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Deformation near a liquid contact line on an elastic substrate

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The equilibrium configuration of a liquid drop on a solid is determined by local energy balance. For a very stiff substrate, energy balance is represented by Young's equation. The equilibrium configuration near a line separating three fluids, in contrast, is determined by a balance of forces—their surface tensions—which is represented graphically by Neumann's triangle. We argue that these two are limiting cases of the more general situation of a drop on an elastic substrate in which both configurational energy balance and force balance must be satisfied independently. By analysing deformation close to the contact line of a liquid drop on an elastic substrate, we show that the transition from the surface tension-dominated regime to the elasticity-dominated regime is controlled by a dimensionless parameter: the ratio of an elasto-capillary length to the characteristic length scale over which surface tension acts. Because of the influence of substrate elasticity, the contact angle is not necessarily given by Young's equation. For compliant solids, we show that the local deformation and stress fields near the contact line are governed by surface tensions. However, if surface tension happens to be different from surface energy, configurational energy balance may not be consistent with force balance.

1. Introduction

When a small liquid drop is placed on a flat and stiff substrate with an isotropic surface, the drop forms a spherical cap with no observable deformation of the substrate (figure 1*a*). If the contact line is free to sample the flat surface, the angle θ_Y made by

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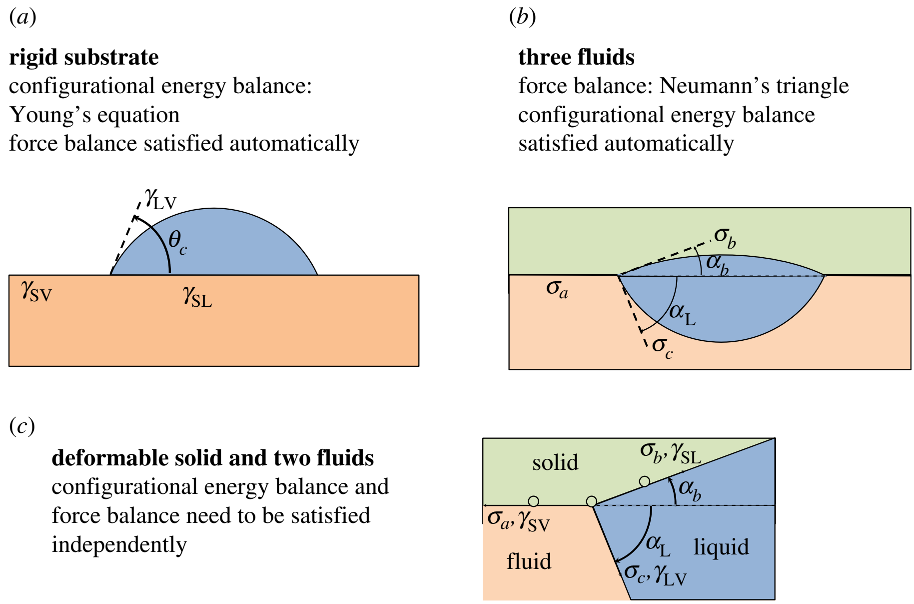

Figure 1. (*a*) On a rigid substrate, the equilibrium shape of a liquid drop with a free contact line is determined by the configurational energy balance; the force balance is satisfied automatically. (*b*) The shape near the contact line separating three fluids is determined by a balance of surface tension forces, which is consistent with the configurational energy balance. (*a*,*b*) represent limiting cases of the more general situation of a liquid drop on an elastic, deformable solid, in which both the configurational energy balance and the force balance need to be satisfied independently. (*c*) If the circles in the figure represent material points attached to the solid, the configurational energy balance means that the free energy is minimized with respect to liquid motion relative to the solid (including attendant changes in solid deformation). Force balance means that a material element surrounding the contact line must be in static equilibrium. (Online version in colour.)

the contact line is given by Young's equation [1]

$$\cos\theta_{\mathrm{Y}} = \frac{\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}}{\gamma_{\mathrm{LV}}}, \tag{1.1a}$$

where γ_{LV}, γ_{SV} and γ_{SL} are the surface *energies* of the liquid/vapour, solid/vapour and solid/liquid interfaces, respectively. In addition to these surface energies, the three surfaces possess surface tensions γ_{LV}, σ_{SV} and σ_{SL}.[1] On the other hand, the angles at which surfaces meet at a contact line between three fluids (figure 1*b*) is governed by the mechanical (force) equilibrium of surface tensions,

$$\sigma_b \sin\alpha_b = \sigma_c \sin\alpha_{\mathrm{L}} \tag{1.1b}$$

and

$$\sigma_a = \sigma_b \cos\alpha_b + \sigma_c \cos\alpha_{\mathrm{L}}. \tag{1.1c}$$

These equilibrium conditions (1.1*b*,*c*), if represented as a set of vectors in two dimensions, form a closed triangle (representing equilibrium) known as Neumann's triangle [1].

For the case of a liquid drop on a compliant solid substrate (e.g. a hydrogel), the Laplace pressure inside the drop and the surface tensions γ_{LV}, σ_{SV} and σ_{SL} can cause significant deformation of the substrate. That liquid surface tension can cause significant deformation in a compliant elastic solid has been known for some time [1–5], and the mechanics of deformation due to liquid surface tension has been examined [6,7], usually without accounting for the resistance to deformation offered by solid surface tension. More recently, Style *et al*. [8] showed that, for very compliant solids, the local deformed shape is governed by the mechanical

[1] For an isotropic surface, the surface stress is an isotropic tensor and will be called surface tension. For a liquid surface, the surface energy and surface tension are numerically equal and can be referred to using the same symbol.

equilibrium of the surface tensions (represented by Neumann's triangle for the two fluids and the solid), not by the configurational energy balance underlying Young's equation (1.1*a*). Nadermann *et al.* [9] have shown that a liquid drop placed under a compliant film deforms it such that the configuration is governed by the force balance at the contact line, i.e. also by Neumann's triangle.

Evidently, two separate principles can be invoked to establish the condition of equilibrium for surfaces adjacent to a contact line: (i) the configurational energy balance, i.e. minimization of potential energy with respect to motion of the contact line relative to the substrate, and (ii) the force balance, which states that the total force and moment acting on a material point due to adjacent material points has to be zero in static equilibrium.

The vertical component of the liquid surface tension exerts a force normal to the substrate surface. This force is resisted by a *combination* of elastic forces and surface tensions. Whereas the elastic forces are related constitutively to bulk strain, the interfacial tensions σ_{SL}, σ_{SV} act on the deformed surface, which is no longer flat. These interfacial tensions provide a vertical component of force *in addition* to the elastic stresses to counteract the vertical component of the liquid/air surface tension. A main result in this work is to show that there is a transition from a surface tension-dominated regime to the elasticity-dominated regime.

If the substrate is perfectly rigid, the force balance is satisfied automatically and trivially, and the configuration energy balance for a contact line which is free to sample all neighbouring points on the surface yields Young's equation [1]. The other extreme case is that of a contact line between three fluids, in which case the force equilibrium (or Neumann's triangle) is the governing condition. Because the three bodies are fluids and their surface energy numerically equals their surface tension, the force and configurational energy balance are *equivalent and consistent* with each other. These are two limiting cases of the more general situation in which the liquid drop lies on an elastic substrate. It is to be expected that, as the substrate stiffness increases, the situation will approach the first limiting case that is governed by Young's equation, independent of the size of the drop. Conversely, as the substrate stiffness decreases, the situation will approach the second limiting case that is governed by the force balance (Neumann's triangle). The configurational energy balance still needs to be satisfied and there may be situations where the two are inconsistent with each other. Between these two limits, the system comprising the contact line and the material in its vicinity must under equilibrium satisfy *both* the configurational energy and the force balance, if the contact line is free to sample different configurations. Specifically, under equilibrium, the forces acting on the contact line must balance each other *and* the location and shape of the contact line must be such that the configuration minimizes energy with respect to virtual changes. In general, these are two separate conditions. These considerations raise a few questions, addressing which is the principal aim of this work:

(a) What combination of materials parameters determines whether elasticity or surface tension dominates the surface shape near the contact line?
(b) If elasticity dominates but the material is not stiff enough to be regarded as rigid, is Young's equation (which ignores elastic energy contributions) still valid?
(c) If surface tension dominates but tensions and energies are not equal, can the force and configurational energy balance be satisfied in a mutually consistent manner?

To study these issues, we have analysed the deformation and stress fields near the contact line of a liquid drop on an elastic half-space. The local fields depend on the contact angle θ_c (figure 1) and the surface tensions γ_{LV}, σ_{SV} and σ_{SL}, as well as the elastic moduli of the substrate. A common practice, valid in the limit of a rigid substrate, is to assume that the contact angle θ_c is given by Young's equation, so that it is completely determined by the surface energies. As will be discussed in more detail below, in situations where the contact line is pinned, the contact angle cannot be determined solely by the surface energies, i.e. $\theta_c \neq \theta_Y$, where θ_Y is defined by (1.1*a*). Even for a free contact line, Young's equation may not be valid for deformable substrates, since the elastic energy stored in the substrate can contribute to the energy balance equation, which is the basis

of Young's equation. For this reason, we do not assume $\theta_c = \theta_Y$ in this work. Since the surface energies need not be the same as the surface tensions, we use different notation to denote the two; the exception being the liquid/vapour interface, where $\gamma_{LV} = \sigma_{LV}$.

In a related recent study, Style & Dufresne [10] carried out a detailed analysis of the stress field caused by an axisymmetric liquid drop on an elastic layer, including the effect of solid surface tensions. They proposed that the key parameter that controls whether the contact angle is governed by Young's equation or by Neumann's triangle is the ratio of the elasto-capillary length γ_{LV}/μ and the radius of the contact line, c,

$$\alpha \equiv \frac{\gamma_{LV}}{\mu c}, \tag{1.2}$$

where μ is the shear modulus of the substrate. The contact angle is given by Young's equation for large α, whereas for small α it is controlled by a balance of surface tensions. Because liquid surface tension is modelled as a line force, their results showed that local deformation fields near the contact line are dominated by the surface tensions, irrespective of the size of the drop or the value of α. Specifically, the usual divergence of displacement owing to a line force acting on an elastic half-space [7,11] is completely suppressed by the interfacial tensions which alone control the local deformation and force balance. Based on this result, they concluded that the local deformation near the contact line is universal [8] and is controlled by the surface tension forces forming a Neumann's triangle; elasticity can be neglected. However, one would expect that, for some range of materials parameters, elasticity would dominate and surface tension would be negligible so that local deformation would no longer depend on interfacial tensions.

In this work, we depart in two important ways from most previous analyses of this problem. Firstly, we introduce a finite region over which the liquid surface tension acts on the elastic substrate [12]. This introduces a new material length scale, ε, and we show that the ratio of the elasto-capillary length to this length scale governs whether the local deformation is dominated by surface tension or by elasticity. Our idea of introducing a molecular length scale was preceded by the recent work of Marchand *et al.* [13]. Using a simulation based on density function theory, they show that the liquid contact angle is selected at a molecular scale. In this work, we used a continuum approach which allows us to study analytically the transition from an elasticity-dominated regime to a surface tension-dominated regime. Secondly, we argue that static equilibrium requires consideration of two separate conditions. For a *free* contact line, the contact angle is such that the *deformed* surface satisfies the local configurational energy balance, which is given by Young's equation only in the limit of a rigid surface. By a free contact line, we mean one that can adjust its location relative to the solid surface without constraint to sample all possible configurations on the surface to arrive at the one that minimizes energy. Simultaneously, the contact angle must be such that the liquid surface tension force is balanced by a combination of solid surface tension and stress in the elastic body. For the problem we consider, the balance of the vertical and horizontal components of the liquid surface tension acting on the solid substrate can be decoupled. We show that, in the limit of vanishing substrate stiffness, the balance of the vertical component of surface tension reduces to equilibrium of surface tensions.

A more subtle issue is the balance of horizontal forces at the contact line. The standard argument is that these forces add up to zero and hence have no effect on substrate deformation. This argument goes as follows: the contact angle obeys Young's law, so it sets itself such that the horizontal component of the liquid/air surface tension, $\gamma_{LV} \cos\theta_Y$, balances $\gamma_{SV} - \gamma_{SL}$. However, this condition represents the configurational energy balance, which is not the same as the force balance since surface tensions need not be the same as surface energies, $\gamma_{SV} - \gamma_{SL} \neq \sigma_{SV} - \sigma_{SL}$. That is, the net horizontal force at the contact line need not be zero even if Young's equation applies. Also, Young's law is based on an un-deformable substrate and does not account for elastic energy, whereas stresses in the elastic body should contribute to horizontal force balance.

The remainder of this article is organized as follows: §2 addresses the difference between the configuration energy balance and the force balance. We argue that a free contact line always satisfies both the local configurational energy balance and the force balance. We also show that

the configurational energy and the force balance might not be satisfied simultaneously for fixed surface energies and tensions, so that the contact line can become unstable. In §3, we formulate the governing equations to determine the stress and deformation field near a contact line. Instead of treating the surface tensions as line forces, we model them as forces distributed over a characteristic length. The ratio of the elasto-capillary length to this length is the dimensionless parameter that governs the transition from the surface tension-dominated to the elasticity-dominated regime. In §4, we summarize our results and discuss the limitations of our model.

2. Energy balance due to configuration change and force balance

The simplest illustration of the configuration energy balance is provided by the derivation of Young's equation (a detailed discussion of Young's equation can be found in Roura & Fort [14]). The usual derivation neglects gravity (small drops) and assumes that the substrate is rigid. The main idea is to compute the free energy change δE due to a virtual displacement δl of the contact line. For an axisymmetric drop, $\delta l = (\delta c)e_r$, where e_r is the unit vector in the radial direction and δc is the change in contact line radius. This virtual displacement causes a change in configuration of the drop, and the work done by the surface tension of the drop is

$$\delta E = \gamma_{\mathrm{LV}}(1 + \cos\theta_c)2\pi c\delta c. \tag{2.1}$$

If the contact line is free, that is, if δl can take on arbitrary values, then for equilibrium the work done by the liquid/air surface tension must be equal to the change in surface energy of the system, which is

$$(\gamma_{\mathrm{LV}} + \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}})2\pi c\delta c. \tag{2.2}$$

Young's equation is obtained by equating (2.1) and (2.2), and for this case $\theta_c = \theta_y$. The key point is that the right-hand side of (2.1) is the energy release due to a virtual advance of the contact line and is valid whether or not the contact line actually moves. However, (2.2) is the equilibrium energy required to move a contact line that is free to sample all configurations. If the contact line is pinned, then the energy release given by (2.1) must exceed (2.2) in order for the contact line to move. Therefore, Young's equation is applicable only for a free contact line on a *rigid* substrate. The rigidity of the substrate is needed to rule out stored elastic energy, which would otherwise enter the energy balance equation through equation (2.1).

What about force balance? If the substrate is truly rigid and the drop is small enough such that gravity can be neglected, then there is a net vertical force

$$f = 2\pi c\gamma_{\mathrm{LV}} \sin\theta_c k, \tag{2.3}$$

owing to surface tension of the drop. (In the next section, this will be replaced by distributed forces.) The liquid drop also applies a Laplace pressure

$$p = 2\gamma_{\mathrm{LV}}\frac{\sin\theta_c}{c}, \tag{2.4}$$

which is required to maintain the drop itself in static equilibrium. Because of the Laplace pressure, the net force on the substrate is exactly zero. If we consider deformation close to the contact line, then the Laplace pressure can be neglected, as it is distributed over a length scale (c) much larger than the length over which the surface tension is distributed. In any case, as the substrate cannot deform, it provides *whatever force is needed to maintain itself in equilibrium*. Thus, the net force acting on any segment of the contact line is exactly zero, but it is not possible to relate these forces to the interfacial tensions owing to the rigidity of the substrate [15,16].

Consider the other limit where the 'substrate' is extremely compliant. This can occur if the structure supporting the drop is very flexible, such as a membrane [9] (a very thin sheet with lateral dimension much greater than its thickness), or if the elastic modulus of the substrate is very small in value [17,18]. In either case, the force of liquid surface tension is primarily supported by in-plane membrane tension. In the immediate vicinity of the liquid contact line, there is always a very small region where either the bending elasticity of the substrate or the finite width of the

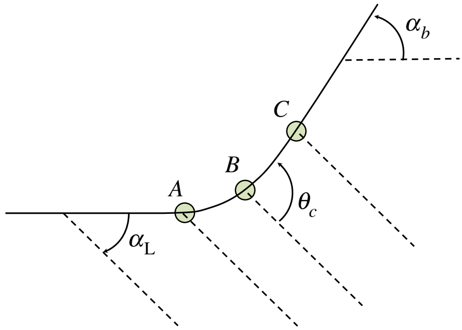

Figure 2. In the surface tension-dominated limit, the force equilibrium fixes angles α_L, α_b. If the contact angle, θ_c, is greater than α_L, but less than $\alpha_\mathrm{L} + \alpha_b$, then the force and configurational energy balance can be satisfied in a consistent manner, and the contact line will come to rest at some point *B* between points *A* and *C*. If $\theta_c < \alpha_\mathrm{L}$, then the force and configurational energy balance cannot be satisfied simultaneously for fixed values of surface energies and tensions. The contact line will move unstably to the left of point *A*. If $\theta_c > \alpha_\mathrm{L} + \alpha_b$, the contact line will move unstably to the right of point *C*. (Online version in colour.)

region over which surface tension acts, ε, smooth out a profile that would otherwise have an infinitely sharp kink at the contact line (figure 2). For a membrane, the extent of this region is determined by bending and is of the order of $d \approx t\sqrt{Et/\gamma_{\mathrm{LV}}}$, where E is Young's modulus of the membrane and t is its thickness [9]. The length scale ε represents a finite region near the interface over which the surface tension develops. The size of this region is determined by the range of intermolecular forces and is expected to be of molecular dimensions [19], say about a nanometre in size. Figure 2 shows the case where d is very small compared with other dimensions (e.g. the size of the drop), but still much larger than ε. At distances large compared with d but still small compared with the size of the drop, the deformed membrane appears to have a kink and this is shown in figure 1*c*. The angle of the liquid–vapour surface tangent with respect to the horizontal line is α_L. Since the drop is in static equilibrium, the force balance requires

$$\sigma_b \sin\alpha_b = \gamma_{\mathrm{LV}} \sin\alpha_\mathrm{L} \tag{2.5a}$$

and

$$\sigma_a = \gamma_{\mathrm{LV}} \cos\alpha_\mathrm{L} + \sigma_b \cos\alpha_b, \tag{2.5b}$$

where σ_a is the tension in the portion of the solid that is in contact with air and σ_b is the tension in the portion of the solid that is in contact with the liquid. Equations (2.5*a*,*b*) imply that the angles α_L and α_b are completely determined by the surface tensions, that is, they are *fixed* by the *force balance*. If surface tensions equal surface energies, then equations (2.5*a*,*b*) also represent the configurational energy balance, but, for solid surfaces, the force and configurational energy balance must be regarded as independent conditions. For example, to analyse the experiments involving a liquid drop on a highly compliant film, Nadermann *et al.* [9] invoked force equilibrium at the contact line. They also, independently, invoked the configurational energy balance by assuming that the liquid surface makes an angle with the solid surface equal to the receding contact angle.

As mentioned earlier, the membrane or solid surface does not have an infinitely sharp kink at the contact line—there is a gradual transition from α_L to α_b—as indicated in figure 2 (from *A* to *B* to *C*). Let θ_c denote the contact angle of the liquid droplet with the solid. Geometry dictates (figure 2) that the following relationship must be satisfied:

$$\alpha_\mathrm{L} \le \theta_c \le \alpha_\mathrm{L} + \alpha_b. \tag{2.6}$$

Suppose the contact line is *free*, and, if elasticity can be neglected, assume that Young's equation applies so that θ_c is given by the configurational energy balance represented by (1.1*a*), so that (2.6) becomes

$$\alpha_\mathrm{L} \le \cos^{-1}\left[\frac{\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}}{\gamma_{\mathrm{LV}}}\right] \le \alpha_\mathrm{L} + \alpha_b. \tag{2.7}$$

As α_L and α_b are completely determined by the surface tensions and as surface energy need not be the same as surface tension, (2.7) may not be satisfied. If this were the case, then the droplet is either pinned in such a way that (2.6) is satisfied (and, by virtue of pinning, the configurational energy balance need not be satisfied) or there will be an instability since the droplet cannot be in static equilibrium (see caption of figure 2).

In summary, the above discussion shows that the force balance and the energy balance (due to the change in configuration) are two *independent* requirements for static equilibrium of a drop on an elastic substrate. For a free contact line, the contact angle is determined by the energy balance due to change in configuration. If the contact line is pinned, then one must supply additional information such as the mechanism of contact pinning to the energy balance equation in order to determine the contact angle.

In the analysis above, we have neglected the contribution of elastic energy to the energy balance equation. Let us relax this condition and account for the elastic energy in the energy balance equation for the case of a water drop on a membrane. As shown by Nadermann *et al.* [9], the membrane tensions and elastic energies are discontinuous across the contact line. Therefore, it is necessary to modify (2.1) to account for the jump in elastic energy across the contact line. Specifically, let W_{SL} and W_{SV} denote the elastic strain energy density ($\mathrm{J\,m^{-2}}$) of the membrane that is in contact with the liquid and air, respectively. The energy release rate given by (2.1) is now modified to

$$\delta E = [\gamma_{LV}(1 + \cos\theta_c) + (W_{SL} - W_{SV})]2\pi c\delta c. \tag{2.8}$$

As the elastic strains are generally non-uniform in the membrane, W_{SL} and W_{SV} in (2.8) should be evaluated at the contact line. For a free contact line, Young's equation now becomes

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta_c + (W_{SL} - W_{SV}), \tag{2.9}$$

with an additional term $W_{SL} - W_{SV}$ which accounts for the contribution of elasticity.

Similarly, we have so far considered force equilibrium at the contact line only in the limiting cases of a rigid material, which provides whatever reaction forces are needed to balance forces, or the other extreme limit of vanishing stiffness, in which case surface tensions form a self-equilibrating Neumann's triangle. We turn next to analysis of the transition between these two limits, i.e. between Young's equation and Neumann's triangle.

3. Stress and deformation fields near the contact line

We assume that the substrate is linearly elastic, isotropic and incompressible with shear modulus μ, and use small strain theory. The deformation near the contact line can be described by plane strain elasticity theory where the contact line is assumed to be infinitely long (out of plane) and the stresses and strains are independent of that direction. As we are only interested in the deformation near the contact line, we place the origin of our coordinate system there. The liquid drop occupies the infinite wedge region in figure 3. We assume θ_c to be given. (It is determined by a consistent solution of the force balance problem analysed in this section and the configurational energy balance.)

The key idea is to replace the line force representation of the liquid/air surface tension by a uniformly distributed traction,

$$p(x) = \begin{cases} \sigma_{LV}\sin\theta_c/2\varepsilon & |x| < \varepsilon \\ 0 & |x| > \varepsilon \end{cases} \quad \text{(vertical)} \tag{3.1}$$

and

$$q(x) = \begin{cases} -\sigma_{LV}\cos\theta_c/2\varepsilon & |x| < \varepsilon \\ 0 & |x| > \varepsilon \end{cases} \quad \text{(horizontal).} \tag{3.2}$$

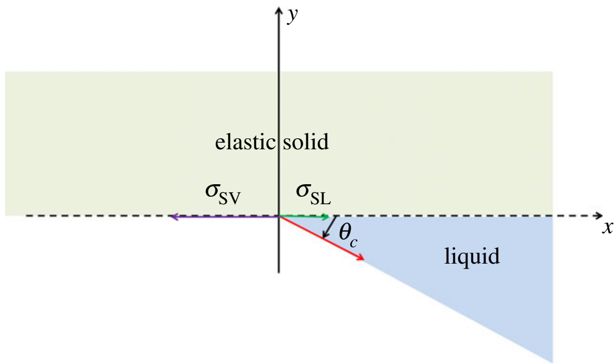

Figure 3. An elastic half-space subjected to surface tension by a liquid drop, which is resisted by a combination of its elasticity and solid surface tensions. (Online version in colour.)

The negative sign in the horizontal traction is due to a standard sign convention. Here, ε is a length scale that reflects the region of dominance of surface tension forces.[2] The solid surface tension should vary continuously from σ_{SV} to σ_{SL} and is represented by a function called $\sigma(x)$ such that

$$\left.\begin{aligned} &\sigma(x \ll -\varepsilon) = \sigma_{SV} \\ \text{and} \qquad &\sigma(x \gg \varepsilon) = \sigma_{SL}. \end{aligned}\right\} \tag{3.3}$$

On the surface $y = 0$, the jump in vertical forces must be balanced by the surface tension-induced curvature forces, that is,

$$p(x) - \sigma_{yy}^{+}(x) = \sigma(x)\frac{\mathrm{d}^2 v}{\mathrm{d}x^2}, \tag{3.4a}$$

where v is the vertical displacement of the surface.[3] The '+' sign in $\sigma_{yy}^{+}(x)$ denotes

$$\sigma_{yy}^{+}(x) \equiv \lim_{y \to 0^+} \sigma_{yy}(x, y = 0^+), \tag{3.4b}$$

that is, $\sigma_{yy}^{+}(x)$ is the vertical 'yy' component of stress just inside the solid surface. The horizontal force balance implies that

$$\frac{\mathrm{d}\sigma}{\mathrm{d}x} = -\sigma_{xy}^{+} + q(x), \tag{3.5}$$

where $\sigma_{xy}^{+}(x)$ is the shear 'xy' component of stress just inside the solid surface. It is useful to restrict attention to incompressible solids, because in that case the vertical surface displacement is independent of the shear surface traction [11]. This allows one to decouple the problems of determining the response to the normal and shear components of the liquid surface tension. From elasticity theory [11], the vertical surface displacement gradient is related to the normal traction by

$$\mathrm{v}_{,x} = \frac{1}{2\pi\mu}\mathrm{PV}\int_{-\infty}^{\infty} \frac{\sigma_{yy}^{+}(t)\mathrm{d}t}{x - t}, \tag{3.6}$$

where PV denotes a principal value integral. Equation (3.6) can be inverted using the Hilbert transform, resulting in

$$\sigma_{yy}^{+}(x) = -\frac{2\mu}{\pi}\mathrm{PV}\int_{-\infty}^{\infty} \frac{\mathrm{v}_{,t}(t)\mathrm{d}t}{x - t}. \tag{3.7}$$

[2]We found that replacing the uniform distribution by a Gaussian with standard deviation of ε made little difference in the results. The uniform distribution has the advantage that we can compare numerical results against an exact solution in both limiting cases.

[3]Note that the symbol σ without subscripts refers to the surface stress or tension ($\mathrm{N\,m^{-1}}$), whereas the symbol σ_{uu} with subscripts refers to a component of the bulk stress ($\mathrm{N\,m^{-2}}$).

Substituting (3.7) into (3.4*a*) gives

$$p(x) + \frac{2\mu}{\pi}\mathrm{PV}\int_{-\infty}^{\infty}\frac{\mathrm{v}_{,t}(t)\,\mathrm{d}t}{x-t} = \sigma(x)\mathrm{v}_{,xx}\,. \tag{3.8}$$

We introduce the normalized variables

$$\left.\begin{aligned} p &= \frac{\sigma_{\mathrm{LV}}}{2\varepsilon}\bar{p}, \quad q = \frac{\sigma_{\mathrm{SV}}}{\varepsilon}, \quad t = \varepsilon\bar{t}, \quad x = \varepsilon\bar{x}, \\ \mathrm{v} &= \frac{\sigma_{\mathrm{LV}}}{4\mu}\bar{\mathrm{v}}, \quad \sigma(x) = \sigma_{\mathrm{SV}}\bar{\sigma}\left(\bar{x}, \frac{\sigma_{\mathrm{SV}}}{\sigma_{\mathrm{SL}}}\right) \quad \text{and} \quad \sigma_{xy}^{+} = \frac{\sigma_{\mathrm{SV}}}{\varepsilon}\bar{\sigma}_{xy}^{+} \end{aligned}\right\} \tag{3.9}$$

to reduce the number of parameters in the calculation. In terms of these normalized variables, (3.8) and (3.5) become

$$\bar{p}(\bar{x}) + \frac{1}{\pi}\mathrm{PV}\int_{-\infty}^{\infty}\frac{\phi(\bar{t})\,\mathrm{d}\bar{t}}{\bar{x}-\bar{t}} = \beta\bar{\sigma}(\bar{x})\phi_{,\bar{x}} \tag{3.10a}$$

and

$$\frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}\bar{x}} = -\bar{\sigma}_{xy}^{+} + \bar{q}(x), \tag{3.10b}$$

where

$$\phi(\bar{t}) \equiv \bar{\mathrm{v}}_{,\bar{t}} \quad \text{and} \quad \beta \equiv \frac{\sigma_{\mathrm{SV}}}{2\mu\varepsilon}. \tag{3.10c}$$

To proceed, we assume that the surface tension interpolates linearly between its two values on either side of the contact line,

$$\bar{\sigma}(\bar{x}) = \begin{cases} 1 & \bar{x} < -1 \\ 1 + [(\sigma_{\mathrm{SL}}/\sigma_{\mathrm{SV}}) - 1](\bar{x}+1)/2 & |\bar{x}| \le 1 \\ \sigma_{\mathrm{SL}}/\sigma_{\mathrm{SV}} & \bar{x} < 1. \end{cases} \tag{3.11}$$

Note that the equations governing the normal (3.10*a*) and horizontal (3.10*b*) surface displacements are decoupled owing to incompressibility of the elastic substrate.

(a) Asymptotic behaviour for small and large $\beta \equiv \sigma_{\mathrm{SV}}/2\mu\varepsilon$

The transition from the surface tension-dominated regime to surface displacements elasticity-dominated regime can be studied by examining the behaviour of the solution of (3.10*a*) for large β (soft substrate) and small β (stiff substrate). First consider large β; (3.10*a*) suggests that

$$\bar{p}(\bar{x}) \approx \beta\bar{\sigma}(\bar{x})\phi_{,\bar{x}}\,, \tag{3.12}$$

in some interval enclosing the origin. Using $\bar{p}(\bar{x}) = 0$ for $|\bar{x}| > 1$, (3.12) implies that

$$\phi_{,\bar{x}}\,(|\bar{x}| > 1) \approx 0 \Rightarrow \phi = \bar{\mathrm{v}}_{,\bar{x}} = \text{const.}, \quad |\bar{x}| > 1. \tag{3.13}$$

Using (3.1) and (3.12), for $|\bar{x}| < 1$, we have

$$\phi = \bar{\mathrm{v}}_{,\bar{x}} = \frac{\sin\theta_c}{\beta}\left[\int_0^{\bar{x}}\frac{\mathrm{d}\bar{x}'}{\bar{\sigma}(\bar{x}')} + \phi(0)\right]. \tag{3.14}$$

Consider the special case where $\sigma_{\mathrm{SV}} = \sigma_{\mathrm{SL}} \Rightarrow \bar{\sigma} = 1$ and $\sin\theta_c = 1$, for which (3.14) reduces to

$$\bar{\mathrm{v}}_{,\bar{x}} = \frac{1}{\beta}[\bar{x} + \phi(0)]. \tag{3.15}$$

For this case, $\bar{\mathrm{v}}_{,\bar{x}}$ is an odd function so that $\phi(0) = 0$. Integrating (3.15), we have

$$\bar{\mathrm{v}}_{,\bar{x}} = \frac{\bar{x}}{\beta} \Rightarrow \bar{\mathrm{v}} = \frac{\bar{x}^2}{2\beta} \quad |\bar{x}| < 1. \tag{3.16}$$

Thus, the vertical displacement directly underneath the contact 'line' is bounded and has a parabolic profile for a very soft substrate. According to (3.13), the deformed surface outside the contact 'line' consists of two planes equally inclined with respect to the vertical y-axis. Were it not

for the regularization of the line force, they would form a kink at the origin. In this limit, the liquid line force is balanced by the vertical component of the interfacial tension in the deformed surface and, as noted by Style & Dufresne [10], the contact angle is governed by Neumann's triangle.

Next, we consider the limit where $\beta \ll 1$ (stiff substrate). For this case, the term on the right-hand side of (3.10*a*) is small and can be neglected, and (3.10*a*) reduces to

$$\bar{p}(\bar{x}) = -\frac{1}{\pi}\mathrm{PV}\int_{-\infty}^{\infty} \frac{\phi(\bar{t})\,\mathrm{d}\bar{t}}{\bar{x}-\bar{t}}. \tag{3.17}$$

Equation (3.17) is the integral equation for a distribution of normal traction on an elastic half-space, for which there is a closed form solution [11]

$$\mathrm{v}_{,x} = \frac{\sigma_{\mathrm{LV}}}{4\pi\varepsilon\mu}\ln\left|\frac{x+\varepsilon}{x-\varepsilon}\right|. \tag{3.18}$$

If we take the limit where $|x| \gg \varepsilon$, the displacement gradient in (3.18) takes the form

$$\mathrm{v}_{,x} \approx \frac{\sigma_{\mathrm{LV}}}{4\pi\mu x}, \tag{3.19}$$

which is the classical solution of a line load on an elastic half-space [11]. Thus, the divergence of the elasticity solution is avoided by treating the line tensions as distributed forces. In this case, the local shape near the contact line is *not* given by Neumann's triangle. In the limit of a rigid substrate, we can equate $\theta_c = \theta_y$, i.e. the geometry of surfaces in contact is governed by Young's equation.

(b) Numerical solution

For arbitrary values of the parameter β, the solution of (3.10*a*,*b*) was obtained numerically. Details of the numerical technique used to solve these equations are given in the electronic supplementary material. We focus on the case $\theta_c = \pi/2$, $\sigma_{\mathrm{SV}} = \sigma_{\mathrm{SL}}$. For this case, the horizontal surface displacement u is identically zero.

Figure 4*a*,*b* plots the vertical displacement and slope of the deformed surface versus the normalized distance from the origin for $\sigma_{\mathrm{LV}}/\sigma_{\mathrm{SV}} = 0.1$ and $\beta = 1000$, 100, 10 and 1. The numerical results are denoted by symbols. The asymptotic solution where $\beta \to \infty$, given by (3.13), (3.15) and (3.16), is shown as solid lines. Note that, for large β, we expect the solution to approach the limit where surface tension completely dominates. (Because in this limit the solution is independent of elastic properties, it is more useful to normalize the displacement by ε, and to plot the displacement gradient $\mathrm{v}_{,x}$ instead of $\bar{v}_{\bar{x}}$.) This expectation is satisfied for $\beta \geq 100$; the slope is practically constant outside the contact 'line', indicating the presence of a kink in the surface profile were it not for the finite width of the contact 'line' (figure 4*b*). Indeed, the numerical results show that the 'kink' is replaced by a parabolic profile, consistent with (3.16).

The numerical results for the vertical displacements and the slope for the same set of parameters, except with $\beta = 0.001$, 0.1, 1.0, 10.0, are shown in figure 5*a*, *b*, respectively. The exact elasticity solution, given by (3.18), is shown by the solid lines. Our solution shows that elasticity dominates for $\beta < 0.1$. Together, the results shown in figures 4 and 5 support our argument that there are two 'universal' profiles and the transition between these profiles is governed by a single parameter, β. For small values of β, liquid surface tension is balanced primarily by elasticity; for sufficiently small values of β the contact condition is then governed solely by Young's equation. For large values of β, liquid surface tension is balanced primarily by solid surface tension and the shape of contacting surfaces is given by Neumann's triangle.

By choosing the parameters just discussed, $\sin(\theta_c) = 1$, $\sigma_{\mathrm{SL}}/\sigma_{\mathrm{SV}} = 1$ and $\sigma_{\mathrm{LV}}/\sigma_{\mathrm{SV}} = 0.1$, we were able to use small displacement theory and ignore horizontal displacements, u, since they vanish. This case suffices to answer question (a) raised in the Introduction. That is, for large values of

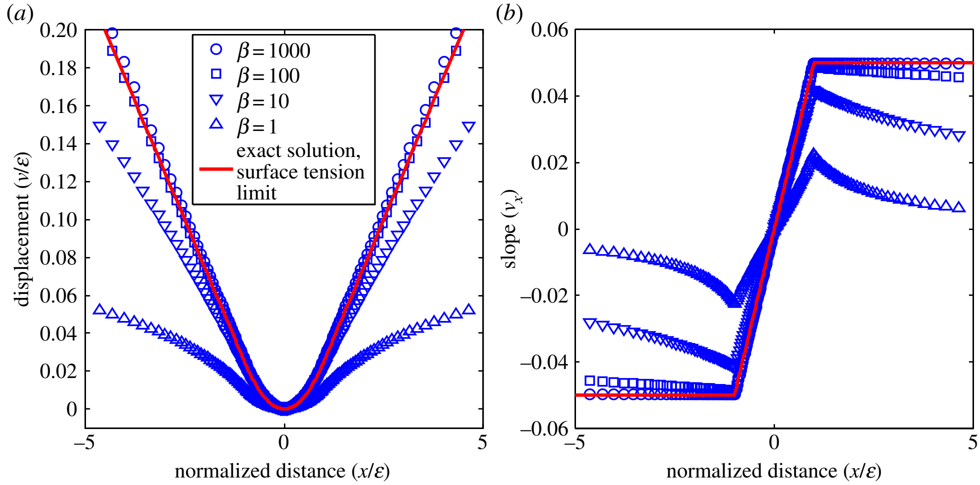

Figure 4. (*a*) Surface vertical displacement v and (*b*) its gradient $v_{,x}$ for $\sin(\theta_c) = 1$, $\sigma_{SL}/\sigma_{SV} = 1$ and $\sigma_{LV}/\sigma_{SV} = 0.1$, and a number of values of $\beta = 1000, 100, 10, 1$. For large values of β, the numerical solution approaches the exact solution (equations (3.13), (3.15) and (3.16)). Outside the region where surface tension forces act, the solid surface is straight with the slope given by the balance of tensions, i.e. Neumann's triangle. (Online version in colour.)

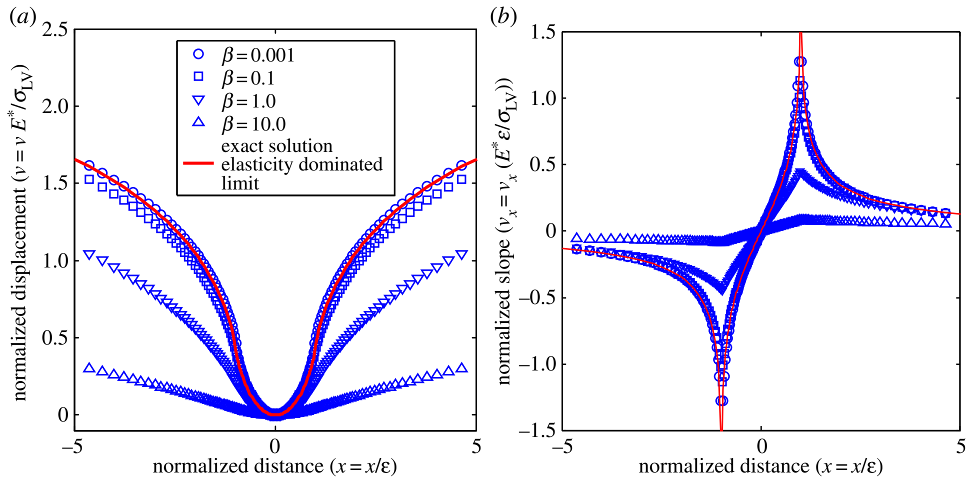

Figure 5. (*a*) Surface vertical displacement and (*b*) its gradient for $\sin(\theta_c) = 1$, $\sigma_{SL}/\sigma_{SV} = 1$ and $\sigma_{LV}/\sigma_{SV} = 0.1$, and a number of values of $\beta = 0.001, 0.1, 1.0, 10.0$. Note that the normalization used in this figure is different from the one in figure 4. For small values of β, the numerical solution approaches the exact solution for the case dominated by elasticity (equation (3.18)). (Online version in colour.)

the parameter $\beta \equiv \sigma_{SV}/2\mu\varepsilon$ surface tension determines the geometry of the contacting surfaces whereas for small values elasticity dominates. (Questions (b) and (c) were addressed in the previous section.)

Within small strain, linear elasticity our formulation can also handle situations such as $\sigma_{SV} \neq \sigma_{SL}$ and/or $\sin(\theta_c) \neq 1$, either of which results in horizontal as well as vertical surface displacements. Thus, one expects a non-symmetrical deformed surface when $\sigma_{SV} \neq \sigma_{SL}$, even if $\theta_c = \pi/2$. However, the small strain theory turns out to be of limited applicability in the limit of large β, because the condition $\sigma_{SV} \neq \sigma_{SL}$ causes significant rotations of the surface in the vicinity of the contact line. (See the electronic supplementary material for a more detailed discussion.)

4. Discussion and summary

In this work, we examined the conditions that determine equilibrium of surfaces near the contact line of a liquid drop on a deformable elastic substrate. We argued that two well-known limiting cases are governed by two different conditions. Specifically, if the substrate is rigid and the contact line free, the contact shape is determined by the configurational energy balance, represented by Young's equation. For deformable substrates, the contact line is additionally subjected to the condition of force balance in which the liquid surface tension is balanced by a combination of elastic tractions and solid surface tensions. In the limit of a highly compliant solid substrate, the three surface tensions must balance each other. Thus, in general, both the configurational energy balance and the force balance need to be satisfied independently. If, as can occur for solids, surface tensions differ from surface energies, it is possible that a consistent solution cannot be found that satisfies both these conditions, which can cause an instability.

By analysing the deformation of an elastic half-space subjected to (distributed) liquid surface tension tractions, we showed that the transition from elasticity-controlled to surface-tension-controlled shape is governed by a single dimensionless parameter β that is the ratio of the elasto-capillary length and the distance over which surface tension acts. For large values of this parameter, surface tension dominates, whereas for small values the shape is dominated by elasticity. If we take $\varepsilon \approx 1\,\mathrm{nm}$; $\sigma_{\mathrm{SV}} \approx 0.05\,\mathrm{N\,m^{-1}}$, then β ranges in value from about 10^5 for compliant gels with shear modulus in the kPa range to 10^{-4} for stiff materials with shear modulus in the hundreds of GPa. We analysed mainly the symmetric case where the two solid surface tensions are identical and the contact angle $\theta_c = \pi/2$, $\sigma_{\mathrm{SV}} = \sigma_{\mathrm{SL}}$, which allowed us to decouple the force balance condition from the configurational energy balance. In general, one would need to account for interplay between the vertical and horizontal force balance, and between both force balances and the configurational energy balance, which will probably require more involved numerical analysis, including also the effect of large deformations.

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References

1. deGennes P-G, Brochard-Wyart F, Quere D. 2002 *Capillarity and wetting phenomena. Drops, bubbles, pearls, waves*. New York, NY: Springer Science+Business Media, Inc.
2. Carré A, Gastel JC, Shanahan MER. 1996 Viscoelastic effects in the spreading of liquids. *Nature* **379**, 432–434. (doi:10.1038/379432a0)
3. Roman B, Bico J. 2010 Elasto-capillarity: deforming an elastic structure with a liquid droplet. *J. Phys.: Condensed Matter* **22**, 493101. (doi:10.1088/0953-8984/22/49/493101)
4. Extrand C, Kumagai Y. 1996 Contact angles and hysteresis on soft surfaces. *J. Colloid Interface Sci.* **1840**, 191–200. (doi:10.1006/jcis.1996.0611)
5. Yu Y-S. 2012 Substrate elastic deformation due to vertical component of liquid–vapor interfacial tension. *Appl. Math. Mech. Engl. Ed.* **33**, 1095–1114. (doi:10.1007/s10483-012-1608-x)
6. Lester GR. 1961 Contact angles of liquids at deformable solid surfaces. *J. Colloid Sci.* **16**, 315–326. (doi:10.1016/0095-8522(61)90032-0)
7. Rusanov AI. 1975 [Theory of wetting of elastically deformed bodies. I. Deformation with a finite contact-angle.] *Colloid J. USSR* **37**, 614–622. [In Russian.]
8. Style RW *et al.* 2013 Universal deformation of soft substrates near a contact line and the direct measurement of solid surface stresses. *Phys. Rev. Lett.* **110**, 066103. (doi:10.1103/PhysRevLett.110.066103)
9. Nadermann N, Hui C-Y, Jagota A. 2013 Solid surface tension measured by a liquid drop under a solid film. *Proc. Natl Acad. Sci. USA* **110**, 10 541–10 545. (doi:10.1073/pnas.1304587110)
10. Style RW, Dufresne ER. 2012 Static wetting on deformable substrates, from liquids to soft solids. *Soft Matter* **8**, 7177–7184. (doi:10.1039/c2sm25540e)
11. Johnson KL. 1985 *Contact mechanics*. Cambridge, UK: Cambridge University Press.

12. Shanahan MER, Gennes PGD. 1987 Equilibrium of the triple line solid/liquid/fluid of a sessile drop. In *Adhesion* (ed. KW Allen), pp. 71–91. London, UK: Elsevier Applied Science.
13. Marchand A *et al.* 2012 Contact angles on a soft solid: from Young's law to Neumann's law. *Phys. Rev. Lett.* **109**, 236101. (doi:10.1103/PhysRevLett.109.236101)
14. Roura P, Fort J. 2004 Local thermodynamic derivation of Young's equation. *J. Colloid Interface Sci.* **272**, 420–429. (doi:10.1016/j.jcis.2004.01.028)
15. Cahn JW, Larche F. 1982 Surface stress and the chemical equilibrium of small crystals—II. Solid particles embedded in a solid matrix. *Acta Metall.* **30**, 51–56. (doi:10.1016/0001-6160(82)90043-8)
16. Larche FC, Cahn JW. 1985 The interactions of composition and stress in crystalline solids. *Acta Metall.* **33**, 332–357. (doi:10.1016/0001-6160(85)90077-X)
17. Style RW *et al.* 2013 Surface tension and contact with soft elastic solids. *Nat. Commun.* **4**, 2728. (doi:10.1038/ncomms3728)
18. Xu X, Jagota A, Hui C-Y. In press. Effect of surface tension on the adhesive contact of a rigid sphere to a compliant substrate. *Soft Matter*. (doi:10.1039/C4SM00216D)
19. Rowlinson JS, Widom B. 1989 *Molecular theory of capillarity*. New York, NY: Oxford University Press.