A general stability criterion for droplets on structured substrates

M Brinkmann[1,2]**, J Kierfeld**[1] **and R Lipowsky**[1]

[1] MPI für Kolloid und Grenzflächenforschung, D-14424 Potsdam, Germany
[2] Interdisciplinary Research Institute, c/o IEMN, F-59652 Villeneuve d'Ascq, France

Abstract
Wetting morphologies on solid substrates, which may be chemically or topographically structured, are studied theoretically by variation of the free energy which contains contributions from the substrate surface, the fluid–fluid interface and the three-phase contact line. The first variation of this free energy leads to two equations—the classical Laplace equation and a generalized contact line equation—which determine stationary wetting morphologies. From the second variation of the free energy we derive a general spectral stability criterion for stationary morphologies. In order to incorporate the constraint that the displaced contact line must lie within the substrate surface, we consider only normal interface displacements but introduce a variation of the domains of parametrization.

PACS numbers: 02.30.Xx, 68.08.Bc, 47.20.Dr

List of symbols

α	Vapour or low density phase
β	Wetting liquid or high density phase
δ^n	nth variation
δ_c^1	Variation including variation of arguments on contact line
δ_s^2	Restricted second variation at a stationary shape
ε	Small real number, subscript for varied quantities
θ	Local contact angle
σ	Rigid substrate
ω	Torsion of a surface along its boundary
ψ	Normal displacement field
Λ	Line tension

μ	Eigenvalue to second variation of free energy
Σ	Surface tension
$A = \|\mathscr{A}\|$	Area of surface $\mathscr{A}$
$\mathscr{C}$	Plane curve
c_1, c_2	Principal curvatures
$c_\parallel$	Normal curvature, parallel to three-phase contact line
$c_\perp$	Normal curvature, perpendicular to three-phase contact line
$\mathcal{F}$	Free energy, general
$\tilde{\mathcal{F}}$	Free energy, pressure ensemble
$\mathcal{F}_\Lambda$	Free energy of three-phase contact line
$\mathcal{F}_\Sigma$	Interfacial free energy
$\mathscr{I}$	Interval $[0, L_{\alpha\beta\sigma}]$
G	Gaussian curvature
$\tilde{g}$	Metric tensor or first fundamental form
g_{ij}	Components of metric tensor
h^i_j	Components of extrinsic curvature tensor
$\mathscr{L}_{\alpha\beta\sigma}$	Three-phase contact line
$L = \|\mathscr{L}\|$	Length of space curve $\mathscr{L}$
L^*_β	Length scale of line tension
L_β	Linear dimension of droplet
ℓ	Arclength parameter
$\ell_{\alpha\beta}$	Width of $\alpha\beta$ interface
$\ell_{\alpha\beta\sigma}$	Width of three-phase contact line
ℓ_G	Capillary length
(s^1, s^2)	Coordinates on $\alpha\beta$ interface
(t^1, t^2)	Coordinates on substrate σ
$S_\varepsilon T_\varepsilon$	Coordinates of the varied three-phase contact line
$\mathscr{D}, \mathscr{G} \subset \mathbb{R}^2$	Domain of parametrization
M	Mean curvature
∇	Covariant operator
$\nabla^2 = \nabla \cdot \nabla$	Laplace–Beltrami operator
$\mathbf{N}$	Surface normal of $\alpha\beta$ interface
$\mathbf{n}$	Conormal of the $\alpha\beta$ interface
$\mathbf{R}$	Vector or parametrization of $\alpha\beta$ interface
$\mathbf{r}$	Vector or parametrization of three-phase contact line
$\mathbf{t}$	Tangent of three-phase contact line
$V = \|\mathscr{V}\|$	Volume of spatial region $\mathscr{V}$
$\mathbf{U}, \mathbf{V} \subset \mathbb{R}^3$	Neighbourhood
W	Wettability of substrate σ
$\mathbf{X}$	Vector or parametrization of substrate σ

1. Introduction

The morphology of droplets wetting a solid substrate is strongly influenced by topographical and/or chemical surface patterns [1]. During the past decade, much effort has been devoted, both theoretically and experimentally, to this interplay between surface structure and wetting morphologies. Experimental techniques such as micro-contact printing [2] or monolayer lithography [3] allow the fabrication of imprinted or structured planar surfaces with tailored patterns of lyophilic and lyophobic surface domains. The resulting wetting morphologies are

governed by the patterns of different wettability over a wide range of droplet volumes, as has been demonstrated in recent experiments on liquid channels [4, 5]. In these experiments, it has also been shown that an increase of the droplet volume beyond a critical value leads to a morphological transition from the liquid channel to a bulged configuration [4, 5]. Such a transition offers the possibility to fuse different microcompartments of liquid in a controlled manner, which is an attractive option for a variety of microfluidic applications [6].

The experimentally observed shapes of wetting droplets are theoretically obtained by minimizing the free energy of the droplet. In general, this free energy contains contributions from the substrate surface, from the fluid–fluid interface and from the line tension of the three-phase contact line. For uniform substrate surfaces, this minimization leads to the classical equations of Laplace and Young–Dupré. For chemically and topographically structured substrate surfaces, a generalized contact line equation has been recently derived by Swain and Lipowsky [7], see further below. These two equations provide necessary conditions for the stationary configurations of the droplet but are not sufficient in order to determine whether these configurations represent *minima* of the free energy and thus experimentally observable shapes. Indeed, stationary droplet configurations may represent saddle points which exhibit one or several unstable directions in the free energy landscape of configurations.

In order to determine the stability of a stationary droplet state, one has to study the second variation of the droplet's free energy. The issue becomes particularly relevant at a morphological transition where two distinct shapes exchange their stability. Such morphological transitions have been found for a variety of domain patterns consisting of circular [8], striped [4, 9] and ring-shaped surface domains [10].

In the micrometre regime, the droplet shapes are governed by their interfacial free energies. Contributions arising from the three-phase contact line are expected to become relevant at a droplet size of about one hundred nanometres [1]. Thus, line tension effects are particularly relevant for small wetting structures such as liquid bridges between wetting droplets [9]. In the general framework of thermodynamics, a line contribution to the free energy of a wetting droplet is defined as an excess free energy related to the structural perturbations along the contact line [11]. Thermodynamic equilibrium implies that the interfacial tensions or free energies are always positive. In contrast, the sign of the line tension may be positive or negative [11]. Within effective interface models, the sign of the line tension is found to depend on the details of the molecular interactions as reflected in the specific form of the interface potentials, see, e.g., [12].

For uniform substrate surfaces, the equation of Young and Dupré represents the condition of mechanical equilibrium of the three-phase contact line between liquid, vapour and substrate. This equation has to be generalized for non-vanishing line tension as was first realized in [13] and extended to certain surface domain geometries in [14, 15]. More recently, Swain and Lipowsky [7] derived a rather general contact line equation which is valid for rigid substrates, both topographically and chemically structured.

Several experimental studies have recently provided evidence for line tension effects on wetting phenomena [16, 17]. In [17], the line tension corrections predicted by the contact line equation in [7] have been determined by AFM measurements of the effective interface potentials close to the contact line as well as contact angle measurements on droplets with highly curved contact lines. Results derived from both methods agree and give a line tension of the order of $|\Lambda| \approx 10^{-10}$ J m^{-1}. Depending on the liquid and the substrate, Λ is observed to have positive or negative sign [17]. In a recent experiment [18], the shape of nanometre-sized polystyrene droplets has been measured using AFM. A systematic comparison between the contact angles of droplets at different sizes shows that, in this case, the line tension attains a value of $|\Lambda| \simeq 0.5 \times 10^{-10}$ J m^{-1}.

In this paper, we start from basic concepts of interface thermodynamics using a general expression for the free energy of a droplet on a structured substrate including interfacial and line free energies. In the framework of differential geometry and variational calculus, we derive the first variation of the free energy and recover the general contact line equation for stationary states as previously derived by Swain and Lipowsky [7]. We then proceed to calculate the second variation of the droplet's free energy for such a stationary configuration and, in this way, obtain a general criterion for the local mechanical stability of stationary droplet shapes.

A major technical difficulty which has to be properly addressed in the variational calculation is that the contact line of the deformed droplet shape must stay within the substrate surface. In order to incorporate this constraint, previous approaches have used shape deformations of the liquid–vapour interface which were parametrized both by normal and by tangential displacements [19–21]. The tangential displacements can then be chosen in such a way that the contact line stays within the substrate surface.

In this paper, we use a different calculational method for the derivation of the second variation of free energy. The shape deformations are entirely parametrized in terms of normal displacements of the initial configuration. Instead of introducing tangential displacements, the necessary shift of the contact line is incorporated by varying the domain of parametrization of the liquid–vapour interface and the wetted substrate. This scheme is rather transparent, and one can easily see how the various terms of the second variation arise from the different terms of the first variation.

The paper is organized as follows. A short summary of the thermodynamic description of fluids wetting a chemically structured substrate is given in section 2. In section 3, we consider general normal displacements of the droplet shape and calculate the variations of general functionals defined on the droplet interface and contact line. The constraint that the contact line should be displaced within the substrate surface is incorporated by introducing variations of the domain of integration. In section 4, the variation of the droplet's free energy is derived in detail. The second variation leads to a general stability criterion as shown in section 5.

2. Free energy

Let us consider a droplet of a liquid β with fixed volume wetting a rigid and inert substrate σ. The wetted substrate is in contact with another third phase, denoted by α. The phase α may be a vapour phase or another liquid phase. We assume that all phases are in thermal and mechanical equilibrium. Concerning chemical equilibrium we may focus on two ideal situations that can be realized in wetting experiments:

(i) The wetting phase β is non-volatile, that is, an exchange of molecules between α and β is *slow* on the time scale of the experiment. Since all liquids are highly incompressible at normal conditions, i.e., at temperatures and bulk pressures far from a critical point, the volume V_β of a β droplet is virtually constant throughout the wetting process. In typical wetting experiments, the β phase may form disconnected droplets. Each β droplet attains a local minimum of the droplet's interfacial and line free energy for its given individual volume. Due to condensation of molecules from the α phase the volume of a β droplet might increase in time and, provided that mechanical equilibration is fast, we may observe a sequence of local minima. If these conditions are fulfilled we will speak of a *volume ensemble* because the droplet volume represents, in principle, an accessible control parameter of the system.

(ii) The exchange of molecules between the surrounding α phase and the β droplet is *fast* and the system reaches *chemical equilibrium*. Whenever the number of particles in the α phase is much larger than in the β phase we can regard the α phase as a reservoir of molecules which fixes the chemical potential of each species in the entire system. In the case of a one-component and simple liquid β coexisting with its vapour α we are able to express the difference between the chemical potential μ, set by α, and the chemical potential μ^0 at coexistence of the bulk phases by the pressure difference $P_\alpha - P_\beta$ across the $\alpha\beta$ interface. Thus, we refer to this situation as the *pressure ensemble*.

In general, the free energy $\mathcal{F}$ of the droplet consists of different contributions related to the bulk of the droplet, its interfaces and the three-phase contact line [1]. Which of these contributions govern its morphology depends on the length scale of the droplet. Also gravitational and van der Waals forces can give relevant contributions to the free energy on large and small scales, respectively.

2.1. Interfacial and contact line energies

At fixed intensive quantities the interfacial free energy $\mathcal{F}_\Sigma$ is homogeneous in the area $A_{ij} = |\mathscr{A}_{ij}|$ of each interface $\mathscr{A}_{ij}$ between adjacent homogeneous phases i and j. Because of chemical inhomogeneities of the substrate walls σ, both surface tensions $\Sigma_{\alpha\sigma}$ and $\Sigma_{\beta\sigma}$ are functions of the position $\mathbf{X}$ on the substrate surface $\mathscr{A}_\sigma$. Thus, we cast the droplet's interfacial free energy into a form

$$\mathcal{F}_\Sigma = \Sigma_{\alpha\beta} A_{\alpha\beta} + \int_{\mathscr{A}_{\beta\sigma}} \mathrm{d}A \, [\Sigma_{\beta\sigma}(\mathbf{X}) - \Sigma_{\alpha\sigma}(\mathbf{X})], \tag{1}$$

where $\mathscr{A}_{\beta\sigma}$ is the surface of σ wetted by β.

To proceed with basic definitions, the three-phase contact line $\mathscr{L}_{\alpha\beta\sigma}$ of the droplet is defined as the set of points where the $\alpha\beta$ interface terminates on the surface of σ, i.e. $\mathscr{L}_{\alpha\beta\sigma} = \mathscr{A}_{\alpha\beta} \cap \mathscr{A}_\sigma$. On a chemically homogeneous substrate wall the related free energy $\mathcal{F}_\Lambda$ is simply proportional to the length $L_{\alpha\beta\sigma} = |\mathscr{L}_{\alpha\beta\sigma}|$ of the three-phase contact line. However, on heterogeneous substrate walls one might expect a spatially non-uniform line tension $\Lambda(\mathbf{X})$ and a line integral

$$\mathcal{F}_\Lambda = \int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L \, \Lambda(\mathbf{X}) \tag{2}$$

accounts for the contact line free energy. One may also consider droplets wetting plane and homogeneous crystalline or nano-patterned surfaces where the line tension Λ is expected to become a function of the local orientation of the contact line.

The line free energy $\mathcal{F}_\Lambda$ becomes comparable with the interfacial free energy if the linear dimension, L_β, of the droplet is of the order of the characteristic length [1]

$$L_\beta^* = \Lambda/\Sigma_{\alpha\beta} \simeq \ell_{\alpha\beta\sigma}^2/\ell_{\alpha\beta} \tag{3}$$

as follows from dimensional analysis where $\ell_{\alpha\beta}$ is the width of the $\alpha\beta$ interface and $\ell_{\alpha\beta\sigma}$ is the width of the contact line.

As long as the linear dimension of the droplet satisfies $L_\beta \gg L_\beta^*$, the line free energy is small compared to the interfacial free energies. This does *not* imply, however, that the line tension has no observable consequences in this case. In fact, most estimates of the line tension are based on contact angle measurements in the regime $L_\beta \gg L_\beta^*$ since the contact angle is affected by the tension, see equation (64) below.

The regime $L_\beta < L_\beta^*$ may not be accessible to experimental studies if the width of the contact line is relatively small. The contact line is the intersection of three interfaces which

will, in general, differ in their width. Usually, the width of the $\alpha\beta$ interface is comparable to the size of the molecules in the two fluid phases (exceptions are provided by phase coexistence near a critical point, where the α and β phases become indistinguishable, and by the adsorption of surfactant molecules which increase the effective interfacial width). If the substrate surface is smooth on the molecular scale, the width of the contact line should also be governed by the width of the $\alpha\beta$ interface. In this case, the characteristic length L_β^* is of the order of the molecular size as well, and droplets with linear dimensions $L_\beta < L_\beta^*$ are not accessible.

On the other hand, the magnitude of the line tension may be increased by the effect of long-range van der Waals forces. As shown in appendix E, the corresponding effective interface model leads, in the small gradient approximation, to the line tension contribution

$$\Lambda_{\text{vdW}} \approx \frac{1}{6\pi\theta} \frac{A_H}{l_{\text{pin}}} \tag{4}$$

from van der Waals forces. This contribution depends on the contact angle θ, the Hamaker constant A_H and the wetting layer thickness $l = l_{\text{pin}}$ where the interface potential has a point of inflection. This line tension contribution is large for small contact angle θ, large Hamaker constant A_H and small thickness l_{pin}. A large contribution Λ_{vdW} increases the characteristic size $L_\beta^* \sim \Lambda$, and the regime $L_\beta < L_\beta^*$ may then become accessible.

2.2. Bulk energies

The droplet's body $\mathscr{V}_\beta$ or, to be precise, the space occupied by the liquid β, with volume $V_\beta = |\mathscr{V}_\beta|$ is bounded by the surface $\mathscr{A}_{\alpha\beta}$ to the vapour α, and by the surface $\mathscr{A}_{\beta\sigma}$ to the rigid substrate σ, and thus, is entirely determined by the shape and position of the $\alpha\beta$ interface. An analogue statement holds for the three-phase contact line $\mathscr{L}_{\alpha\beta\sigma}$ and $\mathscr{A}_{\beta\sigma}$, the surface of σ wetted by β. Hence, the droplets free energy is a functional of the $\alpha\beta$ interface that is mathematically described by $\mathscr{A}_{\alpha\beta}$. In order to find locally or globally stable droplet configurations in contact to the substrate walls we have to minimize the free energy

$$\mathcal{F} = \mathcal{F}_\Sigma + \mathcal{F}_\Lambda \tag{5}$$

under the subsidiary constraint $V_\beta = V$ allowing for a droplet volume that is equal to the value of V. The volume ensemble can be seen as analogous to a canonical ensemble since the number of particles in the incompressible phase β is fixed.

Provided that, in contrast to the volume ensemble, the pressure difference $\Delta P = P_\alpha - P_\beta$ between the fluid phases α and β is prescribed while V_β is not fixed, i.e, the pressure ensemble applies to the system, an additional term $\Delta P V_\beta$ in the free energy

$$\tilde{\mathcal{F}} = \mathcal{F}_\Sigma + \mathcal{F}_\Lambda + \Delta P V_\beta \tag{6}$$

accounts for the work done or received during an exchange of volume with an external reservoir. In the volume ensemble, however, the pressure difference ΔP is a Lagrange multiplier which has to be chosen such that the constraint of a constant volume is fulfilled. At fixed volume, the last term in (6) is a constant and does not contribute to the free energy[3].

In the grand canonical ensemble, the pressure difference is fixed by the supersaturation $\Delta\mu = \mu - \mu^0$ with μ being the actual, fixed value of the chemical potential in the container and μ^0 being the chemical potential at coexistence of bulk phases α and β. A quantitative

---

[3] Note that ΔP is the pressure difference between vapour α and liquid phase β which is set by the external reservoir and identical to the pressure difference across the droplet's $\alpha\beta$ interface if and only if the droplet is in mechanical equilibrium.

relation between the pressure difference ΔP and the shift $\Delta \mu$ in the chemical potential at coexistence is given by the equation

$$\Delta \mu = \frac{\Delta P}{\rho_\alpha^0 - \rho_\beta^0} + \mathcal{O}[(\Delta P)^2], \qquad (7)$$

with particle number densities ρ_i^0 of phases $i \in \{\alpha, \beta\}$ at bulk coexistence.

Gravity does not affect the shape of droplets which are significantly smaller than the capillary length

$$\ell_G = \sqrt{\frac{2\Sigma_{\alpha\beta}}{a(\rho_\beta - \rho_\alpha)}}, \qquad (8)$$

where relevant contributions to the droplet free energy come from the interfaces and, for droplets in the submicrometre regime, from the three-phase contact lines between adjacent bulk phases [1]. Effects of gravity can be eliminated on a macroscopic length scale performing wetting experiments with two liquids of nearly the same mass densities ρ_α and ρ_β as well as in space crafts or drop towers where the acceleration a is typically reduced by a factor of 10^{-4} to 10^{-6} compared to normal conditions on earth. The capillary length ℓ_G is typically of the order of millimetres or even larger.

3. Droplet shape

Small deformations of a liquid droplet β that is freely suspended in a fluid α can be represented by normal displacements of the $\alpha\beta$ interface with respect to the initial droplet configuration. However, normal displacements are not sufficient to describe deformations of a droplet β wetting the wall of a substrate σ. The shift of the contact line under general shape variations may have a tangential component with respect to the $\alpha\beta$ interface.

One obvious way to approach this problem is to introduce an additional displacement along a tangential direction close to the boundary of the $\alpha\beta$ interface as first introduced in [19]. The tangential shift together with the normal displacement allows for the constraint of a contact line gliding on the substrate walls. Within such an approach, it is hard to eliminate the tangential displacement field in the final results. It seems that this problem has been overcome in [20, 21] where displacement fields for each order of the variational problem have been introduced including a tangential shift. Due to the constraint of a gliding contact line these fields are not independent and subject to a condition that is derived in a long calculation in [21]. This condition can be employed to eliminate tangential components in the final expressions for free energy variations.

In this paper, we use a different approach to treat the constraint of the contact line gliding on the walls of the substrate σ. By constructing an extension of the $\alpha\beta$ interface beyond the surface of σ and by use of special coordinate systems close to the contact line we were able to vary the domains of parametrizations of the $\alpha\beta$ interface and of the surface of σ that is wetted by β, respectively. This approach turns out to be computationally advantageous as it naturally leads to the occurrence of boundary terms in the variations of physical quantities, like interfacial energies or droplet volume. As we will show in the following, it enables us to split up the variations into terms which are entirely related to either the variation of the $\alpha\beta$ interface or the variation of the contact line. This justifies a classification of these variations into 'surface' and 'boundary' terms which will be marked with superscripts (s) and (b), respectively.

3.1. Parametrizations

It is reasonable to assume that the substrate wall σ, the droplet's $\alpha\beta$ interface and three-phase contact line are smooth, that is, they exhibit no edges or kinks. The $\alpha\beta$ interface of the droplet, we denote by $\mathscr{A}_{\alpha\beta}$, is parametrized by smooth functions $\mathbf{R} = (R^1, R^2, R^3)$ with

$$\mathbf{x} = \mathbf{R}(s^1, s^2) \tag{9}$$

in local coordinates $(s^1, s^2) \in \mathscr{D} \subset \mathbb{R}^2$ that are mapped onto Euclidean vectors $\mathbf{x} = (x^1, x^2, x^3) \in \mathscr{A}_{\alpha\beta} \subset \mathbb{R}^3$. A tangential plane to a given point of $\mathscr{A}_{\alpha\beta}$ is spanned by a pair of linearly independent tangent vectors $\mathbf{R}_i = \partial\mathbf{R}/\partial s^i$ for any regular parametrization. By convention, the local normal vector $\mathbf{N} = (\mathbf{R}_1 \times \mathbf{R}_2)/\sqrt{g}$ on $\mathscr{A}_{\alpha\beta}$ points from the liquid β to the vapour α. In the definition above we used the local surface element $\sqrt{g} = \sqrt{\det g}$ of the metric tensor g, or first fundamental form, with components $g_{ij} = \mathbf{R}_i \cdot \mathbf{R}_j$. Within the formalism of co- and contravariant components, elements of the matrix inverse g^{-1} of g will be written as $(g^{-1})_{ij} = g^{ij}$ in local coordinates. The surface area of $\mathscr{A}_{\alpha\beta}$ is measured by an integral

$$A_{\alpha\beta} = \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A = \int_{\mathscr{D}} \mathrm{d}^2 s \, \sqrt{g}, \tag{10}$$

which is invariant under reparametrizations of the $\alpha\beta$ interface.

The surface $\mathscr{A}_{\beta\sigma}$, i.e., the part of the surface of σ wetted by the liquid β, is parametrized by smooth functions $\mathbf{X} = (X^1, X^2, X^3)$ with

$$\mathbf{x} = \mathbf{X}(t^1, t^2) \tag{11}$$

in local coordinates $(t^1, t^2) \in \mathscr{G} \subset \mathbb{R}^2$ and with a three-dimensional Euclidean vector $\mathbf{x} \in \mathscr{A}_{\beta\sigma} \subset \mathbb{R}^3$. Trivially, an inclusion $\mathscr{A}_{\beta\sigma} \subset \mathscr{A}_\sigma$ holds with the surface of σ here denoted by $\mathscr{A}_\sigma$. Tangent vectors $\mathbf{X}_i = \partial\mathbf{X}/\partial t^i$ define the metric tensor components $g^*_{ij} = \mathbf{X}_i \cdot \mathbf{X}_j$ and a local surface element $\sqrt{g^*} = \sqrt{\det g^*}$. A corresponding normal vector $\mathbf{M} = (\mathbf{X}_1 \times \mathbf{X}_2)/\sqrt{g^*}$ on $\mathscr{A}_{\beta\sigma}$ points from the substrate σ to the liquid β. We will use the convention that all quantities or operators referring to $\mathscr{A}_{\beta\sigma}$ or $\mathscr{A}_\sigma$ are marked with a star to distinguish them from those defined on $\mathscr{A}_{\alpha\beta}$.

The three-phase contact line $\mathscr{L}_{\alpha\beta\sigma} = \mathscr{A}_{\alpha\beta} \cap \mathscr{A}_\sigma$, i.e, the set of points where the liquid β, the vapour α and the substrate σ meet can be described as the rim of either the surface $\mathscr{A}_{\alpha\beta}$ or $\mathscr{A}_{\beta\sigma}$. Smooth functions $\mathbf{r} = (r^1, r^2, r^3)$ represent the contact line as a space curve

$$\mathbf{x} = \mathbf{r}(\ell) \tag{12}$$

with $\ell \in \mathscr{I} \subset \mathbb{R}$ and $\mathbf{x} \in \mathscr{L}_{\alpha\beta\sigma} \subset \mathbb{R}^3$. By reparametrization one may choose the parameter ℓ such that $|\ell|$ is identical to the arclength on the contact line. Hence, we have $\mathscr{I} = [0, L_{\alpha\beta\sigma}]$ with $L_{\alpha\beta\sigma}$, the length of the contact line.

Apart from the local tangent $\mathbf{t} = \dot{\mathbf{r}}/|\dot{\mathbf{r}}|$ to $\mathscr{L}_{\alpha\beta\sigma}$ we will use a conormal vector $\mathbf{n} = \mathbf{t} \times \mathbf{N}^c$ to the surface $\mathscr{A}_{\alpha\beta}$ which forms a right-handed local frame $(\mathbf{n}, \mathbf{t}, \mathbf{N}^c)$ of $\mathbb{R}^3$ in every point of $\mathscr{L}_{\alpha\beta\sigma}$. Here and below, we denote the total derivative with respect to the parameter ℓ by a dot. The vector $\mathbf{N}^c$ is the local surface normal $\mathbf{N}$ of $\mathscr{A}_{\alpha\beta}$ restricted to points of $\mathscr{L}_{\alpha\beta\sigma}$. Provided that the boundary curve $\mathbf{r}(\ell)$ has a positive orientation with respect to the surface normal $\mathbf{N}$ the conormal $\mathbf{n}$ points outwards when seen from $\mathscr{A}_{\alpha\beta}$. A conormal $\mathbf{m} = \mathbf{t} \times \mathbf{M}^c$ to the surface $\mathscr{A}_{\beta\sigma}$ yields a second orthonormal and right-handed frame $(\mathbf{m}, \mathbf{t}, \mathbf{M}^c)$ of $\mathbb{R}^3$ with $\mathbf{M}^c$, the surface normal $\mathbf{M}$ of $\mathscr{A}_{\beta\sigma}$ restricted to points of $\mathscr{L}_{\alpha\beta\sigma}$. The local contact angle θ between $\mathscr{A}_{\alpha\beta}$ and $\mathscr{A}_{\beta\sigma}$ is defined by a scalar product

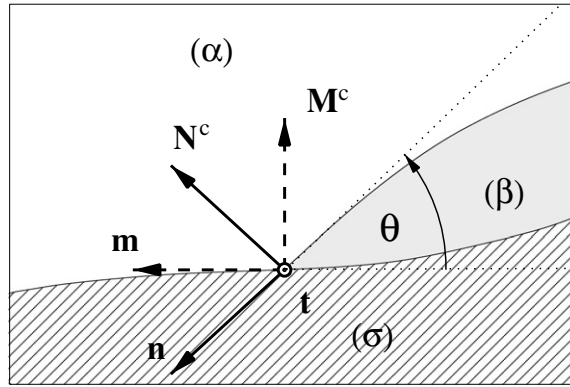$$\cos\theta = \mathbf{n} \cdot \mathbf{m} = \mathbf{N}^c \cdot \mathbf{M}^c, \tag{13}$$

Figure 1. Cut through a droplet β on a substrate σ, perpendicular to the contact line $\mathscr{L}_{\alpha\beta\sigma}$. The droplet β is surrounded by a vapour phase α. In points on $\mathscr{L}_{\alpha\beta\sigma}$ we denote the surface normal of the $\alpha\beta$ interface $\mathscr{A}_{\alpha\beta}$ by $\mathbf{N}^c$ and the surface normal to the substrate $\mathscr{A}_\sigma$ by $\mathbf{M}^c$. The outward-pointing normal $\mathbf{n}$ is perpendicular to $\mathbf{t}$ and $\mathbf{N}^c$ yielding a local orthonormal local frame of $\mathbb{R}^3$. The local frame $(\mathbf{n}, \mathbf{t}, \mathbf{N}^c)$ on $\mathscr{A}_{\alpha\beta}$ is tilted by the local contact angle θ against the corresponding local frame $(\mathbf{m}, \mathbf{t}, \mathbf{M}^c)$ on $\mathscr{A}_\sigma$.

as illustrated in figure 1. The relative orientation of $\mathscr{A}_{\alpha\beta}$ and $\mathscr{A}_{\beta\sigma}$ with respect to the parametrization of $\mathscr{L}_{\alpha\beta\sigma}$ implies that $\mathbf{n} = \mathbf{m}$ and $\mathbf{N}^c = \mathbf{M}^c$ provided $\theta = 0$ holds.

By the divergence theorem one can rewrite the droplet volume as a surface integral over $\mathscr{A}_{\alpha\beta}$ and $\mathscr{A}_{\beta\sigma}$. We have

$$V_\beta = \int_{\mathscr{V}_\beta} \mathrm{d}V = \frac{1}{3} \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A\, \mathbf{R} \cdot \mathbf{N} - \frac{1}{3} \int_{\mathscr{A}_{\beta\sigma}} \mathrm{d}A\, \mathbf{X} \cdot \mathbf{M}$$

$$= \frac{1}{3} \int_{\mathscr{D}} \mathrm{d}^2 s\, \sqrt{g}\, \mathbf{R} \cdot \mathbf{N} - \frac{1}{3} \int_{\mathscr{G}} \mathrm{d}^2 t\, \sqrt{g^*} \mathbf{X} \cdot \mathbf{M}, \tag{14}$$

which turns out to be a computationally advantageous starting point when varying the $\alpha\beta$ interface. The signs in front of the first and the second term are due to the different orientations of the normal $\mathbf{N}$ to $\mathscr{A}_{\alpha\beta}$ and the normal $\mathbf{M}$ to $\mathscr{A}_{\beta\sigma}$ when seen from the bulk of β.

3.2. Extending surfaces

We are able to construct a small stripe $\mathscr{S}_{\alpha\beta}$ along the contact line $\mathscr{L}_{\alpha\beta\sigma}$ that provides a smooth continuation $\bar{\mathscr{A}}_{\alpha\beta} = \mathscr{A}_{\alpha\beta} \cup \mathscr{S}_{\alpha\beta}$ of the $\alpha\beta$ interface beyond the contact line, see also appendix A. Here, the term 'smooth' means in particular that the normal curvature is defined in any point and along any direction in the corresponding local tangential plane on the extended surface $\bar{\mathscr{A}}_{\alpha\beta}$. A continuation $\bar{\mathscr{A}}_{\beta\sigma} = \mathscr{A}_{\beta\sigma} \cup \mathscr{S}_{\beta\sigma}$ of the wetted surface of σ can be easily constructed since $\mathscr{A}_{\beta\sigma}$ is embedded in the smooth substrate wall $\mathscr{A}_\sigma$. Both continuations are necessary to account for variations in the position of the contact line under small deformations of the droplet. It is convenient to introduce special parametrizations $\mathbf{x} = \mathbf{R}(s^1, s^2)$ on $\bar{\mathscr{A}}_{\alpha\beta}$ and $\mathbf{x} = \mathbf{X}(t^1, t^2)$ on $\bar{\mathscr{A}}_{\sigma\beta}$ in the vicinity of $\mathscr{L}_{\alpha\beta\sigma}$, for details see appendix A. Given a parametrization of $\mathscr{L}_{\alpha\beta\sigma}$ as a space curve $\mathbf{x} = \mathbf{r}(\ell)$ we have

$$\mathbf{r}(\ell) = \mathbf{R}(S(\ell), \ell) = \mathbf{X}(T(\ell), \ell), \tag{15}$$

with $s^1 = S(\ell) = 0$, $t^1 = T(\ell) = 0$ and $s^2 = t^2 = \ell$ for all $\ell \in \mathscr{I}$. As the second coordinate is now given by the parameter ℓ we may introduce the simplifying notation $s = s^1$ and $t = t^1$ that is clear as long as we refer to this special coordinate system.

Both coordinate systems arise naturally in the construction of the extensions that we outline in appendix A. The absolute value $|s|$ is the arclength on a coordinate line defined by $\ell = \text{const}$ between a particular point $\mathbf{x} = \mathbf{R}(s, \ell)$ and the contact line. The point $\mathbf{x}$ will be located on the extending stripe $\mathscr{S}_{\alpha\beta}$ if the coordinate s satisfies the inequality $0 \leqslant s < \bar{S}(\ell)$, and $\mathbf{x}$ will lie on $\mathscr{A}_{\alpha\beta}$ if $s < 0$ holds. The rim of the extending stripe is parametrized in these coordinates by a function $s = \bar{S}(\ell)$. Analogue statements hold for the extending stripe $\mathscr{S}_{\beta\sigma}$ and coordinates (t, ℓ) of $\mathscr{A}_{\beta\sigma}$. Here, the rim of the extending stripe is given by a function $t = \bar{T}(l)$ in local coordinates. Now, for the domains of parametrization $\mathscr{D} \subset \mathbb{R}^2$ and $\mathscr{G} \subset \mathbb{R}^2$ with

$$\mathscr{A}_{\alpha\beta} = \mathbf{R}(\mathscr{D}) \qquad \mathscr{A}_{\beta\sigma} = \mathbf{X}(\mathscr{G}), \tag{16}$$

we can find extended domains $\bar{\mathscr{D}} \subset \mathbb{R}^2$ and $\bar{\mathscr{G}} \subset \mathbb{R}^2$ such that

$$\bar{\mathscr{A}}_{\alpha\beta} = \mathbf{R}(\bar{\mathscr{D}}) \qquad \bar{\mathscr{A}}_{\beta\sigma} = \mathbf{X}(\bar{\mathscr{G}}). \tag{17}$$

Expressed in the special coordinates the domains parametrizing the extending stripes $\mathscr{S}_{\alpha\beta}$ and $\mathscr{S}_{\beta\sigma}$ assume the particular form

$$\bar{\mathscr{D}} \backslash \mathscr{D} = [0, \bar{S}] \times \mathscr{I} \qquad \bar{\mathscr{G}} \backslash \mathscr{G} = [0, \bar{T}] \times \mathscr{I}. \tag{18}$$

As shown appendix A the local tangent $\mathbf{t}$ to the contact line satisfies

$$\mathbf{t} = \mathbf{R}_2|_{s=0} = \mathbf{X}_2|_{t=0}, \tag{19}$$

i.e, is identical to the second local tangent vector on the $\alpha\beta$ interface and of the surface of σ wetted by β, respectively, in points on the contact line. The remaining tangent vectors

$$\mathbf{R}_1|_{s=0} = \mathbf{n} \qquad \mathbf{X}_1|_{t=0} = \mathbf{m} \tag{20}$$

in points on the contact line represent the local conormal $\mathbf{n}$ to the $\alpha\beta$ surface and the local conormal $\mathbf{m}$ to the wetted surface of σ, respectively.

3.3. Variation of shape

To test for stationarity or local stability of the $\alpha\beta$ interface we have to impose small deformations to the $\alpha\beta$ interface before calculating changes in the interfacial free energy. Given a parametrization $\mathbf{R}$ of the extended $\alpha\beta$ interface $\bar{\mathscr{A}}_{\alpha\beta}$ we represent the varied, extended $\alpha\beta$ interface $(\bar{\mathscr{A}}_{\alpha\beta})_\varepsilon$ by

$$\mathbf{x} = \mathbf{R}_\varepsilon(s^1, s^2) = \mathbf{R}(s^1, s^2) + \delta\mathbf{R}(s^1, s^2), \tag{21}$$

with $(s^1, s^2) \in \bar{\mathscr{D}}$ and $\mathbf{x} \in (\bar{\mathscr{A}}_{\alpha\beta})_\varepsilon \subset \mathbb{R}^3$. We choose a displacement $\delta\mathbf{R} = \varepsilon\psi\mathbf{N}$ along the surface normal $\mathbf{N}$ of the unvaried surface $\bar{\mathscr{A}}_{\alpha\beta}$ where $\psi(s^1, s^2)$ is a smooth function of coordinates s^i on the extended surface $\bar{\mathscr{A}}_{\alpha\beta}$ and ε is a small and real number. Now, in order to describe the *physical part* of the varied $\alpha\beta$ interface $(\mathscr{A}_{\alpha\beta})_\varepsilon \subset (\bar{\mathscr{A}}_{\alpha\beta})_\varepsilon$, the domain of parametrization $\mathscr{D}$ is varied to $\mathscr{D}_\varepsilon \subset \bar{\mathscr{D}}$ with $(\mathscr{A}_{\alpha\beta})_\varepsilon = \mathbf{R}(\mathscr{D}_\varepsilon) \subset (\bar{\mathscr{A}}_{\alpha\beta})_\varepsilon$. The latter inclusions presuppose that $|\varepsilon|$ is sufficiently small. This procedure can be seen as cutting off the redundant part of the varied extended $\alpha\beta$ interface that is lying in the bulk of the substrate σ. The remaining physically relevant part $(\mathscr{A}_{\alpha\beta})_\varepsilon$ of the $\alpha\beta$ interface is bounded by the varied contact line $(\mathscr{L}_{\alpha\beta\sigma})_\varepsilon$ that is defined by the relation $(\mathscr{L}_{\alpha\beta\sigma})_\varepsilon = (\mathscr{A}_{\alpha\beta})_\varepsilon \cap \mathscr{A}_\sigma$. Under the shift of the contact line, the surface of σ that is wetted by β has to be varied to $(\mathscr{A}_{\beta\sigma})_\varepsilon = \mathbf{X}(\mathscr{G}_\varepsilon) \subset \bar{\mathscr{A}}_{\beta\sigma}$ with a corresponding varied domain $\mathscr{G}_\varepsilon \subset \bar{\mathscr{G}}$.

It is one of the central issues of this paper to calculate the variation of the domains $\mathscr{D}$ and $\mathscr{G}$ of parametrization from this geometrical constraint. Equation (15) serves as a starting point to determine the coordinates of the varied contact line. This condition can be rewritten as

$$\mathbf{r}_\varepsilon(\ell) = \mathbf{R}_\varepsilon(S_\varepsilon(\ell), \ell) = \mathbf{X}(T_\varepsilon(\ell), \ell) \tag{22}$$

in coordinates $s = S_\varepsilon(\ell)$ and $t = T_\varepsilon(\ell)$ of the varied contact line $(\mathcal{L}_{\alpha\beta\sigma})_\varepsilon$ on the varied extended $\alpha\beta$ interface $(\bar{\mathscr{A}}_{\alpha\beta})_\varepsilon$ and the extended wetted surface $\bar{\mathscr{A}}_{\beta\sigma}$ of σ, respectively. The varied domains of parametrization $\mathscr{D}_\varepsilon$ and $\mathscr{G}_\varepsilon$ are expressed in the form

$$\bar{\mathscr{D}} \backslash \mathscr{D}_\varepsilon = [S_\varepsilon, \bar{S}] \times \mathscr{I} \qquad \bar{\mathscr{G}} \backslash \mathscr{G}_\varepsilon = [T_\varepsilon, \bar{T}] \times \mathscr{I} \tag{23}$$

using the special coordinate systems. Differentiation of equation (22) with respect to the small parameter ε yields with equation (20) the relation

$$\delta^1 \mathbf{r} = \mathbf{n} \delta^1 S + \mathbf{N}^c \psi = \mathbf{m} \delta^1 T. \tag{24}$$

The notation $\delta^1(\cdot) = \frac{\mathrm{d}}{\mathrm{d}\varepsilon}(\cdot)\big|_{\varepsilon=0}$ is an abbreviation for the first variation of a function under the deformation of the $\alpha\beta$ interface. By subsequent scalar multiplication of equation (24) with $\mathbf{n}$, $\mathbf{N}^c$ and $\mathbf{m}$, and by comparison with the definition of the local contact angle θ defined in (13) we find

$$\delta^1 \mathbf{r} = \mathbf{m} \delta^1 T \qquad \delta^1 S = \psi \cot \theta \qquad \delta^1 T = \frac{\psi}{\sin \theta}, \tag{25}$$

where all quantities refer to the unvaried contact line. The requirement of smooth curvatures on the contact line, as guaranteed by continuation of the $\alpha\beta$ interface described in the preceding section and appendix A, ensures that the variations (25) are uniquely defined.

3.4. Surface and boundary terms

As a first application of formula (25) we will calculate the variation of a general class of functionals

$$\mathcal{E}\{\mathscr{A}_{\alpha\beta}\} = \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A \, E = \int_{\mathscr{D}} \mathrm{d}^2 s \, \sqrt{g} E, \tag{26}$$

that depend on the configuration $\mathscr{A}_{\alpha\beta}$ of the $\alpha\beta$ interface. The geometrical quantity E defined on the extended surface $\bar{\mathscr{A}}_{\alpha\beta}$ is a function of local coordinates $(s^1, s^2) \subset \bar{\mathscr{D}}$. Note that the first and the second variation of the functional $\mathcal{E}_\varepsilon = \mathcal{E}\{(\mathscr{A}_{\alpha\beta})_\varepsilon\}$ which depends on the real number ε through the varied $\alpha\beta$ interface $(\mathscr{A}_{\alpha\beta})_\varepsilon$ are defined by

$$\delta^1 \mathcal{E}\{\psi\} = \frac{\mathrm{d}\mathcal{E}_\varepsilon}{\mathrm{d}\varepsilon}\bigg|_{\varepsilon=0} \qquad \delta^2 \mathcal{E} = \frac{\mathrm{d}^2 \mathcal{E}_\varepsilon}{\mathrm{d}\varepsilon^2}\bigg|_{\varepsilon=0}. \tag{27}$$

In particular, this definition implies that the iterated first variation is identical to the second variation $\delta^1(\delta^1 \mathcal{E}) = \delta^2 \mathcal{E}$.

To continue, we calculate the first variation of $\mathcal{E}$ as the first derivative

$$\delta^1 \mathcal{E}\{\psi\} = \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left(\int_{\mathscr{D}_\varepsilon} \mathrm{d}^2 s \sqrt{g_\varepsilon} E_\varepsilon \right) \bigg|_{\varepsilon=0} = \int_{\mathscr{D}} \mathrm{d}^2 s \, \delta^1(\sqrt{g}) E$$
$$+ \int_{\mathscr{D}} \mathrm{d}^2 s \sqrt{g} \delta^1 E + \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left(\int_{\mathscr{D}_\varepsilon} \mathrm{d}^2 s \sqrt{g} E - \int_{\mathscr{D}} \mathrm{d}^2 s \sqrt{g} E \right) \bigg|_{\varepsilon=0}. \tag{28}$$

The last term in the general expression (28) comes from the variation of the domain of parametrization (23) which is due to the shift of the contact line. In the special coordinate system defined in section 3.2 and using first variations as given in (25) we may expand the first coordinate of the contact line as $S_\varepsilon = \varepsilon \psi \cot \theta + \mathcal{O}(\varepsilon^2)$ around $\varepsilon = 0$. By construction of the coordinate system we have $\sqrt{g} = 1 + \mathcal{O}(s)$ around $s = 0$, as follows from (19) and (20). The last term of (27) leads to a 'boundary' term

$$\delta^1 \mathcal{E}^b\{\psi\} = \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left(\int_{\mathscr{D}_\varepsilon} \mathrm{d}^2 s \sqrt{g} E - \int_{\mathscr{D}} \mathrm{d}^2 s \sqrt{g} E \right) \bigg|_{\varepsilon=0}$$
$$= \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left(\int_{\mathscr{I}} \mathrm{d}\ell \int_0^{S_\varepsilon} \mathrm{d}s \sqrt{g} E \right) \bigg|_{\varepsilon=0} = \int_{\mathscr{I}} \mathrm{d}\ell \, E \cot \theta \, \psi. \tag{29}$$

to the first variation of the functional $\mathcal{E}$. The remaining terms in (28) give rise to a 'surface' term

$$\delta^1 \mathcal{E}^{\mathrm{s}} \{\psi\} = \int_{\mathcal{D}} \mathrm{d}^2 s \, \delta^1(\sqrt{g}) E + \int_{\mathcal{D}} \mathrm{d}^2 s \, \sqrt{g} \delta^1 E. \tag{30}$$

Note that this surface term would be zero if the surface $\mathscr{A}_{\alpha\beta}$ itself were not varied. We conclude that an equivalent surface term in the first variation of an analogous class of functionals

$$\mathcal{E}^* \{\mathscr{A}_{\alpha\beta}\} = \int_{\mathscr{A}_{\beta\sigma}} \mathrm{d}A \, E^* = \int_{\mathscr{G}} \mathrm{d}^2 t \, \sqrt{g^*} E^*, \tag{31}$$

which are defined as an integral over the surface of σ wetted by β, is absent, i.e., we have

$$\delta^1 \mathcal{E}^{*\mathrm{s}} \{\psi\} = 0. \tag{32}$$

Here, we use an expansion $T_\varepsilon = \varepsilon \psi / \sin \theta + \mathcal{O}(\varepsilon^2)$ of the first coordinate of the varied contact line around $\varepsilon = 0$ to show that the boundary term to the first variation of the functional (31) is given by

$$\delta^1 \mathcal{E}^{*\mathrm{b}} \{\psi\} = \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left(\int_{\mathscr{G}_\varepsilon} \mathrm{d}^2 s \, \sqrt{g^*} E^* - \int_{\mathscr{G}} \mathrm{d}^2 t \, \sqrt{g^*} E^* \right) \bigg|_{\varepsilon=0}$$

$$= \frac{\mathrm{d}}{\mathrm{d}\varepsilon} \left(\int_{\mathscr{I}} \mathrm{d}\ell \int_0^{T_\varepsilon} \mathrm{d}t \, \sqrt{g^*} E^* \right) \bigg|_{\varepsilon=0} = \int_{\mathscr{I}} \mathrm{d}\ell \, \frac{E \psi}{\sin \theta}. \tag{33}$$

An expansion $\sqrt{g^*} = 1 + \mathcal{O}(t)$ can be performed around $t = 0$, as follows again from relations (19) and (20).

To proceed with the computation of the surface term (30), we calculate the first variation $\delta^1(\sqrt{g})$ of the local surface element using the Gauss–Weingarten map which assumes the form

$$\partial_i \mathbf{N} = h_i^j \mathbf{R}_j \tag{34}$$

in local coordinates. We find local tangent vectors to the varied $\alpha\beta$ interface

$$(\mathbf{R}_\varepsilon)_i = \mathbf{R}_i + \mathbf{R}_j h_i^j \varepsilon \psi + \mathbf{N} \varepsilon \partial_i \psi, \tag{35}$$

where, in our definition, all elements h_i^j of the extrinsic curvature tensor are positive on a spherical surface. From equation (35) we derive the expression

$$(g_\varepsilon)_{ij} = g_{ij} + 2h_{ij} \varepsilon \psi + \mathcal{O}(\varepsilon^2) \tag{36}$$

for the varied components $(g_\varepsilon)_{ij}$ of the metric tensor g_{ij}, and we are able to compute the first variation of the local surface element $\sqrt{g}$. Given a non-singular matrix a and an arbitrary matrix b, the useful identity

$$\frac{\mathrm{d}}{\mathrm{d}\varepsilon} \det(a + \varepsilon b)|_{\varepsilon=0} = \mathrm{Tr}(a^{-1} b) \det(a) \tag{37}$$

allows us to calculate a directional derivative of a determinant. By use of formula (37) and the expansion (36) we obtain

$$\delta^1(\sqrt{g}) = \sqrt{g} h_i^i \psi = 2\sqrt{g} M \psi \tag{38}$$

as the first variation of the local surface element. The trace $M = h_i^i / 2$ is the mean curvature and equals the mean value of the two principal curvatures. Since the trace of the extrinsic curvature tensor is invariant under any reparametrization which conserves the orientation of the surface, the mean curvature represents a local geometrical invariant of a surface [22].

Inserting equation (38) into the surface term (30) and with the boundary term (29) we arrive at a general expression

$$\delta^1 \mathcal{E} \{\psi\} = \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A \, 2M E \psi + \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A \, \delta^1 E + \int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L \, E \cot \theta \, \psi \tag{39}$$

for the first variation of the functional $\mathcal{E}$ which itself is a functional of the normal displacement field ψ on $\bar{\mathscr{A}}_{\alpha\beta}$. The first variation of the analogous functional $\mathcal{E}^*\{\mathscr{A}_{\alpha\beta}\}$ of the wetted surface of σ, however, is given by a boundary term

$$\delta^1 \mathcal{E}^*\{\psi\} = \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \, \frac{E^*\psi}{\sin\theta}. \tag{40}$$

Finally, we compute the variation of a general class of functionals $\mathcal{B}$ which are defined as an integral over the contact line. Since the substrate σ is rigid and thus its surface is not varied the contact line is entirely determined by the shape and position of the $\alpha\beta$ interface. Dropping, for the moment, the assumption that ℓ is an arclength parameter on the contact line we may write

$$\mathcal{B}\{\mathscr{A}_{\alpha\beta}\} = \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \, B = \int_{\mathscr{I}} d\ell \, |\dot{\mathbf{r}}| B, \tag{41}$$

where B is a function of local geometrical quantities. These quantities, for instance, depend on the position on the varied $\alpha\beta$ interface and on the surface of σ and, hence, change under a shift of the contact line. The variation of the functional $\mathcal{B}$ leads to two terms

$$\delta^1 \mathcal{B}\{\psi\} = \int_{\mathscr{I}} d\ell \, |\dot{\mathbf{r}}| \delta_c^1 B + \int_{\mathscr{I}} d\ell \, \delta_c^1(|\dot{\mathbf{r}}|) B, \tag{42}$$

where the first term arises from the variation of the geometrical quantity that is due to the variation of the $\alpha\beta$ interface and the accompanying shift of the contact line. The subscript c indicates a total variation under the shift of the contact line including all arguments. The second term describes the effect of local lengthening or shortening of the contact line under the normal displacement by ψ. The first variation of the line element becomes

$$\delta_c^1(|\dot{\mathbf{r}}|) = \frac{\dot{\mathbf{r}} \cdot \delta^1 \dot{\mathbf{r}}}{|\dot{\mathbf{r}}|} = \mathbf{t} \cdot (\dot{\mathbf{m}}\delta^1 T + \mathbf{m}\delta^1 \dot{T}), \tag{43}$$

where we used the identity (24) and the Leibnitz rule. With the definition of the geodesic curvature

$$c_g^* = \frac{\mathbf{t} \cdot \dot{\mathbf{m}}}{|\dot{\mathbf{r}}|} = -\frac{\dot{\mathbf{t}} \cdot \mathbf{m}}{|\dot{\mathbf{r}}|} \tag{44}$$

of the contact line with respect to the surface of σ and the orthogonality relation $\mathbf{m} \cdot \mathbf{t} = 0$ we can rewrite expression (43) as

$$\delta_c^1(|\dot{\mathbf{r}}|) = \mathbf{t} \cdot \dot{\mathbf{m}}\delta^1 T = |\dot{\mathbf{r}}| \frac{c_g^*\psi}{\sin\theta}. \tag{45}$$

The first variation of the functional $\mathcal{B}$ is then given by

$$\delta^1 \mathcal{B}\{\psi\} = \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \left(\delta_c^1 B + \frac{c_g^* B \psi}{\sin\theta} \right), \tag{46}$$

where we still have to compute the total variation $\delta_c^1 B$ of the integrand B while allowing for the tangential shift of the contact line.

First, we consider the situation where the integrand B depends on the *position* of the contact line on the varied extended $\alpha\beta$ interface and the surface of σ, i.e., on the functions $S_\varepsilon(\ell)$ and $T_\varepsilon(\ell)$. Since, by definition, the second coordinate ℓ is not varied, we have

$$\delta_c^1 B = \left. \frac{dB_\varepsilon(S_\varepsilon, T_\varepsilon, \ell)}{d\varepsilon} \right|_{\varepsilon=0} = \delta^1 B + (\partial_s B)\delta^1 S + (\partial_t B)\delta^1 T \tag{47}$$

for the total first variation of the integrand B due to the variational shift of the contact line. The first variation of the coordinates of the contact line, $\delta^1 S$ and $\delta^1 T$, is given in (25).

In the other situation, the integrand B does not depend on the position of the contact line but on the *direction* of the contact line on the substrate wall, i.e., on the unit vector $\mathbf{m}$. This situation is of interest when considering homogeneous but anisotropic substrates σ. For simplicity, we assume that the anisotropic surface of σ is planar so that we can describe the orientation by a single angle ϕ between the conormal $\mathbf{m}$ and a fixed unit vector $\mathbf{e}$ lying in the plane of the surface, i.e., $\cos\phi = \mathbf{m} \cdot \mathbf{e}$. This leads to a first variation

$$\delta_c^1(\cos\phi) = -\sin\phi\,\delta_c^1\phi = \mathbf{e}\cdot\delta_c^1\mathbf{m}. \tag{48}$$

The first variation of the conormal is calculated in appendix C with the result $\delta_c^1\mathbf{m} = -\mathbf{t}\delta^1\dot{T}$ for a planar substrate, see equation (C.16). By the simple relation $\sin\phi = -\mathbf{t}\cdot\mathbf{e}$ we conclude that $\delta_c^1\phi = -\delta^1\dot{T}$. We are now able to calculate the first variation of the quantity B under the rotation of the contact line induced by the shift. Instead of relation (47) being valid for a spatially dependent B we now have

$$\delta_c^1 B = \left.\frac{\mathrm{d}B_\varepsilon(\phi_\varepsilon)}{\mathrm{d}\varepsilon}\right|_{\varepsilon=0} = \delta^1 B - (\partial_\phi B)\delta^1\dot{T} \tag{49}$$

for the total first variation of an integrand B due to the rotation of the contact line under the variation.

4. Variation of free energy

Using the results for the variation of generic functionals derived in the preceding section we will now calculate first and second variations of the interfacial free energy and line energy for droplets wetting a rigid substrate wall. The result for the second variation is valid only for stationary droplet shapes but this restriction may be of no significance since applied to test for local stability.

In the pressure ensemble, a stationary configuration of the $\alpha\beta$ interface is reached whenever the first variation of the total free energy vanishes under any small deformation. In contrast, for non-volatile and incompressible droplets the volume ensemble holds and thus a constraint of a constant volume has to be imposed on the class of configurational variations of the $\alpha\beta$ interface. In principle, the conditions of stationarity do not reveal any information about the local or global stability of the droplet.

The volume term in the free energy (6) can be seen, depending on the ensemble, either as a Langrangian term or as an energy term that accounts for the exchange of volume with an external reservoir. This observation implicates that the set of stationary configurations with fixed volume and the set of stationary configurations at fixed Laplace pressure are identical. But because of the constraint of constant volume, the set of locally mechanically stable configurations in the pressure ensemble is a subset of all locally mechanically stable configurations in the volume ensemble. In what follows, we will focus our attention mostly on the volume ensemble.

As opposed to local stability, global stability can only be inferred if *all* branches of stationary configurations in the wetting geometry are known. Wetting geometries which allow such an exhaustive analytical solution of the first variational problem are rare and, in many cases, exhibit non-analytical solutions as well. In a numerical investigation, this has been demonstrated by Lenz and Lipowsky for droplets wetting a planar lyophobic substrate which is decorated with a lyophilic ring [10].

4.1. First variation

A general expression of the first variation including both interfacial free energy and line free energy has been derived by Swain and Lipowsky [7]. The condition for a mechanical equilibrium of the $\alpha\beta$ interface is still given by the equation of Laplace while the equation of Young–Dupré has to be modified due to line tension. Effects of line tension are strong whenever the curvature of the contact line is large, as it is the case for small droplets, or if the line tension depends strongly on the position on the substrate. Already some decades ago, Gretz considered the equilibrium shape of small spherical droplets on a chemically homogeneous substrate including line tension [13]. He derived a quantitative expression for the deviation of the local contact angle at mechanical equilibrium of a small droplet from a macroscopic droplet. Our calculation, however, allows us to consider the first variation of *arbitrarily* shaped droplets.

As introduced in section 2 we write the free energy of small droplets in the form

$$\tilde{\mathcal{F}} = \mathcal{F}_\Sigma + \mathcal{F}_\Lambda + \Delta P V_\beta, \tag{50}$$

where the influence of gravity has been neglected. We assume, for the moment, that the droplet exchanges volume with an external reservoir at a given pressure difference $\Delta P = P_\alpha - P_\beta$ between the fluid phase α and the wetting liquid β. If we do not allow changes in the droplet volume V_β the last term in the free energy (50) becomes a constant. In this case ΔP can be seen as a Lagrange multiplier, see section 2.

According to equation (1) we split the interfacial free energy $\mathcal{F}_\Sigma$ into the free energies $\mathcal{F}_{\alpha\beta}$ and $\mathcal{F}_{\beta\sigma}$, which are related to the $\alpha\beta$ interface and the surface of σ wetted by β, respectively. The variation of the interfacial free energy $\mathcal{F}_{\alpha\beta} = \Sigma_{\alpha\beta} A_{\alpha\beta}$ can be performed with the general expression (39) for the particular case $E = 1$ which leads to surface and boundary contributions

$$\delta^1 \mathcal{F}_{\alpha\beta}\{\psi\} = \delta^1 \mathcal{F}^s_{\alpha\beta}\{\psi\} + \delta^1 \mathcal{F}^b_{\alpha\beta}\{\psi\}$$

$$= \Sigma_{\alpha\beta} \left(\int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A\, 2M\psi + \int_{\mathscr{L}_{\alpha\sigma}} \mathrm{d}L \cot\theta\, \psi \right). \tag{51}$$

On the other hand, the interfacial free energy which stems from the wetted part of σ is given by an integral

$$\mathcal{F}_{\beta\sigma} = -\Sigma_{\alpha\beta} \int_{\mathscr{A}_{\beta\sigma}} \mathrm{d}A\, W, \tag{52}$$

where the wettability $W = (\Sigma_{\alpha\sigma} - \Sigma_{\beta\sigma})/\Sigma_{\alpha\beta}$ ranges between -1 and 1. As the variation of the $\alpha\beta$ interface leaves the shape of the rigid substrate σ unchanged we find no surface contribution to the first variation, i.e., $\delta^1 \mathcal{F}^s_{\beta\sigma} = 0$, see (32). Therefore, the only contribution to the first variation of the interfacial free energy $\mathcal{F}_{\beta\sigma}$ is due to the boundary and obtained by setting $E^* = W$ in equation (33) as

$$\delta^1 \mathcal{F}_{\beta\sigma}\{\psi\} = \delta^1 \mathcal{F}^b_{\beta\sigma}\{\psi\} = -\int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L\, \frac{W\psi}{\sin\theta}. \tag{53}$$

Another contribution to the total free energy of the droplet comes from line tension and, thus, is sensitive to the variation of the three-phase contact line only. According to equation (46) the first variation of the line energy (2) consists of two terms

$$\delta^1 \mathcal{F}_\Lambda\{\psi\} = \int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L\, \delta^1_c \Lambda + \int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L\, \frac{c^*_g \Lambda \psi}{\sin\theta}. \tag{54}$$

The first term in (54) describes variations of the line energy which emerge from a positional change of the contact line and the chemical inhomogeneity on the surface of σ. Applying equation (47) we find

$$\delta_c^1 \Lambda = (\partial_t \Lambda) \delta^1 T = \frac{\psi \mathbf{m} \cdot (\nabla^* \Lambda)}{\sin \theta},$$ (55)

where we used the covariant derivative $\nabla^* = \mathbf{X}^i \partial_i$ defined on the extended surface $\bar{\mathscr{A}}_{\beta\sigma}$. The first variation of the line energy is then given by

$$\delta^1 \mathcal{F}_\Lambda \{\psi\} = \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \frac{\psi}{\sin \theta} (\Lambda c_g^* + \mathbf{m} \cdot \nabla^* \Lambda).$$ (56)

The last term of the free energy $\tilde{\mathcal{F}}$ in the volume ensemble contains the volume V_β of the liquid droplet. By definition the pressure difference ΔP is fixed by the external volume reservoir and, thus, is not varied. A variation of the droplet volume can be easily performed in the representation by surface integrals (14) with the result

$$\delta^1 V_\beta \{\psi\} = \frac{1}{3} \int_{\mathscr{A}_{\alpha\beta}} dA (\mathbf{N} \cdot \delta^1 \mathbf{R} + \delta^1 \mathbf{N} \cdot \mathbf{R}) + \frac{1}{3} \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \, \mathbf{r} \cdot (\cos \theta \mathbf{N}^c - \mathbf{M}^c) \frac{\psi}{\sin \theta},$$ (57)

where we applied the identities (15), (39) and (40). The varied $\alpha\beta$ interface is represented through normal displacements, and following equation (21) we have $\delta^1 \mathbf{R} = \psi \mathbf{N}$. The first variation of the normal $\mathbf{N}$ to the $\alpha\beta$ interface is given by the simple expression $\delta^1 \mathbf{N} = -\nabla \psi$, as shown in appendix B, see equation (B.5). Here, $\nabla = \mathbf{R}^i \partial_i$ is the covariant derivative on the extended surface $\mathscr{A}_{\alpha\beta}$. Then, by use of Gauss theorem

$$-\int_{\mathscr{A}_{\alpha\beta}} dA \, \mathbf{R} \cdot \nabla \psi = \int_{\mathscr{A}_{\alpha\beta}} dA \, \psi \nabla \cdot \mathbf{R} - \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \, \mathbf{n} \cdot \mathbf{r} \psi$$ (58)

on $\mathscr{A}_{\alpha\beta}$ and employing the identity $\nabla \cdot \mathbf{R} = \mathbf{R}^i \cdot \mathbf{R}_i = \delta_i^i = 2$ we arrive at the first variation

$$\delta^1 V_\beta \{\psi\} = \int_{\mathscr{A}_{\alpha\beta}} dA \, \psi + \frac{1}{3} \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \, \mathbf{r} \cdot (\mathbf{N}^c \cos \theta - \mathbf{n} \sin \theta - \mathbf{M}^c) \frac{\psi}{\sin \theta}.$$ (59)

The vector decomposition $\mathbf{M}^c = \mathbf{N}^c \cos \theta - \mathbf{n} \sin \theta$ (compare figure 1) on the contact line shows that the boundary term of the first variation is zero. Hence, we find a first variation of the droplet volume that is simply given by

$$\delta^1 V_\beta = \delta^1 V_\beta^s = \int_{\mathscr{A}_{\alpha\beta}} dA \, \psi,$$ (60)

and has no boundary term.

Collecting the terms from the first variations of the free energies of the $\alpha\beta$ interface (51), the wetted surface of σ (53), the line energy (56) and the droplet volume (60) we finally arrive at the expression

$$\begin{aligned} \delta^1 \tilde{\mathcal{F}} \{\psi\} &= \delta^1 \mathcal{F}_\Sigma \{\psi\} + \delta^1 \mathcal{F}_\Lambda \{\psi\} + \Delta P \delta^1 V_\beta \{\psi\} \\ &= \int_{\mathscr{A}_{\alpha\beta}} dA (2\Sigma_{\alpha\beta} M + \Delta P) \psi \\ &\quad + \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \frac{\psi}{\sin \theta} [\Sigma_{\alpha\beta} (\cos \theta - W) + \Lambda c_g^* + \mathbf{m} \cdot \nabla^* \Lambda] \end{aligned}$$ (61)

as the first variation of the droplet free energy in the pressure ensemble which consists of a surface and a line integral. Since the normal displacement field ψ on the $\alpha\beta$ interface is arbitrary, we can infer from the condition $\delta^1 \tilde{\mathcal{F}} \{\psi\} = 0$ of mechanical equilibrium that the

arguments of both the surface integral and the line integral in (61) have to vanish identically. This leads to the equation of Laplace

$$2\Sigma_{\alpha\beta}M = -\Delta P = P_\beta - P_\alpha \quad \text{on} \quad \mathscr{A}_{\alpha\beta}, \tag{62}$$

and the generalized equation of Young and Dupré

$$\Sigma_{\alpha\beta}\cos\theta = \Sigma_{\alpha\sigma} - \Sigma_{\beta\sigma} - \Lambda c_g^* - \mathbf{m}\cdot\nabla^*\Lambda \quad \text{on} \quad \mathscr{L}_{\alpha\beta\sigma} \tag{63}$$

for stationary droplet shapes. The latter result was obtained first in its general form by Swain and Lipowsky [7]. Here, the local equilibrium contact angle θ is not only a function of the position, but also depends on the orientation $\mathbf{m}$ and geodesic curvature c_g^* of the contact line with respect to the surface of the substrate.

In the following, we will briefly discuss the somewhat different situation of a homogeneous and planar, but *anisotropic* surface of a crystalline or nanopatterned substrate σ. The conormal $\mathbf{m}$ and a fixed direction $\mathbf{e}$ on the surface of σ form an angle ϕ which was already introduced in (3.4). A variation of the line energy now leads to

$$\delta^1\mathcal{F}_\Lambda = \int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L[c_g^*\Lambda\delta^1 T - (\partial_\phi\Lambda)\delta^1\dot{T}], \tag{64}$$

where the dot denotes a derivative with respect to an arclength parameter ℓ on the contact line. Note that on a planar surface of σ we find a relation $c_g^* = \dot{\phi}$. By a partial integration with respect to the arclength parameter ℓ for a closed (or periodic) contact line on the planar surface we arrive at the first variation

$$\delta^1\mathcal{F}_\Lambda = \int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L\, c_g^*\left(\Lambda + \partial_\phi^2\Lambda\right)\delta^1 T, \tag{65}$$

and the following generalization of the equation of Young and Dupré:

$$\Sigma_{\alpha\beta}\cos\theta = \Sigma_{\alpha\sigma} - \Sigma_{\beta\sigma} - c_g^*\left(\Lambda + \partial_\phi^2\Lambda\right) \quad \text{on} \quad \mathscr{L}_{\alpha\beta\sigma}. \tag{66}$$

It may happen on a surface of a crystalline or periodically nanopatterned substrate that the second derivative $\partial_\phi^2\Lambda$ becomes large and positive for certain contact line orientations. Since the cosine of the contact angle ranges between -1 and 1 the geodesic curvature c_g^* of the contact line with respect to the surface of σ has to go to small positive values in a small range of orientations which leads to a strong faceting of the droplet's three-phase contact line. Such faceting effects have recently been observed for liquid alloy droplets wetting a Si surface [23].

4.2. Second variation

The second variation of the free energy can be obtained by iterated variation of the result (61) for the first variation. Although the calculation is in principle straightforward using the techniques we have provided for treating boundary terms arising from the contact line, a much simpler expression for the second variation can be obtained if we restrict ourselves to the calculation of the second variation for *stationary* droplet shapes for which the first variation has to vanish. Consequently, the conditions of Laplace (62) and Young–Dupré (63) have to be fulfilled. In the following, we will write for the 'restricted second variation', i.e., the second variation evaluated at a stationary shape, the symbol $\delta_s^2(.)$ to distinguish from the ordinary operator $\delta^2(.)$ of second variation. Then, we obtain from iterated variation of the first variation (61) at such a stationary shape the expression

$$\delta_s^2\tilde{\mathcal{F}}\{\psi\} = \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A\,\psi\delta^1(2\Sigma_{\alpha\beta}M + \Delta P)$$

$$+ \int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L\,\frac{\psi}{\sin\theta}\delta_c^1[\Sigma_{\alpha\beta}(\cos\theta - W) + \Lambda c^* + \mathbf{m}\cdot\nabla^*\Lambda]. \tag{67}$$

The final result for the restricted second variation has a much simpler form compared to the full second variation because the arguments in the surface and in the line integral of (61) are zero in any point of the $\alpha\beta$ interface and contact line, respectively, for a stationary droplet shape. Hence, variations of the domain of integration and the variation of the local surface or line element need not be considered in (67). Using the result (B.12) for the first variation of the mean curvature we find

$$\delta_s^2 \tilde{\mathcal{F}}_\Sigma^s \{\psi\} = \Sigma_{\alpha\beta} \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A \, 2\psi \delta^1 M$$

$$= \Sigma_{\alpha\beta} \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A \, \psi [-\nabla^2 + (2G - 4M^2)]\psi \tag{68}$$

as the surface contribution to the restricted second variation of the free energy in the pressure ensemble. The second-order differential operator $\nabla^2 = \nabla \cdot \nabla$ is the Laplace–Beltrami operator on $\mathscr{A}_{\alpha\beta}$.

The second term in (67) gives the boundary contributions to the restricted second variation and leads to four terms: the first term describes the variation of the local contact angle θ under the deformation of the $\alpha\beta$ interface; a second term arises from the position-dependent wettability W on the substrate and the shift of the contact line; the third and the fourth term are related to the change of the geodesic curvature and the position-dependent line tension.

Expressed in an orthonormal coordinate system, as given by the special coordinate systems close to the contact line introduced in section 3.2, the co- and the contravariant components of any tensor become identical and the components of the curvature tensor can be identified with local normal curvatures or torsions of the surface in the directions of the coordinate lines.

In the following, we will denote the components of the extrinsic curvature tensor on the contact line by special symbols. In particular, we use $c_\perp = h_1^1$ for the normal curvature of the $\alpha\beta$ interface perpendicular to the contact line, $\omega = h_2^1 = h_1^2$ for the torsion or winding of the $\alpha\beta$ interface along the contact line, and $c_\parallel = h_2^2$ for the normal curvature parallel to the contact line. Corresponding symbols $c_\perp^*$, ω^* and $c_\parallel^*$ are introduced with respect to the special orthonormal coordinate system on the surface of σ.

Employing the general result for the first total variation (47) of a quantity defined on the contact line and from the definition of the local contact angle (13) we find

$$\delta_c^1(\cos\theta) = \mathbf{M}^c \cdot \delta^1 \mathbf{N} + \frac{\cos\theta \mathbf{M}^c \cdot \partial_s \mathbf{N} + \mathbf{N}^c \cdot \partial_t \mathbf{M}}{\sin\theta} \psi, \tag{69}$$

where the first variation $\delta^1 \mathbf{N}$ and the derivatives $\partial_s \mathbf{N}$ and $\partial_t \mathbf{M}$ are taken on the contact line. By use of the Gauss–Weingarten equation (34) together with (19) and (20), the first variation of the surface normal (B.5), and some trigonometry the above expression simplifies to

$$\delta_c^1(\cos\theta) = \sin\theta \, \mathbf{n} \cdot \nabla\psi + (c_\perp^* - c_\perp \cos\theta)\psi. \tag{70}$$

A further contribution to the second term in the restricted second variation of the free energy (67) arises from a position-dependent wettability W of the substrate wall. The first variation under the shift of the contact line is simply given by

$$\delta_c^1 W = (\partial_t W)\delta^1 T = \frac{\psi \mathbf{m} \cdot \nabla^* W}{\sin\theta}. \tag{71}$$

Whenever we deal with large droplets of linear dimension $L_\beta \gg L_\beta^*$, line energies become irrelevant, and we can neglect all terms which contain the line tension Λ. In this case, the boundary contribution to the restricted second variation of the free energy reduces to

$$\delta_s^2 \mathcal{F}_\Sigma^b \{\psi\} = \int_{\mathscr{L}_{\alpha\beta\sigma}} \mathrm{d}L \, \psi (\Sigma_{\alpha\beta} \mathbf{n} \cdot \nabla + u_\Sigma)\psi, \tag{72}$$

coming from the interfacial energies where u_Σ denotes the expression

$$u_\Sigma = \Sigma_{\alpha\beta} \left(\frac{c_\perp^*}{\sin\theta} - c_\perp \cot\theta - \frac{\mathbf{m} \cdot \nabla^* W}{\sin^2\theta} \right),$$ (73)

defined on the contact line and depending on normal curvatures $c_\perp$ and $c_\perp^*$ as well as the derivative of the wettability W in the direction of the conormal $\mathbf{m}$.

If we consider the local stability of small droplets with linear dimension in the range $L_\beta \simeq L_\beta^*$ we have to include the remaining last two terms in (67), both related to line energy, into our consideration. Iterated variation leads to the restricted second variation

$$\delta_s^2 \mathcal{F}_\Lambda\{\psi\} = \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \, \frac{\psi}{\sin\theta} \delta_c^1(\mathbf{m} \cdot \nabla^* \Lambda + c_g^* \Lambda).$$ (74)

The first term can be further transformed into

$$\delta_c^1(\mathbf{m} \cdot \nabla^* \Lambda) = \nabla^* \Lambda \cdot \delta_c^1 \mathbf{m} + \mathbf{m} \cdot (\nabla^* \otimes \nabla^* \Lambda) \cdot \mathbf{m} \delta^1 T,$$ (75)

containing the first variation of the conormal with respect to the surface of σ. The second term leads to two new terms

$$\delta_c^1(c_g^* \Lambda) = \Lambda \delta_c^1 c_g^* + c_g^* \mathbf{m} \cdot (\nabla^* \Lambda) \delta^1 T,$$ (76)

which account for the variation of geodesic curvature c_g^* and the coupling of the geodesic curvature to the position-dependent line tension Λ. The lengthy calculations of the first variation of the geodesic curvature c_g^* and the first variation of the conormal $\mathbf{m}$ with respect to the substrate are presented in appendix C with the result

$$\delta_c^1 c_g^* = -\delta^1 \ddot{T} - \left(c_g^{*2} + G^* \right) \delta^1 T$$ (77)

and

$$\delta_c^1 \mathbf{m} = -\mathbf{t}\, \delta^1 \dot{T} - \mathbf{M}^c c_g^* \delta^1 T.$$ (78)

The first variation of the two bracketed terms in expression (74) becomes

$$\delta_c^1(\mathbf{m} \cdot \nabla^* \Lambda + c_g^* \Lambda) = -\Lambda \delta^1 \ddot{T} - \dot{\Lambda} \delta^1 \dot{T}$$
$$+ \left[c_g^* \mathbf{m} \cdot \nabla^* \Lambda + \mathbf{m} \cdot (\nabla^* \otimes \nabla^* \Lambda) \cdot \mathbf{m} - \Lambda \left(c_g^{*2} + G^* \right) \right] \delta^1 T.$$ (79)

Recalling that the first factor in (74) is simply given by $\psi/\sin\theta = \delta^1 T$ we may perform a partial integration in the parameter ℓ along the closed contact line which yields a symmetric representation

$$\delta_s^2 \mathcal{F}_\Lambda\{\psi\} = \int_{\mathscr{L}_{\alpha\beta\sigma}} dL[\Lambda(\delta^1 \dot{T})^2 + v(\delta^1 T)^2]$$ (80)

of the restricted second variation of the line energy where v_Λ is an abbreviation for

$$v_\Lambda = c_g^* \mathbf{m} \cdot \nabla^* \Lambda + \mathbf{m} \cdot (\nabla^* \otimes \nabla^* \Lambda) \cdot \mathbf{m} - \Lambda \left(c_g^{*2} + G^* \right).$$ (81)

In a similar manner, the surface term of the second variation (68) assumes a symmetric form after an integration by parts which eliminates the term $\psi \mathbf{n} \cdot \nabla\psi$ under the line integral in (72).

Including both the interfacial and the line energy contributions, the restricted second variation of the free energy of a droplet wetting a rigid substrate σ can be cast into the final form

$$\delta_s^2 \tilde{\mathcal{F}}\{\psi\} = \Sigma_{\alpha\beta} \int_{\mathscr{A}_{\alpha\beta}} dA[(\nabla\psi) \cdot (\nabla\psi) + (2G - 4M^2)\psi^2]$$
$$+ \int_{\mathscr{L}_{\alpha\beta\sigma}} dL \frac{\Lambda(\dot{\psi} - \dot{\theta}\psi \cot\theta)^2 + (v_\Lambda + u_\Sigma \sin^2\theta)\psi^2}{\sin^2\theta},$$ (82)

where the functions u_Σ and v_Λ, defined by (73) and (81), respectively, depend on the normal curvatures $c_\perp$ and $c_\perp^*$ as well as on the geodesic curvature c_g^* of the contact line and the Gaussian curvature G^* with respect to the surface of σ, and derivatives of the wettability W and line tension Λ in the direction of the conormal $\mathbf{m}$.

The restricted second variation (82) of the droplet's free energy is the main result of this paper. It agrees with the result given in [20] with details of its derivation in [21]. As expected, expression (82) is symmetric in the displacement field ψ on the $\alpha\beta$ interface. Note also that we have eliminated the pressure difference ΔP in equation (82) as the restricted second variation is taken at a stationary configuration and as we have implicitly made use of the Laplace equation (62).

In the case of a uniform line tension, the function (81) depends only on the line tension Λ and on the intrinsic curvature of the substrate wall and contact line, that is, the Gaussian curvature G^* and the geodesic curvature c_g^*. Introducing ripples to the boundary of the $\alpha\beta$ interface lengthens the contact line as indicated by the first term in the boundary integral (82). This term has the same sign as the line energy.

5. Spectral stability criterion

The second variation of the free energy of a locally stable droplet has to be non-zero and positive for any deformation of the $\alpha\beta$ interface that is compatible with the constraint of a constant droplet volume. Hence, positivity of the restricted second variation $\delta_s^2 \tilde{\mathcal{F}}\{\psi\}$ implies local stability of the droplet. The final, symmetric form (82) shows that the restricted second variation of the free energy is a quadratic form in the displacement field ψ and positivity can be inferred from its spectrum of eigenvalues μ on the subspace of volume-conserving displacements ψ. The smallest eigenvalue yields the desired information about local stability. A droplet configuration is locally stable if and only if the smallest eigenvalue is positive. The spectrum of eigenvalues can be found by diagonalizing the quadratic form $\delta_s^2 \tilde{\mathcal{F}}\{\psi\}$ on the subspace of volume-conserving displacements ψ using the well-known extremal property of eigenfunctions, which establishes the equivalence to an eigenvalue problem for a partial differential equation with specific boundary conditions [24].

For non-volatile and incompressible liquids, the droplet volume has to be conserved under any deformation of the $\alpha\beta$ interface. For the stability analysis of configurations that are stationary under such a constraint we have to test the restricted second variation (82) for positivity on a subspace of displacements that enforces the volume-constraint up to *linear* order in ψ as shown in appendix D.

The expression of the first variation of the droplet volume (57) shows that this condition is equivalent to

$$\delta^1 V_\beta\{\psi\} = \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A\, \psi = 0, \tag{83}$$

which defines a linear subspace $\mathcal{U}_\perp$ of all displacement fields on the $\alpha\beta$ interface. The displacement field is normed by

$$\int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A\, \psi^2 = 1, \tag{84}$$

and all fields ψ that satisfy (84) are said to belong to the unit sphere $\mathcal{S}$ of elongation fields on the $\alpha\beta$ interface.

Now, the quadratic form $\delta_s^2 \tilde{\mathcal{F}}\{\psi\}$ can be diagonalized by extremizing on the restricted set $\mathcal{S}$ of normalized displacement fields ψ on the $\alpha\beta$ interface [24]. The associated Lagrange

multiplier for the restriction to $\mathcal{S}$ is the eigenvalue μ. For non-volatile liquids with conserved volume, further restriction of $\mathcal{S}$ to the subset $\mathcal{S}_\perp = \mathcal{S} \cap \mathcal{U}_\perp$ of fields has to be considered in the stability analysis instead of $\mathcal{S}$. Equivalently, we can introduce another Lagrange multiplier ν, and find that the quadratic form $\delta_s^2 \tilde{\mathcal{F}}\{\psi\}$ is diagonalized by displacement fields ψ which are local extrema of the functional

$$\mathcal{Q}\{\psi\} = \delta_s^2 \mathcal{F}\{\psi\} - \mu \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A\, \psi^2 - \nu \int_{\mathscr{A}_{\alpha\beta}} \mathrm{d}A\, \psi, \tag{85}$$

where, so far, no restrictions are made upon ψ. Both parameters μ and ν have to be chosen such that the subsidiary conditions of normalization (84) and of conserved volume (83) are satisfied for an extremal field ψ. The extremizing displacement field ψ is an eigenfunction in the subspace of volume-conserving displacements ψ, and the parameter μ the corresponding eigenvalue of the second variation $\delta_s^2 \mathcal{F}\{\psi\}$ restricted to $\mathcal{U}_\perp$. We finally conclude after a partial integration of the symmetric form $\mathcal{Q}\{\psi\}$ that the extremal condition $\delta^1 \mathcal{Q}\{\psi\} = 0$ is equivalent to the inhomogeneous version of a partial differential eigenvalue equation

$$-\nabla^2 \psi + (2G - 4M^2)\psi = \mu\psi + \nu \quad \text{on} \quad \mathscr{A}_{\alpha\beta}. \tag{86}$$

The partial integration of $\mathcal{Q}\{\psi\}$ further shows that the displacement field ψ has to fulfil a linear boundary condition

$$\mathbf{n} \cdot \nabla \psi + \frac{1}{\Sigma_{\alpha\beta}} \left(\frac{v_\Lambda}{\sin^2\theta} + u_\Sigma \right) \psi + r\{\psi\} = 0 \quad \text{on} \quad \mathscr{L}_{\alpha\beta\sigma}, \tag{87}$$

where the function $r\{\psi\}$ on the contact line has a form

$$r\{\psi\} = -\frac{1}{\Sigma_{\alpha\beta} \sin\theta} \frac{\mathrm{d}}{\mathrm{d}\ell} \left[\frac{\mathrm{d}}{\mathrm{d}\ell} \left(\frac{\Lambda\psi}{\sin\theta} \right) \right]. \tag{88}$$

If the smallest eigenvalue μ to a solution ψ of the partial differential equation (86) with boundary condition (87) is positive, the restricted second variation (82) is also positive, which implies local stability of the stationary configuration.

A uniform local contact angle θ and line tension Λ in (88) yields the simplified expression $r\{\psi\} = -\Lambda\ddot{\psi}/(\Sigma_{\alpha\beta} \sin^2\theta)$, which applies to simple droplet morphologies on plane substrates with uniform wettability and line tension, as we will consider in a following publication.

6. Conclusion

In this work, we have derived the most general form of the second variation (82) of the free energy for a *stationary* droplet wetting a rigid substrate with spatially heterogeneous surface topography, wettability and line tension. A new variational technique was introduced to treat the motion of the contact line under arbitrary deformations of the droplet's liquid–vapour interface. Within this variational technique it is sufficient to consider only normal displacements of the liquid–vapour interface. Using this formalism, we are able to recover expression (61) for the first variation of the free energy which has been obtained previously by Swain and Lipowsky [7] and leads to a generalized equation of Young and Dupré (63) for heterogeneous substrates including line tension effects. We have also considered the situation of a homogeneous but *anisotropic* line tension for a planar substrate. In this case, we obtain expression (65) for the first variation of the free energy and a different generalization (66) of the equation of Young and Dupré which can give rise to a faceting of wetting morphologies.

Starting from the result (82) for the restricted second variation we derived the partial differential equation (86) with boundary conditions (87) which allows a systematic stability analysis of stationary droplet shapes and will be applied to a simple wetting geometry in a following publication.
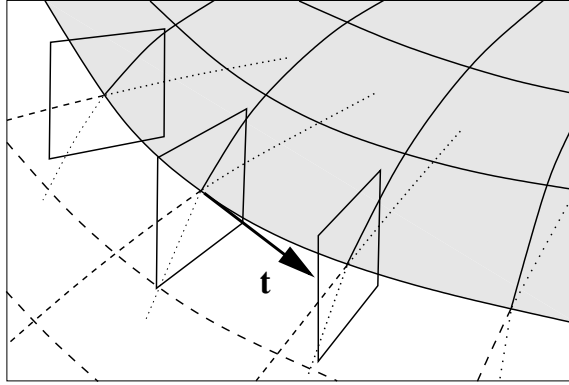
Figure 2. Illustration of the construction of the extending stripes $\mathscr{S}_{\alpha\beta}$ and $\mathscr{S}_{\beta\sigma}$. As outlined in appendix A we construct an array of planes $\mathscr{P}$ perpendicular to the tangent $\mathbf{t}$ of $\mathscr{L}_{\alpha\beta\sigma}$. Provided that the contact line $\mathscr{L}_{\alpha\beta\sigma}$ is smooth the planes $\mathscr{P}$ do not intersect each other in a sufficiently small neighbourhood $\mathbf{U}(\mathbf{x})$ around a point $\mathbf{x} \in \mathscr{L}_{\alpha\beta\sigma}$.

Our variational scheme may be useful in a variety of other contexts. Possible applications include the stability analysis of fluid membrane vesicles adsorbed onto a substrate with spatially heterogeneous chemical composition. Due to the presence of additional bending energies, an expression for the second variation of the elastic free energy for a fluid membrane that includes all boundary contributions is much harder to obtain and remains an open problem to which the variational technique developed in this paper might be successfully applied.

Appendix A. Coordinates and extending stripe

A smooth extension of the $\alpha\beta$ interface can be constructed in the following way. At first, we consider an array of planes where each plane $\mathscr{P}$ is perpendicular to the tangent $\mathbf{t}$ of the contact line $\mathscr{L}_{\alpha\beta\sigma}$ in the point of intersection, see figure 2. Furthermore, each plane $\mathscr{P}$ intersects the surface $\mathscr{A}_{\alpha\beta}$ in the vicinity of $\mathscr{L}_{\alpha\beta\sigma}$ and generates a curve $\mathscr{C}_{\alpha\beta} = \mathscr{P} \cap \mathscr{A}_{\alpha\beta}$ which ends on $\mathscr{L}_{\alpha\beta\sigma}$. Since the planes do not intersect each other in a sufficiently small neighbourhood $\mathbf{U}(\mathbf{r}_0) \in \mathbb{R}^3$ of a given point $\mathbf{r}_0 \in \mathscr{L}_{\alpha\beta\sigma}$, any point $\mathbf{x} \in \mathscr{A}_{\alpha\beta} \cap \mathbf{U}(\mathbf{r}_0)$ belongs to exactly one curve $\mathscr{C}_{\alpha\beta}$.

In the next step, each curve $\mathscr{C}_{\alpha\beta}$ of intersection will be continued by a small piece of a circular arc $\bar{\mathscr{C}}_{\alpha\beta} \subset \mathscr{P}$ pointing in the direction of the conormal $\mathbf{n}$ of the interface $\mathscr{A}_{\alpha\beta}$. The curvature of the arc $\bar{\mathscr{C}}_{\alpha\beta}$ shall be identical to the curvature $c_\perp$ in the end point of $\mathscr{C}_{\alpha\beta}$ on $\mathscr{L}_{\alpha\beta\sigma}$. Hence, $\mathscr{C}_{\alpha\beta} \cup \bar{\mathscr{C}}_{\alpha\beta}$ is a smooth curve in the plane $\mathscr{P}$ perpendicular to $\mathbf{t}$ as indicated in figure 2.

Finally, by collecting all curves $\bar{\mathscr{C}}_{\alpha\beta}$ into a stripe $\mathscr{S}_{\alpha\beta}$ we have constructed a regular extension of the surface $\mathscr{A}_{\alpha\beta}$ in a sufficiently small neighbourhood of $\mathbf{r}_0$. In order to show this proposition we parametrize the contact line by an arclength parameter ℓ and the curve $\mathscr{C}_{\alpha\beta} \cup \bar{\mathscr{C}}_{\alpha\beta}$ by the arclength parameter s. The coordinates s shall satisfy $s > 0$ on the continuation $\bar{\mathscr{C}}_{\alpha\beta}$, $s < 0$ on $\mathscr{C}_{\alpha\beta}$, and consequently $s = 0$ on $\mathscr{L}_{\alpha\beta\sigma}$. Since by definition, the conormal $\mathbf{n}$ and the tangent $\mathbf{t}$ of the contact line $\mathscr{L}_{\alpha\beta\sigma}$ are orthonormal we can argue by continuity that the tangent vectors $\mathbf{R}_1$ and $\mathbf{R}_2$ are linearly independent in a sufficiently small neighbourhood $\mathbf{V}(\mathbf{r}_0) \subset \mathbf{U}(\mathbf{r}_0)$. Smoothness of the extended surface $\bar{\mathscr{A}}_{\alpha\beta} = \mathscr{A}_{\alpha\beta} \cup \mathscr{S}_{\alpha\beta}$ is guaranteed by the construction and the fact that $\mathbf{n}$, $\mathbf{t}$ and $c_\perp$ are smooth functions of the arclength parameter ℓ on $\mathscr{L}_{\alpha\beta\sigma}$.

Appendix B. Variation of surface normal and mean curvature

We will start our calculation with the variation of the surface normal $\mathbf{N}$ of the $\alpha\beta$ interface. As $\mathbf{N} \cdot \mathbf{N} = 1$ we find

$$\mathbf{N} \cdot \delta^1 \mathbf{N} = 0. \tag{B.1}$$

Variation of the orthogonality relation $\mathbf{R}_i \cdot \mathbf{N} = 0$ gives

$$\begin{aligned} 0 &= \delta^1 \mathbf{R}_i \cdot \mathbf{N} + \mathbf{R}_i \cdot \delta^1 \mathbf{N} \\ &= \partial_i \psi + \mathbf{R}_i \cdot \delta^1 \mathbf{N}, \end{aligned} \tag{B.2}$$

where we used (35). Due to (B.2), we can make an ansatz

$$\delta^1 \mathbf{N} = a^j \mathbf{R}_j \tag{B.3}$$

for the variation of the surface normal with numerical coefficients a^j. These coefficients can be determined by inserting the ansatz (B.3) into (B.2), which leads to

$$a^j = -g^{ij} \partial_i \psi. \tag{B.4}$$

We obtain the final result

$$\delta^1 \mathbf{N} = -\mathbf{R}_j g^{ij} \partial_i \psi = -\mathbf{R}^i \partial_i \psi = -\nabla \psi, \tag{B.5}$$

where $\nabla = \mathbf{R}^i \partial_i$ is the covariant operator on $\bar{\mathscr{A}}_{\alpha\beta}$. As expected, $\delta^1 \mathbf{N}$ is oriented perpendicular to the unit surface normal $\mathbf{N}$ of the $\alpha\beta$ interface.

Using the covariant operator $\nabla = \mathbf{R}^i \partial_i$, the mean curvature M can be expressed as

$$2M = \nabla \cdot \mathbf{N} = \mathbf{R}^i \cdot \partial_i \mathbf{N}, \tag{B.6}$$

which leads directly to a first variation

$$2\delta^1 M = \delta^1 \mathbf{R}^i \cdot \partial_i \mathbf{N} + \mathbf{R}^i \cdot \partial_i (\delta^1 \mathbf{N}). \tag{B.7}$$

From variation of the orthogonality relation $\mathbf{R}^i \cdot \mathbf{R}_j = \delta^i_j$ we conclude $\delta^1 \mathbf{R}^i \cdot \mathbf{R}_j = -\mathbf{R}^i \cdot \delta^1 \mathbf{R}_j$ and by use of expression (34) we arrive at

$$\delta^1 \mathbf{R}^i \cdot \partial_i \mathbf{N} = \delta^1 \mathbf{R}^i \cdot \mathbf{R}_j h^j_i = -\delta^1 \mathbf{R}_j \cdot \mathbf{R}^i h^j_i. \tag{B.8}$$

The relation $\mathbf{R}^i \cdot \mathbf{N} = g^{ij} \mathbf{R}_j \cdot \mathbf{N} = 0$ provides together with the first variation (35) a further transformation into

$$\delta^1 \mathbf{R}^i \cdot \partial_i \mathbf{N} = -\mathbf{R}_k \cdot \mathbf{R}^i h^j_i h^k_j \psi - \mathbf{N} \cdot \mathbf{R}^i h^j_i \partial_j \psi = -h^j_i h^i_j \psi. \tag{B.9}$$

By explicit calculation one may check that the double sum can be rewritten as

$$-h^i_j h^j_i = 2G - 4M^2. \tag{B.10}$$

Together with (B.5) the second term on the right-hand side of equation (B.7) yields the simple expression

$$\mathbf{R}^i \cdot \partial_i (\delta^1 \mathbf{N}) = -\mathbf{R}^i \cdot \partial_i \mathbf{R}^j \partial_j \psi = -\nabla^2 \psi, \tag{B.11}$$

with the Laplace–Beltrami operator $\nabla^2 = \nabla \cdot \nabla$ on the $\bar{\mathscr{A}}_{\alpha\beta}$. Finally, we arrive at the first variation

$$\delta^1 M = -\tfrac{1}{2} \nabla^2 \psi + (G - 2M^2) \psi \tag{B.12}$$

of mean curvature.

Appendix C. Variation of conormal and geodesic curvature

To compute the first variation of the conormal $\mathbf{m}$, we make an ansatz

$$\delta_c^1 \mathbf{m} = a_m \mathbf{m} + a_t \mathbf{t} + a_M \mathbf{M}^c, \tag{C.1}$$

with three unknown coefficients a_m, a_t and a_M. Scalar multiplication of (C.1) with $\mathbf{m}$ and using the variation of $\mathbf{m} \cdot \mathbf{m} = 1$ gives the first coefficient

$$a_m = \mathbf{m} \cdot \delta_c^1 \mathbf{m} = 0. \tag{C.2}$$

By scalar multiplication of equation (C.1) with $\mathbf{t}$ and, again, using the variation of an orthogonality relation $\mathbf{t} \cdot \mathbf{m} = 0$ we find

$$a_t = \mathbf{t} \cdot \delta_c^1 \mathbf{m} = -\mathbf{m} \cdot \delta_c^1 \mathbf{t}, \tag{C.3}$$

where the first variation of the tangent vector

$$\delta_c^1 \mathbf{t} = \delta_c^1 (\dot{\mathbf{r}}/|\dot{\mathbf{r}}|) = \mathbf{m} \delta^1 \dot{T} + \dot{\mathbf{m}} \delta^1 T - \mathbf{t} c_g^* \delta^1 T \tag{C.4}$$

can be calculated using (43). To proceed, we make an ansatz for the derivative of the conormal

$$\dot{\mathbf{m}} = b_m \mathbf{m} + b_t \mathbf{t} + b_M \mathbf{M}^c \tag{C.5}$$

with coefficients b_m, b_t and b_M and find the first and the second coefficient to be

$$b_m = \mathbf{m} \cdot \dot{\mathbf{m}} = 0 \quad \text{and} \quad b_t = \mathbf{t} \cdot \dot{\mathbf{m}} = c_g^*. \tag{C.6}$$

Using the orthogonality $\mathbf{M}^c \cdot \mathbf{m} = 0$ the third coefficient can be transformed into

$$b_M = \mathbf{M}^c \cdot \dot{\mathbf{m}} = -\dot{\mathbf{M}}^c \cdot \mathbf{m}. \tag{C.7}$$

The total derivative of the surface normal $\mathbf{M}^c$ of the substrate σ on the contact line with respect to the arclength ℓ is given by

$$\dot{\mathbf{M}}^c = \mathbf{m} \omega^* + \mathbf{t} c_\parallel^*, \tag{C.8}$$

where ω^* is the torsion along the contact line and $c_\parallel^*$ the normal curvature parallel to the contact line. Thus, we have

$$b_M = -\omega^* \tag{C.9}$$

for the third coefficient and consequently

$$\dot{\mathbf{m}} = \mathbf{t} c_g^* - \mathbf{M}^c \omega^*. \tag{C.10}$$

Inserting the relation above into equation (C.4), the first variation of the tangent becomes

$$\delta_c^1 \mathbf{t} = \mathbf{m} \delta_c^1 \dot{t} - \mathbf{M}^c \omega^* \delta^1 T. \tag{C.11}$$

Consequently, the second coefficient in the ansatz (C.1) is

$$a_t = -\delta^1 \dot{T}. \tag{C.12}$$

The third and the last coefficient can be transformed into

$$a_M = \delta_c^1 \mathbf{m} \cdot \mathbf{M}^c = -\mathbf{m} \cdot \delta_c^1 \mathbf{M}^c. \tag{C.13}$$

The first variation of the surface normal to the substrate σ under a variation of the contact line is

$$\delta_c^1 \mathbf{M}^c = \mathbf{m} c_\perp^* \delta^1 T, \tag{C.14}$$

and we finally arrive at

$$a_M = -c_\perp^* \delta^1 T. \tag{C.15}$$

Reinserting all coefficients back into ansatz (C.1) gives

$$\delta_c^1 \mathbf{m} = -\mathbf{t}\, \delta^1 \dot{T} - \mathbf{M}^c c_\perp^* \delta^1 T \qquad (\text{C.16})$$

for the first variation of the conormal $\mathbf{m}$ to the wetted surface of σ.

Our next task will be to calculate the variation of the geodesic curvature c_g^* with respect to the surface of σ. By the use of (43) and the definition (44) of the geodesic curvature we have

$$\delta_c^1 c_g^* = -\mathbf{m} \cdot \delta_c^1 \dot{\mathbf{t}} - \dot{\mathbf{t}} \cdot \delta_c^1 \mathbf{m} - c_g^{*2} \delta^1 T. \qquad (\text{C.17})$$

From the orthogonality $\mathbf{t} \cdot \mathbf{M}^c = 0$, we can easily derive

$$\dot{\mathbf{t}} \cdot \mathbf{M}^c = -\mathbf{t} \cdot \dot{\mathbf{M}}^c = -c_\parallel^* \qquad (\text{C.18})$$

and end up with

$$-\dot{\mathbf{t}} \cdot \delta_c^1 \mathbf{m} = \dot{\mathbf{t}} \cdot \mathbf{M}^c c_\perp^* \delta^1 T = -c_\perp^* c_\parallel^* \delta^1 T \qquad (\text{C.19})$$

for the second term on the right-hand side of equation (C.17). In order to calculate the first term, we derive the first variation of the tangent vector (C.11) with respect to the arclength parameter, yielding

$$\delta_c^1 \dot{\mathbf{t}} = \dot{\mathbf{m}}\, \delta^1 \dot{T} + \mathbf{m}\, \delta^1 \ddot{T} - (\mathbf{m}\, \omega^{*2} + \mathbf{t}\, c_\parallel^* \omega^* + \mathbf{M}^c \dot{\omega}^*) \delta^1 T$$

and eventually, after scalar multiplication with the conormal $\mathbf{m}$, the relation

$$-\mathbf{m} \cdot \delta_c^1 \dot{\mathbf{t}} = \omega^{*2} \delta^1 T - \delta^1 \ddot{T}. \qquad (\text{C.20})$$

Using the definition of the Gaussian curvature

$$G^* = c_\perp^* c_\parallel^* - \omega^{*2} \qquad (\text{C.21})$$

on the surface of σ in points of the contact line we finally arrive at

$$\delta_c^1 c_g^* = -\delta^1 \ddot{T} - \left(c_g^{*2} + G^*\right)\delta^1 T \qquad (\text{C.22})$$

for the first variation of the geodesic curvature of the contact line with respect to σ.

Appendix D. Volume constraint for stationary droplet configurations

If we like to enforce the volume constraint up to a second order in ε we have to introduce a normal variation of the $\alpha\beta$ interface

$$\delta \mathbf{R} = (\varepsilon \psi + \varepsilon^2 \phi)\mathbf{N} \qquad (\text{D.1})$$

with fields ψ and ϕ such that $\delta^1 V_\beta\{\psi\} = 0$ in a linear order and $\delta^1 V_\beta\{\phi\} + \delta^2 V_\beta\{\psi\} = 0$ in quadratic order in the small parameter ε. Inserting the field $\chi = \psi + \varepsilon\phi$ into an expansion of the free energy

$$\tilde{\mathcal{F}} = \tilde{\mathcal{F}}_0 + \delta^1 \tilde{\mathcal{F}}\{\chi\}\varepsilon + \tfrac{1}{2}\delta^2 \tilde{\mathcal{F}}\{\chi\}\varepsilon^2 + \mathcal{O}(\varepsilon^3) \qquad (\text{D.2})$$

and rearranging the terms in powers of ε shows that only the field ψ appears in the quadratic order of the expansion (D.2) of the free energy $\tilde{\mathcal{F}}$ as long as the preceding linear term vanishes. Hence, it is sufficient to enforce the volume constraint up to a linear order if we like to consider the restricted second variation (82) for stationary droplet configurations in the volume ensemble.

Appendix E. Van der Waals contribution to line tension

In this appendix, we will briefly consider the wetting of homogeneous substrate surfaces in the presence of van der Waals forces. Such interactions can be included in the framework of effective interface models which include long-ranged interface potentials [1, 25]. In general, van der Waals forces may favour incomplete or complete wetting corresponding to non-zero and zero contact angle, θ, respectively. For partial wetting and non-zero contact angle, these forces are described by an *attractive* interface potential $U(l)$ which has a minimum at $l = l_{\min}$ and decays as

$$U(l) \approx \frac{A_H}{12\pi} \frac{1}{l^2} \tag{E.1}$$

for large l with the Hamaker constant A_H [26]. Such an interface potential must also have a point of inflection which we denote by $l = l_{\mathrm{pin}}$.

The potential depth $U_{\min} \equiv U(l_{\min})$ is related to the interfacial free energies via

$$|U_{\min}| = \Sigma_{\alpha\beta} + \Sigma_{\beta\sigma} - \Sigma_{\alpha\sigma} = \Sigma_{\alpha\beta}(1 - \cos(\theta)) \approx \tfrac{1}{2}\Sigma_{\alpha\beta}\theta^2 \tag{E.2}$$

where the asymptotic equality reflects the small gradient expansion.

Within this effective interface model, the line tension is given by

$$\Lambda \approx \sqrt{2\Sigma_{\alpha\beta}} \left(\int_{l_{\min}}^{l_{\mathrm{pin}}} \mathrm{d}l \; \sqrt{U(l) + |U_{\min}|} + \int_{l_{\mathrm{pin}}}^{\infty} \mathrm{d}l \; \frac{U(l)}{\sqrt{U(l) + |U_{\min}|}} \right). \tag{E.3}$$

The first integral represents the contribution from the short-ranged forces as previously discussed in [1]. The second integral represents the contribution from the long-ranged forces.

If we insert the asymptotic behaviour $U(l) \approx A_H/(12\pi l^2)$ and the small gradient expression $|U_{\min}| \approx \tfrac{1}{2}\Sigma_{\alpha\beta}\theta^2$ into the second integral, we get the line tension contribution

$$\Lambda_{\mathrm{vdW}} \approx \frac{1}{6\pi\theta} \frac{A_H}{l_{\mathrm{pin}}} \tag{E.4}$$

from the van der Waals forces. This contribution becomes large in the limit of small contact angles θ, i.e., in the limit of complete wetting. For $\theta \geqslant 1/6\pi \simeq 3°$, this line tension contribution satisfies $\Lambda_{\mathrm{vdW}} \leqslant A_H/l_{\mathrm{pin}}$.

References

[1] Lipowsky R, Lenz P and Swain P S 2000 *Colloids Surf.* A **161** 3
[2] Xia Y and Whitesides G M 1998 *Angew. Chem. Int. Ed.* **37** 550
[3] Burmeister F, Schäfle C, Matthes T, Böhmisch M, Boneberg J and Leiderer P 1997 *Langmuir* **13** 2983
[4] Gau H, Herminghaus S, Lenz P and Lipowsky R 1999 *Science* **283** 46
[5] Darhuber A A, Troian S M, Miller S M and Wagner S 2000 *J. Appl. Phys.* **87** 7768
[6] Whitesides G M and Stroock A 2001 *Phys. Today* **54** 42
[7] Swain P S and Lipowsky R 1998 *Langmuir* **14** 6772
[8] Lenz P and Lipowsky R 1998 *Phys. Rev. Lett.* **80** 1920
[9] Brinkmann M and Lipowsky R 2002 *J. Appl. Phys.* **92** 4296
[10] Lenz P, Fenzl W and Lipowsky R 2001 *Europhys. Lett.* **53** 618
[11] Rowlinson J S and Widom B 1982 *Molecular Theory of Capillarity* (Oxford: Clarendon)
[12] Indekeu J O 1994 *Int. J. Mod. Phys.* B **8** 309
[13] Gretz R D 1966 *J. Chem. Phys.* **45** 3160
[14] Boruvka L and Neumann A W 1977 *J. Phys. Chem.* **66** 5464
[15] Rusanov A I 1977 *Colloid. J. USSR* **39** 618 (Engl. Transl.)
[16] Duncan D, Li D, Gaydos J and Neumann A W 1995 *J. Colloid Interface Sci.* **169** 256
[17] Pompe T, Fery A H and erminghaus S 1999 *J. Adhes. Sci. Technol.* **13** 1155
[18] Seemann R, Jacobs K and Blossey R 2001 *J. Phys. Condens. Matter* **13** 4915

[19] Lenz P and Lipowsky R 2000 *Euro. Phys. J.* E **1** 249
[20] Rosso R and Virga E G 2003 *Phys. Rev.* E **68** 012601
[21] Rosso R and Virga E G 2004 *J. Phys. A: Math. Gen.* **37** 3989
[22] do Carmo M 1976 *Differential Geometry of Curves and Surfaces* (Englewood, Cliffs, NJ: Prentice-Hall)
[23] Ressel B, Prince K C, Heun S and Homma Y 2003 *J. Appl. Phys.* **93** 3886
[24] Courant R and Hilbert D 1993 *Methods of Mathematical Physics* (Berlin: Springer)
[25] Lipowsky R 1984 *Phys. Rev. Lett.* **52** 1429
[26] Israelachvili J 1992 *Intermolecular and Surface Forces* (London: Academic)