Line tension and excess energy of a wall Plateau border

P. I. C. Teixeira[1,*] and M. A. Fortes[2]

[1]*Faculdade de Engenharia, Universidade Católica Portuguesa Estrada de Talaíde, P-2635-631 Rio de Mouro, Portugal*

[2]*Departamento de Engenharia de Materiais and Instituto de Ciêencia e Engenharia de Matriais e Superfícies, Instituto Superior Técnico Avenida Rovisco Pais, P-1049-001 Lisbon, Portugal*

(Received 2 June 2006; published 12 January 2007)

We have calculated the equilibrium shape of the axially symmetric Plateau border (PB) along which a spherical bubble contacts a flat wall, by numerical integration of Laplace's equation. We found that the (spherical) film prolongation into the PB meets the wall at an internal angle $\phi \leq \pi/2$; the deviation $\Delta\phi \equiv \pi/2 - \phi$ is an increasing function of the liquid fraction and of the liquid-wall contact angle. For the equivalent *dry* bubble (i.e., no PB) this deviation can be accounted for in terms of a negative line tension τ associated with the PB, and which can be determined from $\Delta\phi$. We have also calculated the (negative) PB excess energy ϵ, defined as the energy per unit length of the PB's liquid-gas and liquid-wall interfaces minus that of the film prolongation into the PB and of the dry wall. For $A^{1/2}/x_I \lesssim 0.4$ (where A is the PB cross-sectional area and x_I is the radius of the extrapolated contact line), it was found that $|\epsilon| \propto A^{1/2}$. Finally, we derived a general relationship involving ϵ, τ and A which yields $\tau = \epsilon/2$ when $|\epsilon| \propto A^{1/2}$, i.e., for not too large PBs; larger PBs have $|\tau| < |\epsilon|/2$.

DOI: 10.1103/PhysRevE.75.011404 PACS number(s): 83.80.Iz, 82.70.Rr

I. INTRODUCTION

A fully dry three-dimensional (3D) liquid foam at stable equilibrium satisfies Plateau's laws [1]: the films are of constant mean curvature and meet at $2\pi/3$ along triple lines. These, in turn, meet at four-connected vertices, or nodes, at the tetrahedral angles, $\cos^{-1}(-1/3)$. The contractile film tension γ of a film of mean curvature κ is balanced by a pressure difference $\Delta p = 2\gamma\kappa$ across the film.

In a fairly dry foam (liquid fraction $\phi_L \lesssim 5\%$, such as is obtained after drainage) the triple lines are decorated with triangular Plateau borders (PBs), where most of the liquid resides, but the films remain of negligible thickness (of order 100 nm, as compared with typical dimensions of order 1 mm for a PB). Whereas in two-dimensional (2D) equilibrium foams the three (circular) film prolongations into a PB always meet at $2\pi/3$ (the so-called "decoration theorem" [2,3]), the same is not in general true in 3D, as was recently shown by the present authors for two highly symmetric bubble clusters (the double bubble and the lens bubble), which contain only spherical or planar films and a circular PB with no vertices [4]. The shapes of the PBs in these wet clusters were obtained by numerical integration of the Laplace equation, taking the tension of the PB liquid surfaces to be $\gamma_L = \gamma/2$. The (positive) calculated deviation $\Delta\phi \equiv \phi - 2\pi/3$ of the angle ϕ at which the prolongations of the two spherical films meet along the triple line was found to be approximately proportional to $A^{1/2}/x_I$, where A is the PB cross-sectional area and x_I is the radius of the circular triple line. $|\Delta\phi| \sim 4°$ for $A^{1/2}/x_I \sim 0.35$, the largest PB considered. Very recently, deviations of up to 2.5° from 120° of the angles between films meeting at a PB were experimentally found by Géminard *et al.* [5], who used a double catenoidal bubble fixed at two identical circular rings.

Let us now consider the equivalent dry foam of a given wet foam: this is obtained by prolonging all films into the PBs and then deleting the PBs. If the film prolongations meet along a single line—the triple line—obviously such a dry foam will not be in equilibrium, as the angle between films at triple lines will not be $2\pi/3$. In order to restore equilibrium we need to endow each triple line with a *line tension* τ which is just the PB contribution (per unit length) to the total energy of the wet foam. In an earlier paper [4] we also calculated the excess energy (per unit length) ϵ of the PB, defined as the energy of the PB surfaces minus the energy of the film prolongations into the PB. This was found approximately to depend on PB size according to

$$-\frac{\epsilon}{\gamma} \approx cA^{1/2}, \tag{1}$$

where the prefactor $c = 0.393$ is close to $c = 0.4016$ for a regular 2D PB with $\gamma_L = \gamma/2$. We also showed in Ref. [4] that if Eq. (1) holds, then

$$\tau = \frac{\epsilon}{2}, \tag{2}$$

a relation which was also used by the authors of Ref. [5] to interpret their experimental results.

In confined foams, which include most real-life foams, there are PBs of a different type—wall PBs—where the films meet the confining walls. These PBs are bounded by two liquid surfaces of tension $\gamma_L = \gamma/2$ and one solid surface (the wall) of tension γ_{WL} (the wall-liquid interfacial tension). Wall PBs affect both the statics and the dynamics of foams: not only do they contribute to the total foam energy, they also exert considerable drag on the walls in foam flow ex-

*Present address: Instituto Superiror de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro 1, P-1950-062 Lisbon, Portugal; and Centro de Física Teórica e Computacional, Universidade de Lisboa, Avenida Professor Gama Pinto 2, P-1649-003 Lisbon, Portugal.

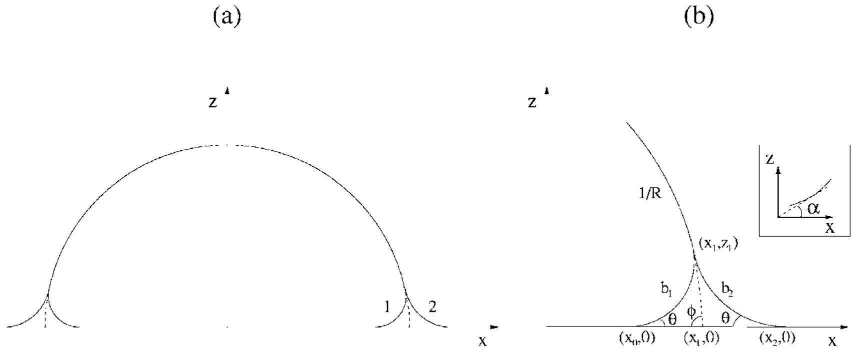

FIG. 1. (a) A bubble at a wall: the contact line is "decorated" with a wall PB. We take the z axis to be the axis of rotational symmetry of the bubble. (b) Definition of key quantities. The dashed line is the film prolongation into the PB, which meets the wall at an angle ϕ. The contact angle of the liquid at the wall is θ.

periments. In fully dry foams the film contact angle at a wall is $\pi/2$. In 2D wet foams, the (circular) film prolongations into a wall PB also meet the wall at $\pi/2$ [6]. However, this appears not to be the case in 3D wet foams in contact with walls: deviations from $\pi/2$ have been reported for a single bubble on a wet porous substrate [7], e.g., $\phi \approx 85°$ (measured inside the bubble and extrapolated to the substrate surface) for a bubble of radius $R=2.4$ mm.

The purpose of this paper is to calculate the deviations from $\pi/2$ of the angle between the film prolongation into a wall PB and the wall. We do this for the simplest possible foam: a single spherical bubble on a flat wall, see Fig. 1(a), as in the experiment described in Ref. [7]. From the angular deviation we find the line tension τ of the wall PB. We also determine the excess energy ϵ of the wall PB and relate it to τ. This is part of our ongoing investigation into how far concepts relating to the decoration theorem can be generalised to 3D (given that the theorem itself is not), and thus allow one to make use, when researching wet foams, of the many mathematical results derived for perfectly dry foams.

II. INTEGRATION OF THE LAPLACE EQUATION FOR THE WALL PB

We start by integrating the Laplace equation numerically, for the two axially symmetric PB liquid-gas interfaces, numbered 1 and 2 [see Fig. 1(a)], as done in Ref. [4] for bulk PBs. We shall assume $\gamma_L=\gamma/2$, which amounts to neglecting the interaction between film surfaces (i.e., the disjoining pressure): the film tension (which, strictly speaking, is not the same as the film energy) is taken to be just twice the tension of the liquid-air surface. This implies that the PB surfaces join the (zero-thickness) film tangentially. Furthermore, we shall neglect gravity in this first treatment: preliminary analytic work [8] suggests that Earth's gravity has very little effect on wall PB shape, i.e., that a sessile and a pendant bubble should have virtually identical wall PBs. We allow for different contact angles θ of the liquid at the wall, according to Young's equation

$$\cos\theta = \frac{\gamma_W - \gamma_{WL}}{\gamma_L}, \tag{3}$$

where γ_W and γ_{WL} are the surface tensions of the wall-gas and wall-liquid interfaces, respectively. If the right-hand side of Eq. (3) is equal to or greater than 1, then $\theta=0°$ and the liquid is said to completely wet the wall; otherwise the wetting is partial.

For the bubble shown in Fig. 1, we take the z axis to be along the symmetry axis of the bubble, and the origin of coordinates to lie on the wall. The radial coordinate (i.e., the distance from a point to the z axis) is x. The bubble film is assumed to have negligible thickness; it is spherical and has (positive) radius R (in a fully dry bubble it would be a hemisphere). The two PB surfaces are numbered 1 and 2, where surface 1 is that located inside the bubble; in the absence of gravity, they have constant mean curvatures b_1 and b_2, respectively [see Fig. 1(b)]. Surface i ($i=1,2$), generically given as $x(z)$, is a solution of the Laplace equation for an axially symmetric fluid interface in zero gravity:

$$(1+\dot{x}^2)^{-3/2}\left(-\ddot{x} + \frac{1+\dot{x}^2}{x}\right) = \frac{\Delta p_i}{\gamma_L} = 2b_i, \tag{4}$$

where the overdot denotes differentiation with respect to z, Δp_i is the pressure difference across the interface, positive if the pressure is higher on the side of the z axis, and $b_i = (1/R_1 + 1/R_2)/2$ is the mean curvature. Thus $b_1 > 0$, but b_2 can have either sign. For $\gamma_L=\gamma/2$, the two PB surfaces meet each other and the film tangentially, at a point of coordinates (x_1, z_1). Equilibrium of pressures requires

$$b_1 + b_2 = 2/R. \tag{5}$$

The two PB surfaces meet the wall at an angle θ, the liquid contact angle. In nonzero gravity (bubble on the upper or lower surface of a horizontal wall) there is an extra term $\pm\rho g z$ on the right-hand side of Eq. (4) (where ρ is the liquid density and g is the acceleration due to gravity) and b_i are now the curvatures of the PB surfaces at the wall ($z=0$). The effect of gravity will be discussed elsewhere.

In order to integrate Eq. (4), we introduce the arc length s along $x(z)$ from a chosen origin. Its origin is taken to be $z=0$, $x=x_0$ for PB surface 1 and $z=z_1$, $x=x_1$ for PB surface 2 [see Fig. 1(b)]. Equation (4) for $x(z)$ is then equivalent to the following set of first-order differential equations:

$$\frac{dx}{ds} = \cos\alpha, \tag{6}$$

$$\frac{dz}{ds} = \sin\alpha, \tag{7}$$

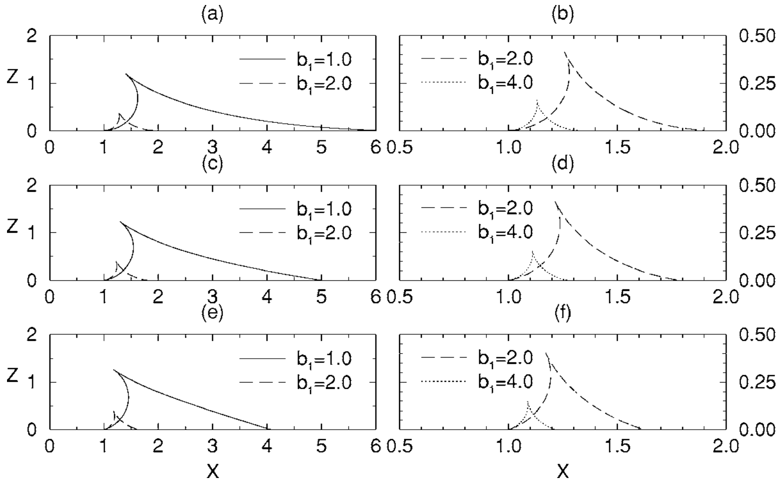

FIG. 2. Shapes of PBs around the bubble at a solid surface for different liquid-solid contact angles θ and inner PB curvatures b_1. (a) and (b) $\theta=0°$; (c) and (d) $\theta=10°$; (e) and (f) $\theta=20°$. The films (not shown) join the PB surfaces tangentally. As b_1 increases, the bubble approaches a hemisphere of radius $R=1$ with a vanishingly small, symmetrical PB.

$$\frac{d\alpha}{ds} = 2b_i - \frac{\sin\alpha}{x}, \tag{8}$$

where $\alpha(0 \le \alpha \le \pi)$ is the angle between the tangent to the $x=x(z)$ curve and the positive x axis [see Fig. 1(b)]: $\tan\alpha = dz/dx$. For a given contact angle θ, and once a length scale has been set (e.g., by fixing $x_0=1$), Eqs. (6)–(8) define a one-parameter family of solutions for the two PB surfaces. We choose b_1 as the parameter and first integrate Eqs. (6)–(8) for PB surface 1, starting from $z=0$, $x=x_0(=1)$, $\alpha=\theta$ (where θ is the contact angle of the liquid at the wall, see Fig. 1(b)) up to a tentative $z=z_1$, $x=x_1$, $\alpha=\alpha_1$. Using x_1 and α_1, the radius R of the spherical film can be calculated from

$$R = \frac{x_1}{\sin\alpha_1}, \tag{9}$$

and b_2 from Eq. (5). With this b_2 we integrate Eqs. (6)–(8) for PB surface 2, with initial conditions $x=x_1$, $z=z_1$, $\alpha=\alpha_1$ (note that z is now decreasing). The resulting profile will reach the wall at $z=0$, $x=x_2$, $\alpha=\alpha_2$. A PB must have $\alpha_2=\pi-\theta$: the liquid contact angle must be the same outside as well as inside the bubble and α is measured anticlockwise. If this is not satisfied, then our choice of z_1 was not correct, so we pick a different z_1 and iterate the above procedure until we get $\alpha_2=\pi-\theta$. Figure 2 shows examples of calculated PB profiles for different b_1 and θ. As remarked in Ref. [7], the PBs are asymmetric: surfaces 1 and 2 have different curvatures, owing to the pressure difference across the bubble film. The corresponding geometrical parameters are collected in Table I. All lengths are in units of x_0, the shortest distance from the PB to the z axis (i.e., the radius of the circle along which the PB surface meets the wall inside the bubble).

III. ANGULAR DEVIATIONS DUE TO WALL PB

The internal angle ϕ between the prolongation of the spherical bubble film and the wall can be obtained from

$$z_1 = R(\cos\alpha_1 - \cos\phi). \tag{10}$$

The calculated ϕ is always less than $\pi/2$. As will be shown below, this is reflected in a negative line tension associated with the wall PB. In Fig. 3 we plot the deviation $\Delta\phi$ of ϕ from its value in the absence of the wall PB, $\pi/2$ vs $A^{1/2}/x_I$. Here A is the PB cross-sectional area, defined by Eq. (14) as the ratio of the PB volume to the length $2\pi x_I$ of the line along which the film prolongation meets the solid wall,

TABLE I. Geometrical parameters pertaining to the PBs of Fig. 2: we take $x_0=1.0$ and fix the contact angle and b_1.

Contact angle	b_1	b_2	x_1	x_2	x_I	R	ϕ
0°	1.0	−0.0219	1.3990	6.1463	2.0232	2.0448	81.66°
	2.0	−0.5253	1.2586	1.9303	1.3531	1.3562	86.11°
	4.0	−2.2572	1.1307	1.3296	1.1471	1.1476	88.26°
10°	1.0	0.0021	1.2869	4.9452	1.9748	1.9957	81.70°
	2.0	-0.4781	1.2141	1.7769	1.3113	1.3142	86.18°
	4.0	−2.2231	1.1089	1.2739	1.1250	1.1255	88.31°
20°	1.0	0.0438	1.1731	4.0497	1.8994	1.9160	82.45°
	2.0	−0.4198	1.1706	1.6218	1.2634	1.2657	86.60°
	4.0	−2.1856	1.0875	1.2172	1.1020	1.1023	88.61°

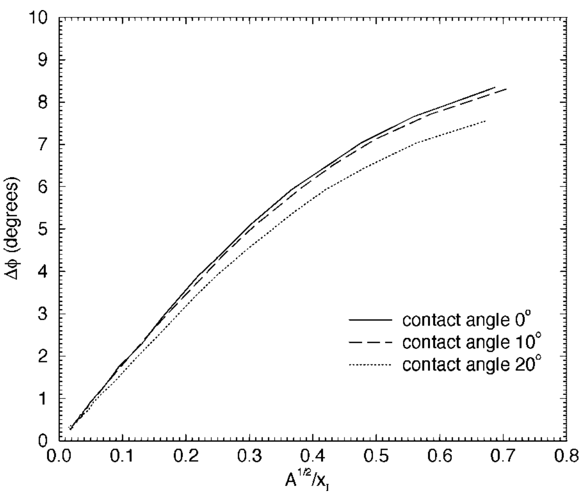

FIG. 3. Deviation of ϕ from its dry bubble value, $\Delta\phi=\pi/2-\phi$ (in degrees) vs $A^{1/2}/x_I$, the bubble liquid fraction. By Eq. (19) this also gives $\tau/\gamma x_I \approx -\Delta\phi$.

henceforth denoted the "contact line." Note that $A^{1/2}/x_I$ is a measure of the liquid fraction of the wet bubble. At a given $A^{1/2}/x_I$, $\Delta\phi$ for the wall PB is slightly larger than for the bulk PBs calculated in Ref. [4]. The radius x_I of the contact line, given by

$$x_I = R\sin\phi, \tag{11}$$

is also listed in Table I. The true PB cross-sectional area A_{CS} is

$$A_{\mathrm{CS}} = \left(\int_0^{z_1} x dz\right)_2 + \left(\int_0^{z_1} x dz\right)_1, \tag{12}$$

and the PB volume V is, likewise,

$$\frac{V}{\pi} = \left(\int_0^{z_1} x^2 dz\right)_2 + \left(\int_0^{z_1} x^2 dz\right)_1, \tag{13}$$

where $(\cdots)_i$ denotes that the integration is to be carried out over PB surface i. This leads to an alternative measure of the PB cross-sectional area as

$$A = \frac{V}{2\pi x_I}. \tag{14}$$

In Fig. 3 we plot $A_{\mathrm{CS}}^{1/2}/x_I$ vs $A^{1/2}/x_I$: the slope is close to unity except for the largest PBs considered. In this paper we adopt A as *the* PB cross-sectional area, as our results are relevant to the case where V is constant and x_I variable.

How well do our results for $\Delta\phi$ agree with experiment? From Fig. 3 in Ref. [7], we obtain by straightforward extrapolation from the PB apex to the wall that $\phi \approx 85°$ for a bubble of radius $R \approx 2.4$ mm on a wet substrate (where the contact angle is unambiguously zero). For this bubble $z_1/R \approx 0.14 \ll 1$, hence the PB is approximately symmetric and $x_I \approx R$ and $z_1 \approx r$, where r is the radius of the PB surfaces, and $A \approx (2-\pi/2)r^2 \approx (2-\pi/2)z_1^2$. This yields $A^{1/2}/x_I \approx 0.09$, for which we predict (see Fig. 4) $\phi = 88.3°$ if $\theta = 0°$.

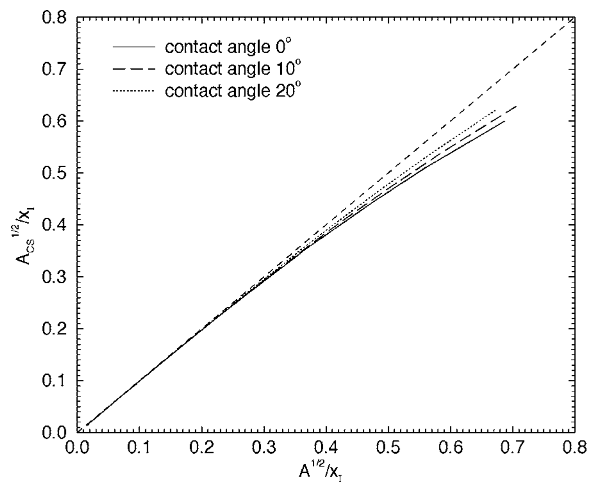

FIG. 4. Nondimensionalized "true" PB cross-sectional area $A_{\mathrm{CS}}^{1/2}/x_I$ vs nondimensionalized PB cross-sectional area found from PB volume $A^{1/2}/x_I$. The thick short-dashed line has slope 1: the two cross-sectional areas are very close for small PBs.

IV. SURFACE ENERGY MINIMISATION WITH TRIPLE LINE TENSION

The deviation from $\pi/2$ of ϕ can be interpreted by assigning a line tension τ to the contact line (of radius x_I) of a dry bubble on a wall. This is defined as the contribution of the PB to the total energy of a unit length of contact line in the dry bubble. The energy E of the wet bubble is then the sum of the surface energy γS of the dry film meeting the wall along a contact line of length $L=2\pi x_I$, plus the energy τL of that contact line

$$E = \gamma S + \tau L. \tag{15}$$

The area S of the dry film (a spherical cap) is

$$S = 2\pi R^2(1-\cos\phi), \tag{16}$$

and the volume it encloses is

$$V_b = \frac{\pi R^3}{3}\left(2 - 3\cos\phi + \cos^3\phi\right). \tag{17}$$

Minimisation of E at fixed V_b yields

$$\frac{\tau}{\gamma x_I} = -\cos\phi. \tag{18}$$

For small deviations $\Delta\phi = \pi/2 - \phi$, this becomes

$$\frac{\tau}{\gamma x_I} \approx -\Delta\phi. \tag{19}$$

The equilibrium condition (18) can be derived directly by balancing the γ and $\tau = \tau\hat{\mathbf{n}}/x_I$ forces acting on the (dry) contact line, where $\hat{\mathbf{n}}$ is the principal unit normal to the contact line, pointing towards its centre (see Fig. 5). A positive line tension τ induces a contractile force τ/x_I per unit length: conversely a negative line tension (as in PBs) tends to expand the contact line. These two cases lead, respectively, to $\phi > \pi/2$ or $\phi < \pi/2$ at equilibrium. From the calculated ϕ of Fig. 4 one can then determine, using Eq. (18) or (19), the

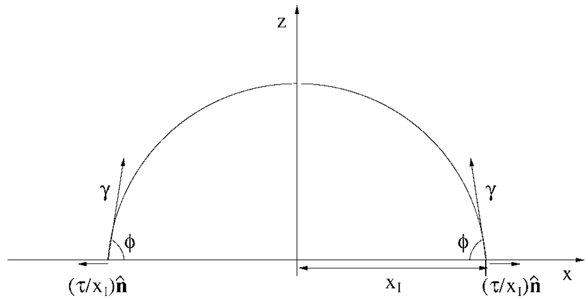

FIG. 5. In the equivalent dry bubble, the (negative) contact line tension enforces $\phi<\pi/2$ in the absence of a PB (vectors not to scale for clarity). $\hat{\mathbf{n}}$ points towards the origin.

reduced line tensions $\tau/\gamma x_I$ and $\tau/\gamma A^{1/2}$ associated with the wall PB, as functions of $A^{1/2}/x_I$.

V. EXCESS ENERGY OF A WALL PLATEAU BORDER

The excess energy ϵ of the wall PB is defined as the energy (per unit length) of the PB surfaces and wetted wall minus the energy (per unit length) of the film prolongations into the PB and of the dry wall. The area of PB surface i is

$$S_i=\left[2\pi\int_0^{z_1} x\sqrt{1+\left(\frac{dx_i}{dz}\right)^2}dz\right]_i, \tag{20}$$

and the wetted area on the wall (a circular ring) is

$$S_W=\pi(x_2^2-x_1^2). \tag{21}$$

Finally, the spherical film prolongation into the PB is a slice of height z_1 of a sphere of radius R; its area is $2\pi R z_1$ or, using Eq. (10),

$$S_{fp}=2\pi R^2(\cos\alpha_1-\cos\phi). \tag{22}$$

Thus the excess energy per unit length, ϵ, of the contact line (of total length $L=2\pi x_I$) is

$$\epsilon=\frac{1}{2\pi x_I}[(S_1+S_2)\gamma_L+S_w(\gamma_{WL}-\gamma_W)-S_{fp}\gamma], \tag{23}$$

or, dividing through by γ_L and using Eq. (3),

$$\frac{\epsilon}{\gamma_L}=\frac{1}{2\pi x_I}[(S_1+S_2)-S_W\cos\theta-2S_{fp}]. \tag{24}$$

In Fig. 6 we plot the dimensionless quantity $\epsilon/(\gamma x_I)$ vs $A^{1/2}/x_I$; the latter quantity is a measure of the fraction of liquid in the bubble. The excess energy is negative and approximately proportional to $A^{1/2}$ for small liquid fractions

$$-\frac{\epsilon}{\gamma_L}=c(\theta)A^{1/2}, \tag{25}$$

where $c(\theta)$ is a constant which is a function of θ. In the limit $A^{1/2}/x_I\to 0$, the bubble expands to infinite radius and the film becomes planar, giving [6]

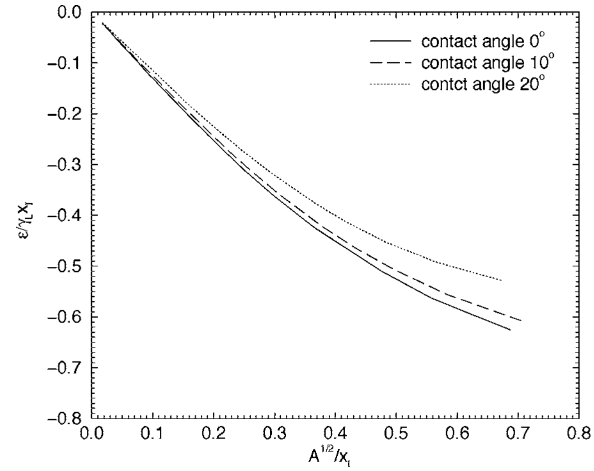

FIG. 6. Excess energy $\epsilon/\gamma_L x_I$ vs PB cross-sectional area $A^{1/2}/x_I$. Except for small PBs ($A^{1/2}/x_I\lesssim 0.3$), the dependence is clearly nonlinear.

$$\frac{\epsilon}{\gamma_L A^{1/2}}=1.743-3.053\cos\theta. \tag{26}$$

For $\theta=0°$, $10°$, and $20°$, this predicts $\epsilon/\gamma_L A^{1/2}=-1.310$, -1.264, and -1.126, respectively, in excellent agreement with $\epsilon/\gamma_L A^{1/2}=-1.307$, -1.256, and -1.150 found from Fig. 6 in the range $A^{1/2}/x_I\lesssim 0.1$.

VI. RELATIONSHIP BETWEEN LINE TENSION AND EXCESS ENERGY

In order to relate the line tension τ and the excess energy ϵ we follow the argument previously adduced in Refs. [5,4] for PBs at a triple line. Consider an infinitesimal change dx_I of the radius of the circular contact line of a dry bubble at a wall, at constant PB volume V. The work performed by τ is then $\tau d(2\pi x_I)$, and the change in the total PB excess energy is $d(2\pi x_I\epsilon)$. Equating these two quantities yields

$$\tau=\epsilon+x_I\left(\frac{\partial\epsilon}{\partial x_I}\right)_V \tag{27}$$

or, since $V=2\pi x_I A$ is kept constant,

$$\tau=\epsilon-A\left(\frac{\partial\epsilon}{\partial A}\right)_V. \tag{28}$$

This is a general relationship involving τ, ϵ, and the PB cross-sectional area A: our only assumptions were a closed triple line (no nodes). It can be rewritten as

$$\tau=\epsilon-\frac{A^{1/2}}{2}\left(\frac{\partial\epsilon}{\partial A^{1/2}}\right)_V, \tag{29}$$

whence it follows that, when $\epsilon\propto A^{1/2}$, we have

$$\tau=\frac{\epsilon}{2}, \tag{30}$$

which is independent of the liquid-wall contact angle θ. As can be seen from Fig. 6, $\epsilon\propto A^{1/2}$ for $A^{1/2}/x_I\lesssim 0.3$, i.e., for

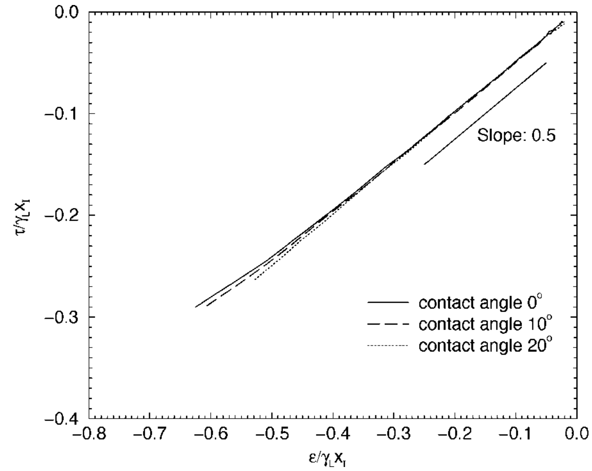

FIG. 7. Line tension $\tau/\gamma_L x_I$ vs excess energy $\epsilon/\gamma_L x_I$: in the linear region near the origin (at the top right-hand corner) the slopes of all curves are close to 0.5 (as shown by the short straight line), thus satisfying the relationship $\tau=\epsilon/2$ found earlier [4].

relatively dry bubbles. For wetter bubbles there are noticeable deviations and Eq. (30) no longer applies. In Fig. 7 we plot τ *vs* ϵ: it is apparent that $|\tau|<|\epsilon|/2$ for wet bubbles, consistently with Fig. 4.

VII. CONCLUDING REMARKS

We have provided a detailed analysis of a wet hemispherical bubble on a wall, neglecting gravity. This analysis amounts to solving Eq. (4) [or, alternatively, Eqs. (6)–(8)] for the two PB surfaces, with appropriate boundary conditions at the film and at the wall (i.e., the contact angle at the wall-liquid interface). We have calculated the deviation $\Delta\phi$ from $\pi/2$ of the angle at which the film prolongation into the PB meets the wall ($\Delta\phi=\pi/2-\phi$). This is positive and can be a few degrees, in agreement with the experimental results of Ref. [7]. $\Delta\phi$ may be accounted for by endowing the equivalent dry bubble with a (negative) line tension, the absolute value of which is an increasing function of PB size relative to bubble size, and of the liquid contact angle θ on the wall. We have related $\Delta\phi$ to τ by minimizing the total energy at constant volume of the dry bubble, and showed that the same relation can be obtained by balancing the film tension force γ and the line tension force $\boldsymbol{\tau}=\tau\hat{\mathbf{n}}/x_I$ at the contact line of radius x_I, along which the film prolongation into the PB meets the wall.

Finally, we derived a general relationship between the line tension τ and the rate of change of the excess energy ϵ with respect to the PB cross-sectional area, at constant liquid fraction, for a closed PB in a foam with no nodes. If $\epsilon \propto A^{1/2}$, which is approximately true for moderately wet bubbles, this general relation implies that $\tau=\epsilon/2$, as found previously for bulk PBs [4]. This result is probably exact only in the dry bubble limit. The next step in our investigation will be to look at the effect of gravity on the angle ϕ between the film prolongation and the wall, and on the relationships between ϵ, τ, and A; this will be addressed in a separate paper.

ACKNOWLEDGMENTS

We thank M. A. C. Teixeira for discussions.

[1] J. A. F. Plateau, *Statique Expérimentale et Théorique des Liquides Soumis aux Seules Forces Moléculaires* (Gauthier Villars, Paris, 1873).
[2] F. Bolton and D. Weaire, Philos. Mag. B **63**, 795 (1991).
[3] D. Weaire, Philos. Mag. Lett. **79**, 491 (1999).
[4] M. A. Fortes and P. I. C. Teixeira, Phys. Rev. E **71**, 051404 (2005).
[5] J. C. Géminard, A. Żywociński, F. Caillier, and P. Oswald, Philos. Mag. Lett. **84**, 199 (2004).
[6] M. A. Fortes and P. I. C. Teixeira, Philos. Mag. Lett. **85**, 21 (2005).
[7] J. F. Rodrigues, B. Saramago, and M. A. Fortes, J. Colloid Interface Sci. **239**, 577 (2001).
[8] M. A.C. Teixeira (unpublished).