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Author for correspondence:

Stefanie Heyden

e-mail: stefanie.heyden@mat.ethz.ch

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Contact lines on stretched soft solids: modelling anisotropic surface stresses

Stefanie Heyden¹, Nicolas Bain¹, Qin Xu², Robert W. Style¹ and Eric R. Dufresne¹

¹Department of Materials, ETH Zürich, 8093 Zürich, Switzerland

²Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

SH, 0000-0002-7035-7975

We present fully analytical solutions for the deformation of a stretched soft substrate due to the static wetting of a large liquid droplet, and compare our solutions to recently published experiments (Xu *et al.* 2018 *Soft Matter* 14, 916–920 (doi:10.1039/C7SM02431B)). Following a Green's function approach, we extend the surface-stress regularized Flamant–Cerruti problem to account for uniaxial pre-strains of the substrate. Surface profiles, including the heights and opening angles of wetting ridges, are provided for linearized and finite kinematics. We fit experimental wetting ridge shapes as a function of applied strain using two free parameters, the surface Lamé coefficients. In comparison with experiments, we find that observed opening angles are more accurately captured using finite kinematics, especially with increasing levels of applied pre-strain. These fits qualitatively agree with the results of Xu *et al.*, but revise values of the surface elastic constants.

1. Introduction

Capillary phenomena of liquids are familiar to us from everyday life and have a long history in theoretical mechanics [1]. There, surface stresses dominate the mechanics of liquids, leading to a range of phenomena from the spherical shape of small water droplets to capillary action within narrow tubes. Their effects are visible to the naked eye because their characteristic scale is set by the capillary length $L_c = \sqrt{\gamma/\rho g} \sim \mathcal{O}(\text{mm})$, which relates the surface energy, γ , to density, ρ and gravitational acceleration, g . In solids, capillary phenomena dominate at length scales much shorter

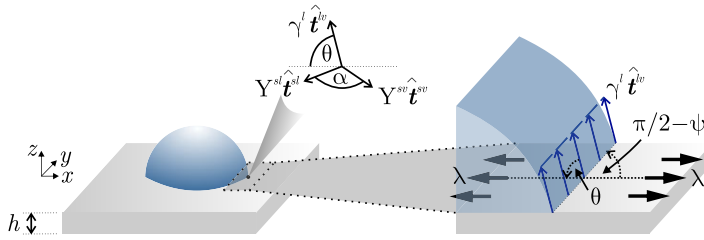


Figure 1. Sketch of the static wetting problem under consideration, illustrating opening angle α of the wetting ridge, contact angle θ , as well as in-plane angle ψ between an applied pre-strain ϵ_{xx} and the contact line generated by liquid surface tension γ_l . (Online version in colour.)

than the elastocapillary length, $l_e \sim \gamma/E$. Here, γ is the surface stress and E denotes the material's Young's modulus. For stiff engineering materials ($E \sim \mathcal{O}(\text{GPa})$), the elastocapillary length is comparable to the atomic scale. Thus, capillary phenomena are rarely significant in stiff materials. Soft materials ($E \sim \mathcal{O}(\text{kPa})$) feature elastocapillary lengths that can reach $\mathcal{O}(10 \mu\text{m})$. Thus, capillary phenomena can become relevant in a variety of settings, e.g. the wetting behaviour on soft substrates [2–6], flattening of nearly plane soft solids [7], stiffening effects in composites with liquid inclusions [8] or soft adhesion [8].

Solid surface stresses have several features that distinguish them from liquid surface stresses. Owing to the ability of liquid molecules to freely rearrange, the surface energy per unit current or deformed area of simple liquids is independent of deformation. Consequently, the surface stress takes on a strain-independent isotropic form, $\gamma_{ij} = \gamma^l \delta_{ij}$. Thus, the terms ‘surface tension’ and ‘surface energy’ are used interchangeably in that context [9]. Solids on the other hand exhibit much more complex surface stresses, including, e.g. anisotropy [10,11] and inelasticity [12,13]. Our understanding of the underlying physical principles governing surface stresses in soft solids, however, is only weakly developed and constitutes an active subject of research [14–22].

To shed light on surface stresses in soft solids, recent experiments have used static wetting techniques [9,21–23]. There, liquid droplets were deposited on soft substrates, and the microscopic geometry of the contact-line (where the three interfaces meet) was precisely measured. As illustrated on the left of figure 1, surface stresses were inferred from a local force balance, ignoring any contributions from bulk elasticity. The net force per unit length of the contact line was assumed to have contributions from the surface tensions of the liquid–vapour interface, γ^{lv}_i , the solid–liquid interface, $\gamma^{sl}_{ij} \hat{t}^{sl}_j$, and the solid–vapour interface, $\gamma^{sv}_{ij} \hat{t}^{sv}_j$ (Einstein's summation convention is implied). Here, γ_{ij} is the surface stress tensor and $\hat{t}_j$ is the tangent vector of each interface normal to the contact line as illustrated in the inset in figure 1. To gain insights into the strain-dependence of surface stresses, recent experiments [21,22] have applied the same approach to stretched substrates as shown in figure 1 on the right. In these experiments, the substrate is stretched in both uniaxial [21] as well as biaxial [22] set-ups preceding droplet deposition.

Data from [22] are shown in figure 2, which depicts the measured static wetting profiles within the direction of applied pre-strain and perpendicular to the direction of applied pre-strain. The slope of the surface converges to a finite value below the elastocapillary length since the tip behaviour of wetting ridges is dominated by surface stresses [24]. Thus, the tip geometry is well described by the opening angle, α . As shown in [22], the opening angles are strain-dependent. A balance of surface stresses at the tip suggests that the surface stresses are also strain dependent. An alternate explanation of these data has emerged, based on nonlinearities within the bulk material, propagated to singular points at the surface [18]. A more recent paper [19], however, argues that the elastic singularity stemming from nonlinear elasticity is too weak to alter the opening angle of the wetting ridge.

Analytical solutions to the static wetting problem trace back to the central formulation of surface elasticity [25,26], as well as classical problems of point and line forces on an elastic half

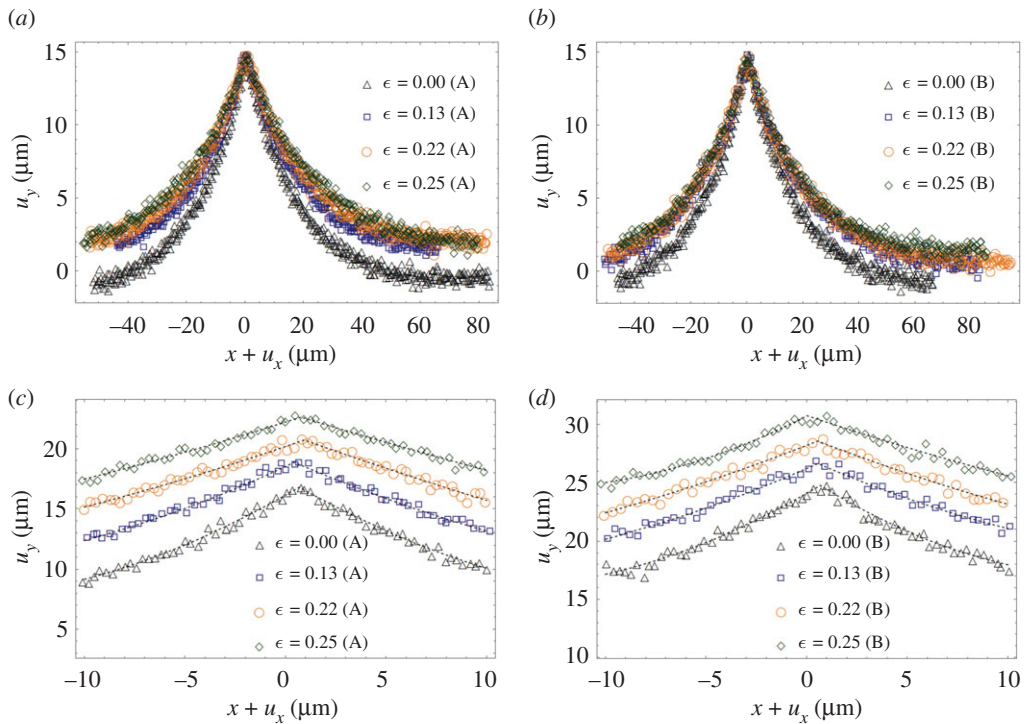


Figure 2. (a,b) Experimental static wetting profiles within the direction of applied pre-strain (A) and perpendicular to the direction of applied pre-strain (B). (c,d) Zoom into the surface stress dominated region of experimental static wetting profiles and corresponding fittings. The data shown here is a subset of experimental static wetting profiles first published in [22]. (Online version in colour.)

space commonly referred to as the Boussinesq and Flamant problem, respectively [27,28]. In addition, Cerruti's problem considers a point force that is tangent to the surface of a half-space [29]. Solutions were subsequently extended to account for anisotropic half-spaces [30,31], as well as isotropic media of finite thickness and possibly multiple layers [32–34].

Here, we extend the analytical solution to the static wetting problem in the large droplet limit to furthermore account for pre-strains of the surface. To predict the fully three-dimensional profile of the wetting ridge, solutions account for varying in-plane angles between the attendant line force and the applied pre-strain. To gain further insight into the characteristics of the strain-dependence of surface stresses, the theory is laid out in both frameworks of linearized and finite kinematics and predicted opening angles of the wetting ridge are compared to available experimental data. We compare our results to published experiments, finding good agreement for data with revised elastic constants.

2. Formulation of the problem

To model substrate deformations upon static wetting in the limit of large droplets, we consider a substrate of finite thickness, h , as shown in figure 1. The substrate is assumed to be neutrally-wetted, such that $\gamma_{ij}^{sv} = \gamma_{ij}^{sl}$. For convenience, both will be referred to as γ_{ij} in the following. We further allow for an emergent anisotropy in surface stresses due to pre-strains applied to the substrate. Solutions account for varying in-plane angles ψ between the applied pre-strain and the in-plane direction perpendicular to the contact line, thus predicting the fully three-dimensional surface profile of a large sessile droplet.

Modelling assumptions (to be introduced in subsequent sections) may be summarized as follows: We consider a linear elastic bulk with a surface rendered anisotropic based on an applied pre-stretch. Surface elasticity is laid out in both frameworks of linear and nonlinear elasticity. The contact line is treated as locally straight (assuming large droplets compared to the elastocapillary length). Surface stresses counteracting tractions applied at the surface are derived assuming small out-of-plane deformations.

(a) Bulk elasticity

We follow a Green's function approach in studying the effect of a line force acting upon an elastic substrate within the linearized kinematics framework. Starting from linear momentum balance, insertion of the Cauchy relations for an isotropic linear elastic material gives the well-known Navier–Lamé equations

$$\left. \begin{aligned} (\lambda + 2\mu)u_{x,xx} + (\lambda + \mu)(u_{y,yx} + u_{z,xz}) + \mu(u_{x,yy} + u_{x,zz}) &= 0 \\ (\lambda + 2\mu)u_{y,yy} + (\lambda + \mu)(u_{x,xy} + u_{z,yz}) + \mu(u_{y,xx} + u_{y,zz}) &= 0 \\ (\lambda + 2\mu)u_{z,zz} + (\lambda + \mu)(u_{x,xz} + u_{y,zy}) + \mu(u_{z,xx} + u_{z,yy}) &= 0, \end{aligned} \right\} \quad (2.1)$$

and

whereby gravitational effects are neglected. For the limiting case of large droplets, the line force generated by the liquid surface tension γ_l may be approximated as a straight contact line as illustrated in figure 1. Under the assumption of plane strain within the in-plane direction parallel to the contact line, the set of equation (2.1) simplifies to

$$\left. \begin{aligned} (\lambda + 2\mu)u_{x,xx} + (\lambda + \mu)u_{z,xz} + \mu u_{x,zz} &= 0 \\ (\lambda + 2\mu)u_{z,zz} + (\lambda + \mu)u_{x,xz} + \mu u_{z,xx} &= 0. \end{aligned} \right\} \quad (2.2)$$

and

Application of Fourier transformations in x leads to a system of ordinary differential equations, which can be recast into matrix form as

$$\begin{pmatrix} \hat{u}_{x,z} \\ \hat{u}_{z,z} \\ \hat{u}_{x,zz} \\ \hat{u}_{z,zz} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ \frac{(\lambda + 2\mu)}{\mu}k^2 & 0 & 0 & -\frac{i(\lambda + \mu)}{\mu}k \\ 0 & \frac{\mu}{(\lambda + 2\mu)}k^2 & -\frac{i(\lambda + \mu)}{(\lambda + 2\mu)}k & 0 \end{pmatrix} \begin{pmatrix} \hat{u}_x \\ \hat{u}_z \\ \hat{u}_{x,z} \\ \hat{u}_{z,z} \end{pmatrix}$$

with wavenumber k . In shorthand notation, a solution to the system

$$\frac{\partial}{\partial z} \hat{u}_j = A_{ij} \hat{u}_j \quad (2.3)$$

may be written in terms of matrix exponentials

$$\hat{u}_j = e^{A_{ij}z} \hat{u}_j^0, \quad (2.4)$$

whereby we find the Jordan normal form of A_{ij} to compute the matrix exponential $B_{ij} = e^{A_{ij}z}$ (the full form of B_{ij} is given in the appendix). Here, $\hat{u}_j^0$ denotes boundary conditions applied at the bottom of the substrate in the form $\hat{u}_x^0 = 0$ and $\hat{u}_z^0 = 0$. The solution may be reformulated as

$$\hat{u}_i = B_{ij} \hat{u}_j^0 = \begin{pmatrix} B_1 & B_2 \\ B_3 & B_4 \end{pmatrix} \hat{u}_j^0, \quad (2.5)$$

with $\hat{u}_i = (\hat{u}_x, \hat{u}_z, \hat{u}_{x,z}, \hat{u}_{z,z})$ and $\hat{u}_i^0 = (0, 0, \hat{u}_{x,z}^0, \hat{u}_{z,z}^0)$. Each block B_i furthermore constitutes a 2×2 matrix, with

$$\begin{pmatrix} \hat{u}_x \\ \hat{u}_z \end{pmatrix} = B_2 \begin{pmatrix} \hat{u}_{x,z}^0 \\ \hat{u}_{z,z}^0 \end{pmatrix}. \quad (2.6)$$

Using this relation, we can replace $\hat{u}_j^0$ with $(0, 0, B_2^{-1}(\hat{u}_x, \hat{u}_z))$, which gives

$$\hat{u}_i = \begin{pmatrix} B_2 & B_2^{-1} \\ B_4 & B_2^{-1} \end{pmatrix} \begin{pmatrix} \hat{u}_x \\ \hat{u}_z \end{pmatrix}. \quad (2.7)$$

In the following, we aim to solve for substrate displacements at the surface $z = h$ only. Note that in the absence of uniaxial pre-strains $\epsilon_{xx}^{\text{pre}}$, $h = h_0$, whereas $h = h_0(1 - \epsilon_{xx}^{\text{pre}}/2)$ otherwise (assuming plane stress conditions during pre-stretch). Traction applied at the surface due to the line force generated by the liquid surface tension γ_l take the form

$$\begin{pmatrix} \sigma_{xz}^h \\ \sigma_{zz}^h \end{pmatrix} = \begin{pmatrix} \gamma_l \cos(\theta) \delta(x) \\ \gamma_l \sin(\theta) \delta(x) \end{pmatrix} \Rightarrow \begin{pmatrix} \hat{\sigma}_{xz}^h \\ \hat{\sigma}_{zz}^h \end{pmatrix} = \begin{pmatrix} \gamma_l \cos(\theta) \\ \gamma_l \sin(\theta) \end{pmatrix}, \quad (2.8)$$

where θ is the contact angle between the applied line force and the substrate's surface. Under the assumption of isotropic linear elasticity, e.g. $\sigma_{ij} = \lambda \epsilon_{kk} \delta_{ij} + 2\mu \epsilon_{ij}$, tractions and displacements may be related via a coefficient matrix S such that

$$\begin{pmatrix} \hat{\sigma}_{xz}^h \\ \hat{\sigma}_{zz}^h \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{13} \\ S_{21} & S_{22} & S_{23} & S_{23} \end{pmatrix} \hat{u}_i^h \\ = \begin{pmatrix} 0 & \frac{iE}{2(1+\nu)}k & \frac{E}{2(1+\nu)} & 0 \\ -\frac{iE\nu}{(1+\nu)(2\nu-1)}k & 0 & 0 & \frac{E(\nu-1)}{(1+\nu)(2\nu-1)} \end{pmatrix} \begin{pmatrix} B_2 & B_2^{-1} \\ B_4 & B_2^{-1} \end{pmatrix} \begin{pmatrix} \hat{u}_x^h \\ \hat{u}_z^h \end{pmatrix}. \quad (2.9)$$

In shorthand notation, we write equation (2.9) as

$$\hat{\tau}_i^h = \hat{Q}_{ij} \hat{u}_j^h, \quad (2.10)$$

and refer to $\hat{Q}_{ij}$ as a generic matrix of spring constants relating tractions $\hat{\tau}_i^h$ applied at the substrate's surface to surface displacements.

(b) Surface stresses

We now proceed to furthermore take into account surface stresses which are counteracting tractions applied at the substrate's surface following [35,36]. Starting from a force balance at the surface, we have

$$[\hat{\sigma}_{ij} \hat{n}_j]_{-}^{+} = -(\delta_{ij} - \hat{n}_i \hat{n}_j) \hat{\gamma}_{ik,j}, \quad (2.11)$$

where $\hat{\sigma}_{ij}$ denotes the Cauchy stress tensor within the bulk material, $\hat{\gamma}_{ik}$ represents the two-dimensional surface stress tensor and $\hat{n}_i$ is the surface normal in the undeformed configuration. For an isotropic linear elastic surface stress tensor, $\hat{\gamma}_{ik} = \gamma^0 \delta_{ik} + \lambda^s \epsilon_{mmm} \delta_{ik} + 2\mu^s \epsilon_{ik}$, equation (2.11) gives

$$\begin{aligned} [\hat{\sigma}_{xz}^h]_{-}^{+} &= [\hat{t}_i \hat{\sigma}_{ij} \hat{n}_j]_{-}^{+} \\ &= -(\delta_{ij} - \hat{n}_i \hat{n}_j) (\hat{\gamma}_{ik} \hat{t}_k)_{,j} + (\delta_{ij} - \hat{n}_i \hat{n}_j) \hat{\gamma}_{ik} \hat{t}_{k,j} \\ &= -(\delta_{ij} - \hat{n}_i \hat{n}_j) (\hat{\gamma}_{ik} \hat{t}_k)_{,j} \\ &= k^2 (\lambda^s + 2\mu^s) \hat{u}_x^h \end{aligned} \quad (2.12)$$

to first order in $\hat{u}_i$, with wavenumber k [37].

To derive surface stresses counteracting normal tractions $[\hat{\sigma}_{zz}^h]_{-}^{+}$ in an equivalent way, we first note that

$$\begin{aligned} [\hat{\sigma}_{zz}^h]_{-}^{+} &= [\hat{n}_i \hat{\sigma}_{ij} \hat{n}_j]_{-}^{+} \\ &= -(\delta_{ij} - \hat{n}_i \hat{n}_j)(\hat{T}_{ik} \hat{n}_k)_{,j} + (\delta_{ij} - \hat{n}_i \hat{n}_j) \hat{T}_{ik} \hat{n}_{k,j} \\ &= 0. \end{aligned} \quad (2.13)$$

We therefore derive an expression for the surface normal $\hat{n}_i$ in a perturbed configuration as

$$\hat{n}_i = \begin{pmatrix} -\hat{u}_{z,x} \\ -\hat{u}_{z,y} \\ 1 \end{pmatrix}. \quad (2.14)$$

Using this relation, surface stresses counteracting tractions $[\hat{\sigma}_{zz}^h]_{-}^{+}$ may be derived as

$$\begin{aligned} [\hat{\sigma}_{zz}^h]_{-}^{+} &= [\hat{n}_i \hat{\sigma}_{ij} \hat{n}_j]_{-}^{+} \\ &= (\delta_{ij} - \hat{n}_i \hat{n}_j) \hat{T}_{ik} \hat{n}_{k,j} \\ &= k^2 \Upsilon^0 \hat{u}_z^h + \mathcal{O}(u^2). \end{aligned} \quad (2.15)$$

Generalizing equation (2.10) to the additional action of surface stresses therefore results in

$$\hat{\tau}_i^h = (\hat{Q}_{ij} + \hat{T}_{ij}) \hat{u}_j^h, \quad \text{with } \hat{T}_{ij} = \begin{pmatrix} k^2(\lambda^s + 2\mu^s) & 0 \\ 0 & k^2 \Upsilon^0 \end{pmatrix}. \quad (2.16)$$

(c) Anisotropic surface stresses based on pre-strain

For an isotropic substrate subjected to uniaxial tension in x and free boundaries in y and z , strains are related as

$$\epsilon_{yy}^{\text{pre}} = -\nu \epsilon_{xx}^{\text{pre}}, \quad (2.17)$$

with ν being the bulk's Poisson ratio. Resultant surface stresses follow as

$$\left. \begin{aligned} \Upsilon_{xx}^{\text{pre}} &= (\lambda^s + 2\mu^s - \nu\lambda^s) \epsilon_{xx}^{\text{pre}} \\ \Upsilon_{yy}^{\text{pre}} &= (\lambda^s - \nu 2\mu^s - \nu\lambda^s) \epsilon_{xx}^{\text{pre}}, \end{aligned} \right\} \quad (2.18)$$

such that total surface stresses are given by $\Upsilon_{ik} = \Upsilon^0 \delta_{ik} + \Upsilon_{ik}^{\text{pre}} + \lambda^s \epsilon_{mm} \delta_{ik} + 2\mu^s \epsilon_{ik}$. To derive the fully three-dimensional profile of the wetting ridge, we introduce an arbitrary in-plane rotation ψ connecting reference (x, y) and rotated (x', y') frames. Surface normals in the perturbed configuration are related as

$$\hat{n}_i = R(\psi)_{ij'} \hat{n}_{j'} = \begin{pmatrix} -\cos(\psi) \hat{u}_{z',x'} \\ -\sin(\psi) \hat{u}_{z',x'} \\ 1 \end{pmatrix}, \quad (2.19)$$

whereby the corresponding gradient is given by

$$\begin{aligned} \hat{n}_{i,j} &= \hat{n}_{i,k'} R(\psi)_{jk'} \\ &= \begin{pmatrix} -\cos^2(\psi) u_{z',x',x'} & -\cos(\psi) \sin(\psi) u_{z',x',x'} & -\cos(\psi) u_{z',x',z'} \\ -\sin(\psi) \cos(\psi) u_{z',x',x'} & -\sin^2(\psi) u_{z',x',x'} & -\sin(\psi) u_{z',x',z'} \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (2.20)$$

Extending equation (2.16) to take into account anisotropy in surface stresses based on an applied pre-strain hence results in

$$\left. \begin{aligned} \hat{t}_i^h &= (\hat{Q}_{ij} + \hat{T}_{ij} + \hat{T}_{ij}^{\text{pre}}) \hat{u}_j^h, \quad \text{with} \\ \hat{T}_{ij}^{\text{pre}} &= \begin{pmatrix} 0 & 0 \\ 0 & k^2(\gamma_{xx}^{\text{pre}} \cos^2(\psi) + \gamma_{yy}^{\text{pre}} \sin^2(\psi)) \end{pmatrix} \end{aligned} \right\} \quad (2.21)$$

(d) Extension to finite deformation

In the following, we extend the model to account for finite pre-strains of the surface and subsequently linearize about the pre-strained configuration preceding droplet deposition. We choose a two-dimensional compressible neo-Hookean strain energy density

$$W^{\text{NH}} = \frac{\mu^s}{2} \left(\frac{I_1}{\det(\mathbf{F})} - 2 \right) + \frac{\kappa^s}{2} (\det(\mathbf{F}) - 1)^2, \quad (2.22)$$

where $I_1 = \text{tr}(\mathbf{F}^T \mathbf{F})$ denotes the first tensor invariant [38]. Linearization about a given finite deformation gives the tangent matrix in spatial form as

$$C_{ijkl} = \det(\mathbf{F})^{-1} F_{ij} F_{il} C_{ijkl}, \quad (2.23)$$

with $C_{ijkl} = \partial(\partial W^{\text{NH}} / \partial F_{ij}) / \partial F_{kl}$ being the tangent stiffness matrix. Note the dependence on deformation gradient $\mathbf{F}$, which in turn renders the resulting tangent matrix anisotropic in the present case of a given uniaxial pre-strain $\mathbf{F} = ((1 + \epsilon_{xx}^{\text{pre}}, 0), (0, 1 - \nu^s \epsilon_{xx}^{\text{pre}}))$. Resultant surface stresses upon subsequent droplet deposition follow as previously derived in equations (2.12) and (2.15), whereby now $\hat{\gamma}_{ij} = C_{ijkl} \epsilon_{kl}$ is a function of new effective moduli $\hat{\gamma}_{ij}(\mu_{\text{eff}}^s, \lambda_{\text{eff}}^s)$. We hence have

$$\hat{T}_{ij} + \hat{T}_{ij}^{\text{pre}} = \begin{pmatrix} k^2(\lambda_{\text{eff}}^s + 2\mu_{\text{eff}}^s) & 0 \\ 0 & k^2(\gamma^0 + \gamma_{xx}^{\text{pre}}(\mu_{\text{eff}}^s, \lambda_{\text{eff}}^s) \cos^2(\psi) + \gamma_{yy}^{\text{pre}}(\mu_{\text{eff}}^s, \lambda_{\text{eff}}^s) \sin^2(\psi)) \end{pmatrix}. \quad (2.24)$$

(e) Calculated surface profiles

Figure 3 illustrates theoretically predicted wetting profiles within the linearized kinematics framework at different strain levels. Note that the reconstruction of the three-dimensional shape of the wetting ridge follows from solving the outlined problem for varying Ψ . The wetting ridge decreases in height with increasing pre-strain levels due to a stiffer material response of the surface. This stiffening effect is more pronounced within the direction of applied pre-strain at $\Psi = 0$. Similarly, opening angles of the wetting ridge increase with increasing pre-strain, showing a more distinct increase at $\Psi = 0$.

3. Comparison with experiments

We now compare the results of these calculations to experiments of Xu *et al.* To minimize systematic errors due to variations in material composition between different samples, we use an experimental subset of the data first published in [22] spanning one sample over a range of pre-strain levels at positions A, B at $\Psi = 0, \pi/2$, respectively (figure 1).

First, we fit the deformation of the substrate far from the contact line to determine the substrate elastic modulus. In this region, where the curvature is small, the liquid surface tension, $\gamma^l = 0.041 \text{ N m}^{-1}$ [21], is balanced by bulk elastic forces with no contribution from solid capillary forces. Fitting ranges are chosen from $20 \mu\text{m}$ to the final data point in each experimental dataset. We find that far-field surface profiles for four values of the pre-strain at both locations A and B can be simultaneously best-fit with a Young's modulus of $E = 2.88 \text{ kPa}$. Figure 4 depicts the tail behaviour of experimental static wetting profiles and the corresponding fittings.

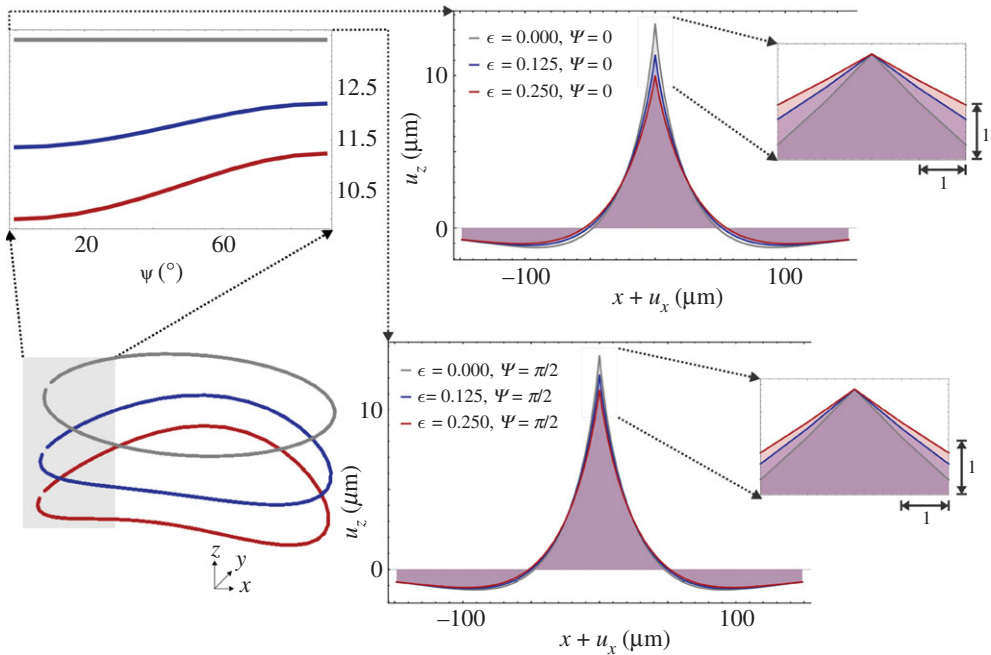


Figure 3. Static wetting on substrates exhibiting anisotropy in surface stresses based on applied pre-strains (linearized kinematics framework). Left: Wetting ridges along in-plane angle Ψ under varying pre-strains of $\epsilon_{xx} = 0.0$, $\epsilon_{xx} = 0.125$ and $\epsilon_{xx} = 0.25$. Right: Corresponding wetting profiles at $\Psi = 0$ and $\Psi = \pi/2$ with inset illustrating the increase in opening angles with increasing pre-strain. Simulations employ values of $\gamma^0 = 0.02 \text{ N m}^{-1}$, $\mu^s = 0.012 \text{ N m}^{-1}$, $\lambda^s = 0.055 \text{ N m}^{-1}$ and $E = 2.88 \text{ kPa}$.

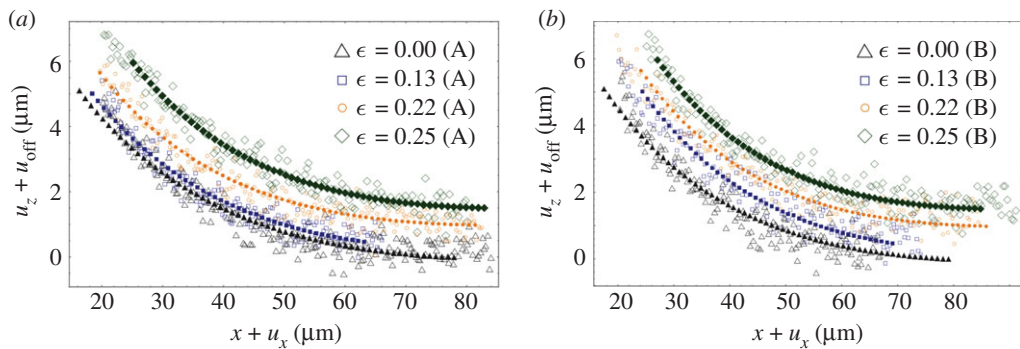


Figure 4. Substrate profiles far from the contact line with their corresponding best fits to the theory described here, with $E = 2.88 \text{ kPa}$. Individual curves are shifted by an offset u_{off} for better visibility. (Online version in colour.)

Subsequently, surface elastic moduli λ^s and μ^s are determined from a comparison of experimental and analytical opening angles at the tip of the wetting ridge, as surface stresses dominate the material behaviour below the elastocapillary length. Opening angles are calculated by fitting surface profiles within $10 \mu\text{m}$ of either side of the ridge tip to quadratic polynomials. The position x_0 of the tip of the wetting ridge is included as a free parameter during the fitting procedure to account for possible shifts in experimental profiles. Fitted profiles are depicted in figure 2, and their opening angles are depicted in figure 5. We note that all tip profiles are well-fit within the linear regime.

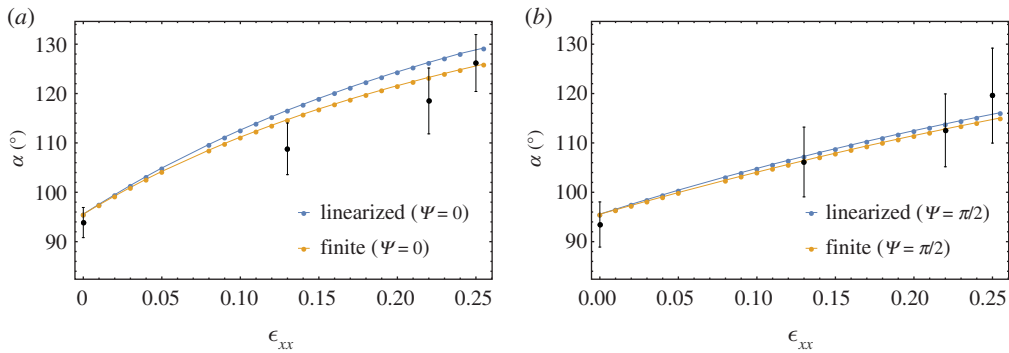


Figure 5. Opening angles of the wetting ridge as predicted from linearized and finite kinematics theory in comparison to opening angles measured in static wetting experiments. Values are depicted for different pre-strain levels ϵ and compared both within the direction of applied pre-strain at $\Psi = 0$ (a) as well as perpendicular to it at $\Psi = \pi/2$ (b). (Online version in colour.)

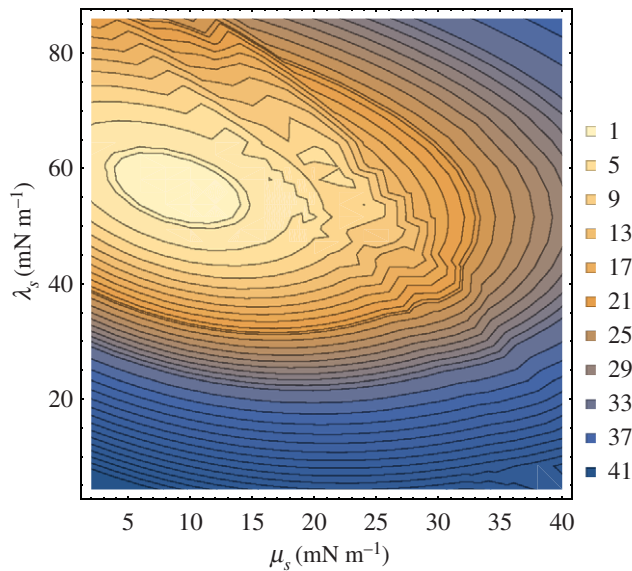


Figure 6. Contour plot showing reduced χ^2 statistics applied to opening angles observed in experiments and simulations for varying surface elastic moduli. The marker located at $(\mu_s = 20 \text{ mN m}^{-1}, \lambda_s = 43 \text{ mN m}^{-1})$ illustrates χ^2 for surface elastic moduli published in [22]. (Online version in colour.)

To find best-fit values of surface elastic moduli, we seed the solution space with test points using a grid of varying discretization. Figure 6 illustrates reduced chi-squared statistics applied to opening angles observed in experiments and simulations within the tested solution space. Lowest contour levels $\chi^2 = 0.95$ indicate that differences in opening angles obtained from experiments and simulations are in accordance with the experimental error variance. Resultant best-fit values are obtained as $\lambda^s = 55 \pm 1 \text{ mN m}^{-1}$ and $\mu^s = 12 \pm 1 \text{ mN m}^{-1}$ (with standard deviations corresponding to a 95% confidence interval). Here, we fixed $\gamma^0 = 0.02 \text{ N m}^{-1}$ and $\gamma^l = 0.041 \text{ N m}^{-1}$ as reported in previous investigations [21,22]. This gives a surface Poisson's ratio of $\nu^s = \lambda^s / (\lambda^s + 2\mu^s) = 0.69$. In two dimensions, Poisson's ratio must lie on the interval $\nu^s \in [-1, 1]$, with $\nu^s = 1$ for an incompressible surface. While our specific values of λ_s and μ_s differ from

Table 1. Opening angles $\alpha^{\text{exp,sub}}$ as determined from an experimental subset of data originally published in [22] and theoretically determined values $\alpha^{\text{theo,lin}}$ and $\alpha^{\text{theo,fin}}$.

$\epsilon_{xx}^{\text{pre}}$	0.0	0.13	0.22	0.25
$\alpha^A_{\text{exp,sub}}$	94 ± 3	109 ± 5	119 ± 6	126 ± 6
$\alpha^A_{\text{theo,lin}}$	96	117	126	129
$\alpha^A_{\text{theo,fin}}$	96	115	123	126
$\alpha^B_{\text{exp,sub}}$	93 ± 5	106 ± 7	113 ± 7	120 ± 9
$\alpha^B_{\text{theo,lin}}$	96	107	114	116
$\alpha^B_{\text{theo,fin}}$	96	106	113	115

the values in [22], our value of the biaxial stretching modulus $\Lambda = 2(\lambda^s + \mu^s)$ is consistent from previously reported values [21,22].

A comparison of the experimental and best-fit opening angles are plotted in figure 5 as a function of applied strain. As expected, both theories of linearized and finite kinematics predict the same opening angle at the tip of the wetting ridge for $\epsilon_{xx} = 0$. In the direction perpendicular to the applied pre-strain, opening angles are recovered within experimental error measures in intermediate as well as high deformation regimes. Within the direction of applied pre-strain, however, linearized kinematics theory consistently overpredicts opening angles of the wetting ridge due to an inherent over-estimation of the material response. Using a finite kinematics model of surface elasticity softens the material response, resulting in decreased values of opening angles. This effect is more pronounced with increasing levels of applied pre-strain. Note that the chosen neo-Hookean strain energy density allows for direct comparison to linearized kinematics theory, as both models of surface elasticity may be formulated in terms of model parameters μ^s and λ^s . Experimental opening angles have furthermore been compared to calculated values based on a two-dimensional Yeoh strain energy density, for which results only display a marginal difference to the chosen neo-Hookean model.

For a detailed comparison, table 1 lists values of both analytically determined opening angles within linearized and finite kinematics theory ($\alpha^{\text{theo,lin}}$ and $\alpha^{\text{theo,fin}}$, respectively). In addition, table 1 lists opening angles calculated from an experimental subset of the data first published in [22], which is used in determining best-fit surface elastic moduli λ^s and μ^s .

4. Conclusion

We have described a theory of strain-dependent surface stresses in the framework of static wetting by extending the generalized Flamant–Cerruti problem. Analytical solutions provide fully three-dimensional surface profiles near a contact line, with an arbitrary orientation relative to the direction of applied stretch. We found that finite kinematics more accurately capture experimental opening angles (especially with increasing levels of applied pre-strain).

To minimize systematic errors, we limited our analysis to a subset of experiments from [22], where a series of surface profiles are measured on a single substrate as a function of strain and location. While we recover re-analysis of these data returns the same value of the surface bi-axial stretching modulus, we find different values of the surface Lamé coefficients.

The origins of surface elasticity in gels are unknown. One simple model described in [9] suggests that surface elasticity of gels can arise due to a thin layer of material near the surface with a modulus much higher than the bulk.

In this picture, two-dimensional Lamé moduli (denoted as s) are related to the three-dimensional Lamé of the putative stiff layer (denoted as l) through $(\mu^s, \lambda^s) = (\mu^l h, (2\mu^l \lambda^l)/(\lambda^l + 2\mu^l)h)$, where h is the thickness of the stiff layer [39]. Substituting our measured values of λ^s and μ^s , we find $\mu^l/\lambda^l = -0.28$. Since elastic moduli must be positive, this is an

unphysical result. This suggests that the surface elastic moduli do not come from such a simple layer, or that nonlinear effects at the contact line [18] need to be explicitly accounted for. In addition, including a compressible layer of finite thickness into the solution procedure constitutes an interesting extension of the presented model.

Possible further extensions of the theory presented in this work include a re-formulation of the problem to allow for bulk elasticity within finite deformations. This extension may leverage further insights into the strain-dependence of surface stresses within the regime of large pre-deformations of the elastic substrate. An examination of different constitutive models of surface elasticity may furthermore give insights into the specific characteristics of strain dependence. Following [20,40], allowing for the effects of compressibility of an interfacial layer of finite thickness represents an additional possible extension. As a secondary measure of comparison, theoretical results could be compared to local strains at the contact line. Current discrepancies between the predicted and measured in-plane displacements are based on the influence of the Laplace pressure difference of the droplet, and could hence be resolved by extending the theory to droplets of arbitrary size. Future experiments on a wider range of materials with different interfacial properties are furthermore needed to differentiate between the two hypotheses of strain-dependent surface stresses versus the effects of bulk nonlinearities being propagated to surfaces of constant surface energy [18]. Possible experimental set-ups in future investigations could include a droplet deposited on a stretched soft solid substrate immersed in a second liquid phase. Varying second liquid phases would thus allow testing of a wide range of surface tensions at the contact line.

Data accessibility. Source code corresponding to this submission is provided as a electronic supplementary material file ‘Static_Wetting_Source’.

Authors' contributions. S.H. carried out the theoretical analysis; S.H., R.S. and E.D. designed the study and wrote the manuscript; N.B. critically revised the manuscript; Q.X. contributed experimental results. All authors gave final approval for publication and agree to be held accountable for the work performed therein.

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Appendix A

The full form of components B_1 through B_4 of the matrix exponential B_{ij} in equation (2.5) is given as

$$\begin{aligned}
 B_1 &= \begin{pmatrix} \cosh(kz) + \frac{kz \sinh(kz)}{(2-4\nu)} & \frac{i(kz \cosh(kz) - \sinh(kz))}{4(-1+\nu)} \\ \frac{2i(kz \cosh(kz) - \sinh(kz))}{8\nu-4} & \cosh(kz) + \frac{kz \sinh(kz)}{(4\nu-4)} \end{pmatrix} \\
 B_2 &= \begin{pmatrix} \frac{kz \cosh(kz) + 3 \sinh(kz) - 4\nu \sinh(kz)}{4k - 4k\nu} & \frac{2iz \sinh(kz)}{8\nu - 4} \\ \frac{iz \sinh(kz)}{4(\nu-1)} & \frac{kz \cosh(kz) - 3 \sinh(kz) + 4\nu \sinh(kz)}{4k\nu - 2k} \end{pmatrix} \\
 B_3 &= \begin{pmatrix} \frac{k(-kz \cosh(kz) + (4\nu-3) \sinh(kz))}{4\nu-2} & \frac{ik^2 z \sinh(kz)}{4(\nu-1)} \\ \frac{2ik^2 z \sinh(kz)}{8\nu-4} & \frac{k(kz \cosh(kz) + (4\nu-3) \sinh(kz))}{4(\nu-1)} \end{pmatrix} \\
 B_4 &= \begin{pmatrix} \cosh(kz) + \frac{kz \sinh(kz)}{(4-4\nu)} & \frac{2i(kz \cosh(kz) + \sinh(kz))}{8\nu-4} \\ \frac{i(kz \cosh(kz) + \sinh(kz))}{4(-1+\nu)} & \cosh(kz) + \frac{kz \sinh(kz)}{(4\nu-2)} \end{pmatrix}.
 \end{aligned}$$

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