, \rho_S^*; \vec{\xi})$ to state $(T, \mathbf{E}, \rho_A^*, \rho_B^*, \rho_S^*; \vec{\xi})$, we get

$$\rho_i^* \mu_i = \rho_i^* \mu_i^* - \frac{1}{2} \mathbb{L}[\mathbf{E}] : \mathbf{E}. \quad (5.18)$$

Substituting (5.18) into (5.15), we obtain

$$\Psi = \rho_i^* \mu_i^* + \mathbf{T} : \mathbf{E} + \frac{1}{2} \mathbb{L}[\mathbf{E}] : \mathbf{E}, \quad (5.19)$$

which agrees with (5.7) with $\Psi = \rho_i^* \mu_i^*$.

2 Derivation of growth rate

Let σ_1 and σ_2 be the principal stresses of the prestress tensor $\mathbf{S}^a = \mathbf{T}^a$, and let \mathbf{e}_1 and \mathbf{e}_2 be orthonormal vectors that agree with the principal stress directions. Let

$$\bar{\sigma} = \frac{1}{2}(\sigma_1 + \sigma_2), \quad \tau = \frac{1}{2}(\sigma_1 - \sigma_2). \quad (5.20)$$

We assume that $\tau \neq 0$. Under the Cartesian coordinate system defined by the basis \mathbf{e}_i ($i = 1, 2$), the stress \mathbf{S}^a is given by

$$\mathbf{S}^a = \bar{\sigma} \mathbf{I} + \begin{pmatrix} \tau & 0 \\ 0 & -\tau \end{pmatrix}. \quad (5.21)$$

By a judicious choice of \mathbf{e}_1 and \mathbf{e}_2 , we can make τ positive or negative as we please.

By the representation theorem for isotropic linear tensor functions [12, Section 52.4.1] and (5.8), we have

$$\mathbf{S}^a = \lambda^a(\text{tr } \mathbf{E}^a)\mathbf{I} + 2\mu^a\mathbf{E}^a, \quad (5.22)$$

where λ^a and μ^a are elastic constants that satisfy

$$\mu^a > 0, \quad \lambda^a + \mu^a > 0 \quad (5.23)$$

and we have used relations (5.9) and (5.8). Moreover, we assume that the initial infinitesimal rotation

$$\mathbf{W}^a = \frac{1}{2}(\mathbf{H}^a - \mathbf{H}^{a\top}) = \mathbf{0}. \quad (5.24)$$

It follows from (5.21) and (5.22) that under the basis \mathbf{e}_i ($i = 1, 2$) the strain \mathbf{E}^a is given by

$$\mathbf{E}^a = \frac{\bar{\sigma}}{2(\lambda^a + \mu^a)}\mathbf{I} + \frac{1}{2\mu^a} \begin{pmatrix} \tau & 0 \\ 0 & -\tau \end{pmatrix}. \quad (5.25)$$

Suppose at some instant a nucleus of spherulitic crystallization is formed and at time t the spherulite occupies a region \mathcal{B}_t^s in the film. In what follows we consider the growth of the spherulitic region and adopt the physical assumption that outside \mathcal{B}_t^s , the amorphous phase can be taken at all time as in a state of a fixed homogeneous stress \mathbf{S}^a .

Let \mathbf{T}^s be the initial stress carried by the the part of the reference configuration where spherulitic crystallization occurred. As was shown in [30, 32], with the presence of the initial stress and in two-dimensional case,

$$\mathbb{D}[\mathbf{T}^s, \mathbf{E}^s] = \beta_1(\text{tr } \mathbf{E}^s)(\text{tr } \mathbf{T}^s)\mathbf{I} + \beta_2(\text{tr } \mathbf{T}^s)\mathbf{E}^s + \beta_3 \left((\text{tr } \mathbf{E}^s)\mathbf{T}^s + (\text{tr } \mathbf{E}^s\mathbf{T}^s)\mathbf{I} \right) \quad (5.26)$$

where $\beta_1, \beta_2, \beta_3$ are material constants. Since we assume that the material point in the crystallized phase remains isotropic, then $\mathbf{T}^s = -p_0\mathbf{I}$ [33]. By (5.13), the stress

tensor in the crystalline phase can be written as

$$\mathbf{S}^s = -p_0\mathbf{I} - p_0\mathbf{H}^s + \tilde{\lambda}^s(\text{tr}\mathbf{E}^s)\mathbf{I} + 2\tilde{\mu}^s\mathbf{E}^s, \quad (5.27)$$

where

$$\tilde{\lambda}^s = \lambda^s - 2p_0\beta_1 - 2p_0\beta_3, \quad (5.28)$$

$$\tilde{\mu}^s = \mu^s - p_0\beta_2, \quad (5.29)$$

and λ^s and μ^s are the elastic constants of the prestressed crystalline phase.

Since $\mathbf{F} = \mathbf{I} + \mathbf{H}$, we have

$$\llbracket \mathbf{F} \rrbracket = \llbracket \mathbf{H} \rrbracket. \quad (5.30)$$

Then by (5.24), $\mathbf{H}^{a+} = \mathbf{E}^a$. The kinematic compatibility condition (2.20) requires that

$$\mathbf{H}^{a+} - \mathbf{H}^{s-} = \mathbf{E}^a - \mathbf{H}^{s-} = \mathbf{a} \otimes \mathbf{m} \quad (5.31)$$

for some vector \mathbf{a} . Let

$$\mathbf{m} = (\cos \theta, \sin \theta) \quad (5.32)$$

under the basis \mathbf{e}_i ($i = 1, 2$). We choose a new orthonormal basis $\mathbf{f}_1, \mathbf{f}_2$ such that $\mathbf{f}_1 = \mathbf{m}$. Under this basis we have

$$\mathbf{a} \otimes \mathbf{m} = \begin{pmatrix} a_1 & 0 \\ a_2 & 0 \end{pmatrix}, \quad (5.33)$$

and the stress and strain tensor in the amorphous phase under the new basis become

$$\mathbf{S}^a = \bar{\sigma}\mathbf{I} + \tau \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ -\sin 2\theta & -\cos 2\theta \end{pmatrix}, \quad (5.34)$$

$$\mathbf{E}^a = \frac{\bar{\sigma}}{2(\lambda^a + \mu^a)}\mathbf{I} + \frac{\tau}{2\mu^a} \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ -\sin 2\theta & -\cos 2\theta \end{pmatrix}, \quad (5.35)$$

respectively. It follows that

$$\begin{aligned}\mathbf{H}^{s^-} &= \mathbf{E}^a - \mathbf{a} \otimes \mathbf{m} \\ &= \frac{\bar{\sigma}}{2(\lambda^a + \mu^a)} \mathbf{I} + \frac{\tau}{2\mu^a} \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ -\sin 2\theta & -\cos 2\theta \end{pmatrix} - \begin{pmatrix} a_1 & 0 \\ a_2 & 0 \end{pmatrix}\end{aligned}\quad (5.36)$$

and

$$\begin{aligned}\mathbf{E}^{s^-} &= \frac{1}{2} \left(\mathbf{H}^{s^-} + (\mathbf{H}^{s^-})^\top \right) \\ &= \frac{\bar{\sigma}}{2(\lambda^a + \mu^a)} \mathbf{I} + \frac{\tau}{2\mu^a} \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ -\sin 2\theta & -\cos 2\theta \end{pmatrix} - \begin{pmatrix} a_1 & a_2/2 \\ a_2/2 & 0 \end{pmatrix}.\end{aligned}\quad (5.37)$$

Then by (5.27), we have

$$\begin{aligned}\mathbf{S}^{s^-} &= \left(\frac{\tilde{\lambda}^s + \tilde{\mu}^s - p_0/2}{\lambda^a + \mu^a} \bar{\sigma} - \tilde{\lambda}^s a_1 - p_0 \right) \mathbf{I} \\ &\quad + \frac{\tilde{\mu}^s - p_0/2}{\mu^a} \tau \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ -\sin 2\theta & -\cos 2\theta \end{pmatrix} + \begin{pmatrix} (p_0 - 2\tilde{\mu}^s)a_1 & -\tilde{\mu}^s a_2 \\ (p_0 - \tilde{\mu}^s)a_2 & 0 \end{pmatrix}.\end{aligned}\quad (5.38)$$

By neglecting inertia effects, (4.17) reduces to

$$\llbracket \mathbf{S}\mathbf{m} \rrbracket + \frac{\partial \boldsymbol{\sigma}}{\partial s} = \mathbf{0}.\quad (5.39)$$

When the radius of the spherulite is sufficiently large, the effect of the interfacial stress $\boldsymbol{\sigma}$ can be neglected. Thus we have $\llbracket \mathbf{S}\mathbf{m} \rrbracket = \mathbf{0}$, i.e. $\mathbf{S}^{a^+}\mathbf{m} = \mathbf{S}^{s^-}\mathbf{m}$ on the interface. With (5.34) and (5.38), we obtain the equations

$$\frac{\tilde{\lambda}^s + \tilde{\mu}^s - p_0/2}{\lambda^a + \mu^a} \bar{\sigma} - p_0 - \tilde{\lambda}^s a_1 + \frac{\tilde{\mu}^s - p_0/2}{\mu^a} \tau \cos 2\theta + (p_0 - 2\tilde{\mu}^s)a_1 = \bar{\sigma} + \tau \cos 2\theta,\quad (5.40)$$

$$-\frac{\tilde{\mu}^s - p_0/2}{\mu^a} \tau \sin 2\theta + (p_0 - \tilde{\mu}^s)a_2 = -\tau \sin 2\theta,\quad (5.41)$$

from which we get

$$a_1 = \frac{1}{p_0 - \tilde{\lambda}^s - 2\tilde{\mu}^s} \left(p_0 + \left(1 - \frac{\tilde{\lambda}^s + \tilde{\mu}^s - p_0/2}{\lambda^a + \mu^a} \right) \bar{\sigma} + \tau \left(1 - \frac{\tilde{\mu}^s - p_0/2}{\mu^a} \right) \cos 2\theta \right), \quad (5.42)$$

$$a_2 = \frac{\left(\frac{\tilde{\mu}^s - p_0/2}{\mu^a} - 1 \right) \tau \sin 2\theta}{p_0 - \tilde{\mu}^s}. \quad (5.43)$$

It follows that

$$\llbracket \mathbf{S} \mathbf{m} \cdot \mathbf{F} \mathbf{m} \rrbracket = a_1 (\bar{\sigma} + \tau \cos 2\theta) - a_2 \tau \sin 2\theta. \quad (5.44)$$

The growth rate relation is given by (5.1) and the Helmholtz free energy densities for the amorphous phase and the crystalline phase are give by (5.11) and (5.14), respectively.

We calculate

$$\mathbf{S}^a : \mathbf{E}^a = \frac{\bar{\sigma}^2}{\lambda^a + \mu^a} + \frac{\tau^2}{\mu^a} \quad (5.45)$$

and

$$\begin{aligned} \mathbb{L}^s[\mathbf{E}^{s^-}] : \mathbf{E}^{s^-} &= \frac{\tilde{\lambda}^s + \tilde{\mu}^s}{(\lambda^a + \mu^a)^2} \bar{\sigma}^2 - \frac{2(\tilde{\lambda}^s + \tilde{\mu}^s)}{\lambda^a + \mu^a} a_1 \bar{\sigma} \\ &\quad + \frac{\tau^2 \tilde{\mu}^s}{(\mu^a)^2} - \frac{2\tilde{\mu}^s \tau}{\mu^a} (a_1 \cos 2\theta - a_2 \sin 2\theta) \\ &\quad + \tilde{\lambda}^s a_1^2 + 2\tilde{\mu}^s a_1^2 + \tilde{\mu}^s a_2^2 \end{aligned} \quad (5.46)$$

and therefore with (5.1) and (5.44)–(5.46),

$$\begin{aligned}
\beta V &= \overset{\star}{\Psi}^a - \overset{\star}{\Psi}^s & (5.47) \\
&+ \frac{1}{2} \left(\frac{\bar{\sigma}^2}{\lambda^a + \mu^a} \left(1 - \frac{\tilde{\lambda}_s + \tilde{\mu}_s}{\lambda^a + \mu^a} \right) + \frac{\tau^2}{\mu^a} \left(1 - \frac{\tilde{\mu}_s}{\mu^a} \right) \right. \\
&+ 2 \frac{\tilde{\lambda}_s + \tilde{\mu}_s}{\lambda^a + \mu^a} \bar{\sigma} a_1 + \frac{2\tilde{\mu}_s \tau}{\mu^a} (a_1 \cos 2\theta - a_2 \sin 2\theta) \\
&\left. - \tilde{\lambda}_s a_1^2 - 2\tilde{\mu}_s a_1^2 - \tilde{\mu}_s a_2^2 \right) + \frac{p_0 \bar{\sigma}}{\lambda^a + \mu^a} - p_0 a_1 \\
&- (a_1 (\bar{\sigma} + \tau \cos 2\theta) - a_2 \tau \sin 2\theta).
\end{aligned}$$

From the expressions of a_1 and a_2 in (5.42), we observe that the growth-rate formula is in the form

$$\beta V = A + B \cos 2\theta + C \cos^2 2\theta, \quad (5.48)$$

where A, B, C are all constants. A straightforward calculation shows that

$$\begin{aligned}
B &= \frac{\tau}{p_0 - \tilde{\lambda}^s - 2\tilde{\mu}^s} \left(1 - \frac{\tilde{\mu}^s - p_0/2}{\mu^a} \right) \left(\left(\frac{\tilde{\mu}^s + \tilde{\lambda}^s}{\lambda^a + \mu^a} - 1 \right) \bar{\sigma} - p_0 + \right. & (5.49) \\
&\left. \left(p_0 + \bar{\sigma} \left(1 - \frac{\tilde{\lambda}^s + \tilde{\mu}^s - p_0/2}{\lambda^a + \mu^a} \right) \left(\frac{\tilde{\mu}^s - \mu^a}{\mu^a - \tilde{\mu}^s - p_0/2} - \frac{p_0}{p_0 - \tilde{\lambda}^s - 2\tilde{\mu}^s} \right) \right) \right)
\end{aligned}$$

and

$$\begin{aligned}
C &= \tau^2 \left(1 - \frac{\tilde{\mu}^s - p_0/2}{\mu^a} \right)^2 & (5.50) \\
&\left(\frac{\tilde{\mu}^s - \mu^a}{\mu^a - \tilde{\mu}^s - p_0/2} \left(\frac{1}{p_0 - \tilde{\lambda}^s - 2\tilde{\mu}^s} - \frac{1}{p_0 - \tilde{\mu}^s} \right) - \frac{\tilde{\lambda}^s/2 + \tilde{\mu}^s}{(p_0 - \tilde{\lambda}^s - 2\tilde{\mu}^s)^2} + \frac{\tilde{\mu}^s}{2(p_0 - \tilde{\mu}^s)^2} \right).
\end{aligned}$$

It is obvious from the explicit expression of B and C that when $\tau = 0$, i.e. the prestress is spherical, we will recover the constant growth rate feature obtained in [1].

A rotation of the Cartesian coordinate system by $\pi/2$ about the normal direction of the planar film changes θ to $\theta + \pi/2$ and the growth-rate formula (5.48) is recast as

$$\beta V = A - B \cos 2\theta + C \cos^2 2\theta. \quad (5.51)$$

Hence, without loss of generality, we may restrict our attention to (5.48) with $B \geq 0$. We are primarily interested in situations defined by $A > 0$, $A \gg B$ and $A \gg |C|$.

Examples of polar plots of βV versus θ for growth-rate formula (5.48) are given in Figure 5.1 and Figure 5.2. For comparison purposes, we include in Figure 5.3 and Figure 5.4 where B and C are of the same order as A . It should be emphasized that these polar plots show the dependence of βV on the direction of the unit outward normal \mathbf{m} of the interface.

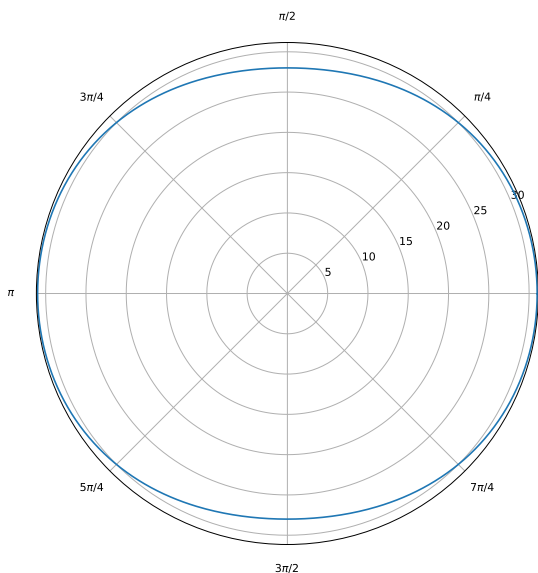


Figure 5.1: $A=30$, $B=1.5$, $C=-0.5$

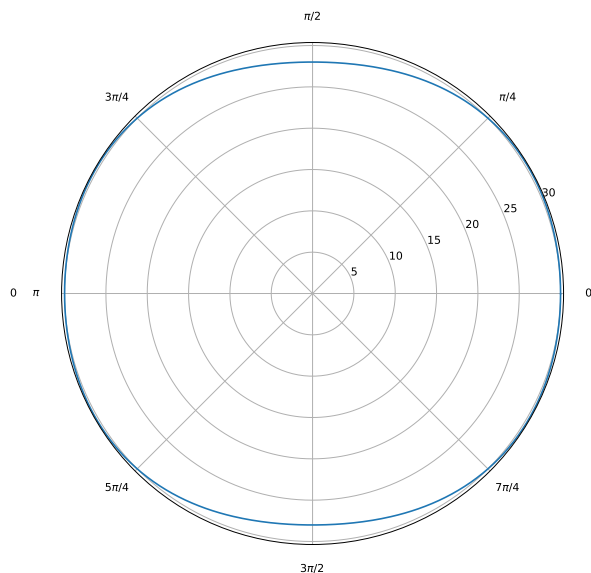


Figure 5.2: $A=30$, $B=1.0$, $C=-1.0$

3 Implication on the shape of the phase boundary

Let the arc-length map $s = s(p, t)$ be prescribed where $s(\cdot, t)$ is the arc-length for the curve $\Sigma(t)$ at time t and p is the parameter. Then

$$\frac{d\theta}{ds} = \kappa \tag{5.52}$$

where θ is defined in (5.32). As was noted in the paragraph containing equation (2.15), under our choice of \mathbf{t} and \mathbf{m} , $\kappa < 0$ for the curve that is the boundary of a strictly convex region.

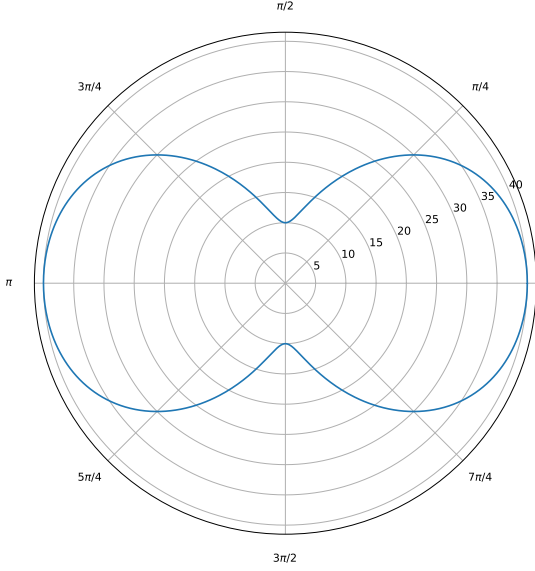


Figure 5.3: $A=30, B=15, C=-5$

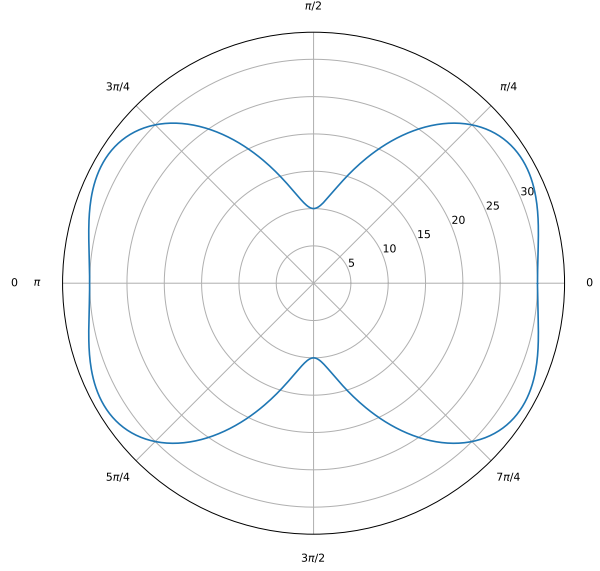


Figure 5.4: $A=30, B=10, C=-10$

The rate of change of curvature following a normal trajectory of the evolving curve is given by [8]

$$\dot{\kappa} = V_{ss} + \kappa^2 V \quad (5.53)$$

where

$$V_{ss} = V_{\theta\theta}\kappa^2 + V_{\theta}\kappa_{\theta}\kappa. \quad (5.54)$$

It is clear from (5.53) and (5.54) that $\dot{\kappa} = 0$ when $\kappa = 0$. Thus if the initial curve $\Sigma(0)$ is the boundary of a convex region, then the region that $\Sigma(t)$ encloses will be convex for all t .

Consider the special case where the initial curve $\Sigma(0)$ is a circle of radius r_0 ; see Figure 5.5. As was noted in the beginning of section 3, we choose a fixed point on the initial curve and measure from it the arc-length to the intersection of $\Sigma(0)$ with the axes \mathbf{e}_1 and \mathbf{e}_2 , which we call s_1 and s_2 , respectively. By symmetry, the normal trajectories starting from s_1 and s_2 will always stay on the axes; see \mathcal{N}_{s_1} and \mathcal{N}_{s_2} in Figure 5.5. Therefore, at time t , the evolving curve $\Sigma(t)$ will intersect with the axis \mathbf{e}_1 at the point $(r_0 + t(A + B + C)/\beta, 0)$ and with the axis \mathbf{e}_2 at the point $(0, r_0 + t(A - B + C)/\beta)$. Note that $(A - B - |C|)/\beta \leq V \leq (A + B + |C|)/\beta$.

The curve will always enclose a convex region and stay between two dashed circles of radius $r_0 + t(A + B + |C|)/\beta$ and $r_0 + t(A - B - |C|)/\beta$. One can compare the predicted shape of a spherulite in Figure 5.5 with the experimental picture in Figure 1.1.

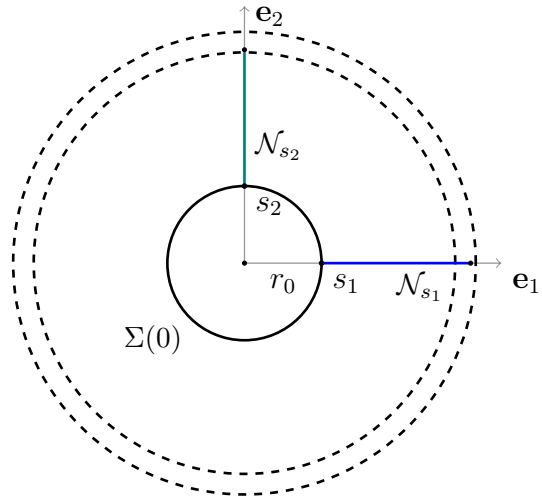


Figure 5.5: A sketch of shape estimation (not to scale)

Chapter 6 Closing Remarks and Future Work

In this dissertation, we have derived the driving force of solvent-vapor induced crystallization with the interface treated as a thermodynamic system of its own right.

We derived the equilibrium condition of a system that consists of two bulk phases, a phase interface, and the vapor with the same constituents. The approach we took was slightly different than the usual practice, namely by minimizing the ballistic free energy and incorporating the interfacial thermodynamic relation (2.50).

We then proceeded to investigating the driving force of the crystallization. In doing so, we treated the interface as a whole thermodynamical system by endowing it with excess quantities. The driving force was identified and was compared with the counterpart proposed in [1].

The last part of the dissertation was focused on the effect of the prestress on the shape of the crystallized spherulite. We derived a new formula for the normal velocity and inferred the shape of the spherulite under it. In [1], the stress tensors in both phases were assumed to be spherical. Under this assumption and with other physically reasonable assumptions, the growth rate was shown to be constant. The implication of a constant growth rate is that the shape of the spherulite would approach that of a disc as time elapses. A comparison between Fig 1.1 and Fig 5.5 might suggest that the present theory delivers a better prediction.

We introduced the “Lagrange description” of the interface and the particle name “ s_0 ” in section 1. This seems counter-intuitive at first glance since the particle labeled by “ s_0 ” pertains to different material points as time evolves. However the Lagrange description was originally used in fluid mechanics. In a gas flow, the gas molecules that occupy a “material point” are constantly in the process of being partially replaced by its peers. In fact, open systems by definition can exchange matter with

the environment and generally will not consist of the same constituents all the time. Therefore we consider the particle name “ s_0 ” well defined [24].

In deriving the formula for the normal velocity V , for the sake of simplicity, we ignored the effect of inertia and interfacial stress. For a better result, one needs to incorporate the aforementioned aspects into the calculation.

In modeling the phase interface, we adopt the model proposed by Gibbs where a dividing surface of zero thickness is introduced and endowed with excess quantities to replace the interfacial region. Other models such as the ones proposed by Guggenheim or Hansen [34] are plausible choices which in fact comprises possible direction of future work.

In one of the experiments reported in [2] and [3], TES ADT and a small-molecule additive were both dissolved in toluene. Different roles played by the additive were postulated and examined; see [35, 36]. In another possible scenario, after crystallization the additive is expelled from the spherulite into the amorphous phase. Therefore building a model that allows diffusion is another possible direction of future work.

In the present work, the thin film is modeled as a 2-dimensional object. However, in reality the film has certain thickness. The effect of thickness of the film on the spherulitic growth remains to be investigated.

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