

Contact Line Elasticity of a Completely Wetting Liquid Rising on a Wall.

E. RAPHAEL (*)^(§) and J. F. JOANNY (**)

(*) *Institute for Polymer and Organic Solids and Materials Department
University of California - Santa Barbara, CA 93106*

(**) *Institut Charles Sadron - 6 rue Boussingault, 67083 Strasbourg Cedex, France*

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Abstract. – We analyze the contact line elasticity of a completely wetting liquid rising on a vertical solid wall. Since the liquid-vapor interface intersects the solid substrate with a vanishing contact angle, the line elasticity is nonlinear and differs significantly from the linear elasticity predicted for a partially wetting liquid. If the line is deformed by a localized force f and displaced from its average position by a distance γ_m , the nonlinear force/displacement relation is given by: $f \propto \gamma_m^3$. This nonlinear elasticity affects both the relaxation modes of the contact line and the contact angle hysteresis.

Introduction. – Wetting phenomena have been studied quantitatively for at least two centuries [1] and are currently a topic of renewed interest [2, 3]. The behavior of a small drop of liquid placed on a solid surface is controlled by the spreading power S which characterizes the competition between the interfacial energies of the liquid-vapor (γ), liquid-solid (γ_{SL}) and solid-vapor (γ_{SV}) interfaces: $S = \gamma_{SV} - \gamma - \gamma_{SL}$. If S is greater than or equal to zero (*total wetting*), the liquid spreads spontaneously onto the solid surface. On the other hand, for $S < 0$ (*partial wetting*), the liquid remains as a drop showing a well-defined contact angle θ_0 between the liquid-vapor interface and the solid surface given by Young's law: $\cos \theta_0 = 1 + S/\gamma$. The wetted portion of the surface is then delimited by a certain contact line L (here a circle) where the three phases meet. The elasticity of the contact line was first constructed by Joanny and de Gennes [4] and is quite anomalous. The energy corresponding to a weak deformation of the line (specified by a displacement $x = \gamma(y)$ measured from the average line position $x = 0$) is of the form

$$u = \frac{1}{2} \gamma \theta_0^2 \sum_q |q| |\bar{\gamma}(q)|^2, \quad (1)$$

^(§) On leave from Laboratoire de la Matière Condensée, Collège de France, 75231 Paris Cedex 05, France.

where $\bar{\gamma}(q)$ is the Fourier transform of $\gamma(y)$:

$$\bar{\gamma}(q) = \int_{-\infty}^{+\infty} dy \exp[-iqy] \gamma(y).$$

The elastic energy (1) does not correspond to a usual line tension which would give an energy $\sim q^2$. The unusual $|q|$ -dependence for a mode of wavelength $2\pi/q$ expresses the fact that the line distortion perturbs the liquid-vapor interface up to a distance of order q^{-1} in the direction normal to the line. Using the elastic energy (1) one can construct the deformation of the contact line $\gamma(y)$ corresponding to a localized force f [4],

$$\gamma(y) = \frac{f}{\pi\gamma\theta_0^2} \log \frac{\Lambda}{|y|}, \quad (2)$$

where Λ is a long-distance cut-off given either by the gravity capillary length or by a macroscopic size. If d is the small linear dimension over which the force is acting, the central value of the distortion γ_m is proportional to the applied force; this defines a contact line spring constant $k = f/\gamma_m$:

$$k = \frac{\pi\gamma\theta_0^2}{\log(\Lambda/d)}. \quad (3)$$

Thus, for a partially wetting liquid, the relation between the force f and the maximal displacement γ_m is *linear*.

Very recently, Cazabat and Heslot have studied experimentally the effect of surface heterogeneities on the behavior of a nonvolatile, completely wetting liquid in the capillary rise geometry [5]. In particular, they have studied the deformation of the contact line in the presence of a nonwetting chemical defect. This situation is very interesting, since it involves the elasticity of the contact line in a case where the liquid-vapor interface intersects the solid substrate with a vanishing contact angle. As already noticed by Cazabat and Heslot, one can expect the line elasticity to be quite different from the form (1) which was established under partial-wetting conditions. Motivated by this experimental work, we present here a theoretical analysis of the contact line elasticity for a nonvolatile, completely wetting liquid rising on a vertical solid surface [6].

Contact line elasticity. – Figure 1 represents the capillary rise of a completely wetting liquid on a chemically homogeneous, vertical solid surface. The liquid rises up to a height $H = \sqrt{2}\kappa^{-1}$ above the free liquid surface [7] where κ^{-1} is the capillary length defined by $\kappa^{-1} = (\gamma/\rho g)^{1/2}$, ρ being the liquid density and g the gravity acceleration. The coordinate system is indicated in fig. 1. Near the contact line the liquid profile is *parabolic*,

$$z_0(x) = x^2 H^{-1} + O(x^3). \quad (4)$$

This is in contrast with the linear profile obtained in the case of a partially wetting liquid.

If the contact line is deformed by some weak external force (see fig. 2), the shape $z(x, y)$ of the liquid-vapor interface changes. In the vicinity of the contact line ($x \ll H$) the balance between the capillary pressure and the hydrostatic pressure can be approximated by

$$\kappa^{-2} \left(\frac{\partial^2 z}{\partial^2 x} + \frac{\partial^2 z}{\partial^2 y} \right) = H - x. \quad (5)$$

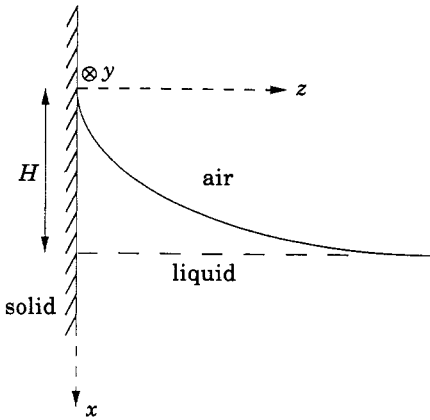


Fig. 1.

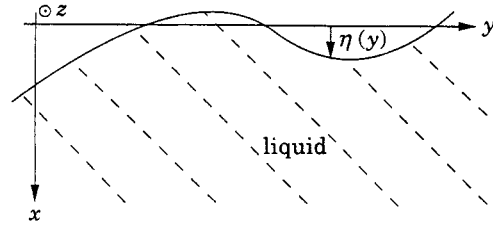


Fig. 2.

Fig. 1. – A nonvolatile, completely wetting liquid rising on a chemically homogeneous, vertical solid surface. The height of the meniscus is given by $H = \sqrt{2}\kappa^{-1}$, where κ^{-1} is the capillary length. The y -axis is perpendicular to the plane of the figure.

Fig. 2. – A deformed contact line L . The distortion is specified by a displacement $x = \eta(y)$ measured from the unperturbed line position $x = 0$.

The interface profile can thus be written in the form

$$z(x, y) = z_0(x) + \int_{-\infty}^{+\infty} \frac{dq}{2\pi} \alpha_q \exp[+iqy] \sinh[|q|(H - x)], \tag{6}$$

where we have used the fact that $z(x, y) - z_0(x)$ must vanish when $x \rightarrow H$. The amplitudes α_q are related to the imposed shape $\eta(y)$ of the contact line through the boundary condition $z(x = \eta(y), y) = 0$. This leads to

$$\alpha_q \sinh[|q|H] = -\frac{\kappa}{\sqrt{2}} \int_{-\infty}^{+\infty} \frac{dk}{2\pi} \tilde{\eta}(q - k) \tilde{\eta}(k) \tag{7}$$

(where terms of higher order in η have been neglected).

The total energy associated with the deformation of the contact line is the sum of a capillary contribution and a gravitational contribution:

$$u = \int_{-\infty}^{+\infty} dy \int_{\eta(y)}^H dx \left[\frac{1}{2} \gamma (\nabla z)^2 - S \right] - \gamma \kappa^2 \int_{-\infty}^{+\infty} dy \int_{\eta(y)}^H dx (H - x) z(x). \tag{8}$$

Inserting eq. (6) into (8) we obtain to second order in α

$$u = \frac{1}{4} \gamma \int_{-\infty}^{+\infty} \frac{dq}{2\pi} \alpha_q \alpha_{-q} |q| \sinh[2|q|H]. \tag{9}$$

Using eq. (7) the energy u can then be expressed directly in terms of the line shape $r_l(y)$:

$$u = \frac{\gamma\kappa^2}{8\pi} \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dy' K(y-y') r_l^2(y) r_l^2(y'), \quad (10)$$

where K is the kernel

$$K(y) = \int_{-\infty}^{+\infty} dq \exp[-iqy] |q| \operatorname{ctgh}[|q|H]. \quad (11)$$

The correction to the system energy due to the deformation of the contact line is therefore proportional to the *fourth* power of the displacement.

The external force required to create the distortion is given by

$$f(y) = \frac{\delta u}{\delta r_l(y)} = \frac{\gamma\kappa^2}{2\pi} r_l(y) \int_{-\infty}^{+\infty} dy' K(y-y') r_l^2(y'). \quad (12)$$

We can now construct the deformation of the contact line $r_l(y)$ corresponding to a localized force f acting over a distance d ($d \ll \kappa^{-1}$). We assume the maximal distortion r_m (see below) to be much smaller than κ^{-1} . From eq. (12) we find

$$r_l(y) = \left(\frac{f}{\gamma\kappa^2\pi} \right)^{1/3} \frac{\log^{1/2} |\operatorname{ctgh}(\pi y/4H)|}{\log^{1/6} |\operatorname{ctgh}(\pi d/4H)|}. \quad (13)$$

Equation (13) indicates that the perturbation generated by the applied force heals on a distance of the order of the capillary length H .

The central value of the distortion is given by

$$r_m = r_l(d) = \left(\frac{f}{\gamma\kappa^2\pi} \right)^{1/3} \log^{1/3} |\operatorname{ctgh}(\pi d/4H)|. \quad (14)$$

We define a nonlinear spring constant $k' = f/r_m^3$:

$$k' = \frac{\gamma\kappa^2\pi}{\log |\operatorname{ctgh}(\pi d/4H)|}. \quad (15)$$

Thus, for a completely wetting liquid rising on a vertical wall, the relation between the applied (localized) force f and the maximal distortion of the contact line r_m is *cubic* (nonlinear elasticity).

The nonlinear response of the contact line predicted by (14) has already been proposed by Pomeau in a different context [8]. He has given a detailed discussion of the thermal fluctuations of a contact line in the case of a completely wetting fluid and shown that the energy of a fluctuation is not a quadratic function of the fluctuation amplitude.

Concluding remarks. – We have shown in this paper that when the contact angle vanishes, the elasticity of a contact line is nonlinear. We have also discussed explicitly the line distortions induced by localized defects. Experiments under way in Paris by Marsh and Cazabat [9] should allow a precise check of our predictions.

The nonlinear elasticity of the contact line is relevant both for contact angle hysteresis and for the relaxation modes of the contact line.

Joanny and de Gennes have considered the contact angle hysteresis due to pinning of the three-phase line by individual impurities for a partially wetting fluid on a horizontal, heterogeneous solid surface [4]. They found that for smooth defects the hysteresis scales as the square of the impurity strength, a prediction checked recently by di Meglio and Quéré [10]. For a completely wetting liquid in the capillary rise geometry, one can show—using the elasticity (10)—that the advancing contact angle scales as the power 4/3 of the heterogeneity (the receding contact angle being equal to zero).

The relaxation modes of a contact line for a partially wetting fluid on a horizontal, homogeneous solid surface have been analysed by de Gennes [11,12]. For a completely wetting liquid in the capillary rise geometry, the relaxation of the line is governed by the balance between the viscous and elastic forces

$$\frac{3l}{\theta_d} \frac{\partial \gamma(y, t)}{\partial t} = \frac{\gamma \kappa^2}{2\pi} \gamma(y, t) \int_{-\infty}^{+\infty} dy' K(y - y') \gamma^2(y'; t), \quad (16)$$

where l is a logarithmic factor which reflects the singularity of the flow field near the contact line [13] and θ_d is the dynamical contact angle given by Tanner law [14,15]: $\theta_d^3 \propto \partial \gamma / \partial t$. In eq. (16) we approximate the logarithmic factor l as a constant; a similar approach was used by de Gennes [11] for the relaxation of a contact line of a partially wetting fluid and seems to describe the experimental results of Ondarçuhu and Veyssié [12] very well. If one starts from a localized distortion $\gamma(y, t = 0) = \text{const } \delta(y)$, and if one looks for a solution of the form $\gamma(y, t) = (\mu t)^\alpha g[y/(\nu t)^\alpha]$ ($g[u]$ being a dimensionless function of the dimensionless variable u), then one obtains $\alpha = -\beta = 1/5$. The relaxation is thus much slower than in the case studied by de Gennes (where $\alpha = -\beta = 1$).

Our model has however some limitations. We have discarded the possible role played by the microscopic film which for $S > 0$ develops ahead of the meniscus [15]. It is however possible to circumvent this difficulty by dealing with a partially wetting fluid with a very small contact angle θ_0 rising on a wall. Indeed, one can show that, though the contact angle is finite, the force/displacement relation becomes nonlinear (eq. (15)) as soon as r_m is greater than $\theta_0 \kappa^{-1}$. We also have linearized the equation giving the interface profile. This is a good approximation in the vicinity of the contact line but a poor approximation for a thick meniscus ($x \approx H$).

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