Triple-line decoration and line tension in simple three-dimensional foam clusters

M. A. Fortes[1] and P. I. C. Teixeira[2]
[1]*Departamento de Engenharia de Materiais and Instituto de Ciência e Engenharia de Materiais e Superfícies, Instituto Superior Técnico Avenida Rovisco Pais, P-1049-001 Lisbon, Portugal*
[2]*Faculdade de Engenharia, Universidade Católica Portuguesa Estrada de Talaíde, P-2635-631 Rio de Mouro, Portugal*
(Received 15 October 2004; revised manuscript received 18 January 2005; published 26 May 2005)

We show that if the triple line around a three-dimensional double bubble or lens bubble is decorated with another bubble or with a Plateau border, then the film prolongations into the decoration no longer meet at $2\pi/3$. These deviations can be accounted for in terms of a line tension that equals half the excess surface energy associated with the decoration.

DOI: 10.1103/PhysRevE.71.051404 PACS number(s): 83.80.Iz, 82.70.Rr

I. INTRODUCTION

A liquid foam is an assembly of gas bubbles bounded by liquid films. The behavior of a foam with a low-viscosity liquid phase (e.g., an aqueous foam or a metal foam, as opposed to a polymeric foam) is dominated by surface tension. Such foams thus serve as models for systems in which the interfacial area [in three dimensions (3D)] or the perimeter [in two dimensions (2D)] is minimized at equilibrium. Besides this fundamental usefulness, foams have many important practical applications, which include food and beverages, toiletries, cleaning products, fire fighting, oil recovery, mixture fractionation, the manufacture of cellular materials, and ore purification by flotation [1].

The theoretical analysis of foams usually starts from the model of a dry, or mathematical, foam. This consists of films of zero thickness (which can be regarded as mathematical surfaces), endowed with a contractile tendency that is described by a film tension, denoted γ (a free energy per unit length of a 2D film, or per unit area of a 3D film). Films join along edges and at vertices, in such a way that the resulting cells (bubbles) fill a region of 2D or 3D space without any gaps.

At equilibrium, a fully dry foam satisfies Plateau's laws [2]: films of constant mean curvature meet at $2\pi/3$ angles at triple lines, and different pressures in the bubbles equilibrate the contractile forces on the films. The energy of such a foam is just the energy of its films. In actual fairly dry foams (liquid content below about 5%), we may still neglect the film thickness, but the triple lines are "decorated" with regions called Plateau borders (PBs), where most of the liquid resides. How the wetness of real physical foams modifies their geometry and energy has been a subject of interest in the past few years. The properties of 2D PBs, including their (negative) excess energy relative to the dry film junctions, have been discussed by Krotov and Rusanov [3] and by Srinivasan *et al.* [4] for equilateral triangular PBs, and by ourselves for general three- and four-sided PBs [5]. The mathematical modeling of triple junctions has been surveyed by Taylor [6]. The effect of PBs on the energy and shear modulus of 3D foams in the dry limit has been analyzed by Kern and Weaire [7]. Very recently, a deviation from $2\pi/3$ of the angles between films meeting at a PB was experimentally found by Géminard *et al.* [8], who interpreted their result in terms of a (negative) line tension associated with the PB. A similar deviation from the dry foam equilibrium angles was reported by Rodrigues *et al.* [9] for a small (millimeter-sized) hemispherical bubble on a plate, which was also explained with resort to a line tension associated with the PB at the plate-film junction. Likewise, Srinivasan *et al.'s*[4] atomistic simulation of grain boundaries yielded a negative excess energy of a trijunction.

Here we expand on the above works by investigating how the geometry of a wet 3D foam differs from that of a dry 3D foam, and in particular how a wet 3D foam can be mimicked by an "equivalent" dry 3D foam endowed with a line tension. This is useful because many rigorous and quasirigorous results are known that apply only to dry foams. We choose to concentrate on two simple 3D bubble clusters, as their shapes can be calculated numerically to great accuracy. We are thus able to show that deviations from the dry foam equilibrium angles occur as a consequence of PBs or bubbles decorating the three-film junctions. Furthermore, we relate the line tension to the excess energy of these decorations.

This paper is organized as follows: in Sec. II we review the properties of PBs in 2D foams. In Sec. III we consider the decoration of the contact line of a 3D double bubble by either a third, toroidal bubble, or a liquid PB; as well as the decoration by an extra bubble or a PB of the contact line around a lens bubble. We integrate Laplace's equation to get the shape of the decorations. In Sec. IV we define and compute the excess energy per unit length ϵ associated with the decorated double bubble and lens bubble of the preceding section, and compare them with those of the corresponding 2D decorations. In Sec. V we perform a direct minimization (at constant volume) of the energy of an undecorated double bubble and of a lens bubble with triple-line tension τ, and show that it leads to the same results as balancing the film and triple-line tensions. Finally, in Sec. VI we check that our numerical calculation satisfies the relationship between ϵ and τ obtained earlier by Géminard and co-workers [8]: the line tension required to reproduce the calculated angles between film prolongations is half the decoration excess energy; i.e., $\tau=\epsilon/2$. Our results are summarized and discussed in Sec. VII.

II. PLATEAU BORDERS IN TWO-DIMENSIONAL FOAMS AND THE DECORATION THEOREM

In fairly dry 2D foams, PBs are three-sided (i.e., triangular) regions connected by films of negligible thickness. They satisfy an important result known as the *decoration theorem* [10,11]: if the three circular films connected to the PB vertices are prolonged into the PB, then at equilibrium they intersect at a single point, at $2\pi/3$ angles. Conversely, a threefold vertex can be decorated with a triangular PB (in fact, an infinite family of triangular PBs) at equilibrium without disturbing the films (although the bubble areas obviously change).

For 2D triangular PBs we can then define an excess energy ϵ_3 as the difference between the energy of the PB surfaces (of tension γ_L, equal to that of the free surface of the bulk liquid) and that of the film prolongations (of tension γ) [5]. (It should be noted that γ_L and γ are here understood to be energies *per unit length*.) In a separate paper [5] we studied the properties of these PBs in the case wherein their surfaces meet the films tangentially; i.e., for $\gamma_L = \gamma/2$. It was found that the (negative) excess energy ϵ_3 is approximately related to the PB area A_3 by

$$\frac{\epsilon_3}{\gamma} = -\left[\left(-\frac{\pi}{2} + \sqrt{3}\right)A_3\right]^{1/2} \simeq -0.402A_3^{1/2}, \qquad (1)$$

which holds exactly for *regular* three-sided PBs. Alternatively, a threefold vertex in a 2D dry foam can be decorated with an additional bubble, of film tension γ; an associated excess energy can then be defined as for a decoration PB. If such a bubble is regular (i.e., equilateral) and has area A_D, its (positive) excess energy is

$$\frac{\epsilon_D}{\gamma} = [2(\pi - \sqrt{3})A_D]^{1/2} \simeq 1.679A_D^{1/2}. \qquad (2)$$

At high liquid fractions, a 2D foam contains PBs with more than three sides, to which the decoration theorem does not in general apply. One cannot then define an excess free energy as for three-sided PBs. In 3D foams, the decoration theorem in general does not hold, in the sense that, as we shall show, film prolongations do not meet at the equilibrium angles. Indeed, it is not even known whether film prolongations (assuming that they can be unambiguously defined) meet along a single line. Conversely, a general triple film junction cannot be decorated without disturbing the film geometry. Exceptions are the two 3D bubble clusters discussed in the next sections: the double bubble and the lens bubble, in which all films are spherical or planar. We will, however, show that, even in these cases where the film prolongations do meet along a single line, they do not do so at the equilibrium $2\pi/3$ angles as in 2D.

III. TRIPLE-LINE DECORATION OF A DOUBLE BUBBLE AND OF A LENS BUBBLE

Figures 1 and 2 show a double bubble and a lens bubble, respectively. In their fully dry equilibrium states, each comprises two spherical films and a flat film, and has axial symmetry. At equilibrium, the three films meet at $2\pi/3$ angles along a circular triple line, as follows from equilibrium of the film tensions γ. The triple line decoration is a toroidal region bounded by three surfaces of tension γ_D, which equals γ in the case of a decoration bubble, or $\gamma/2$ in the case of a decoration PB. In either decorated cluster, each of the films meets two of the surfaces bounding the decoration along a circle; there are thus three such circles.

In what follows we first describe in detail the calculations performed for the double bubble and then indicate how the same can be straightforwardly adapted to deal with the lens bubble. The films remain spherical after decoration; indeed, the equilibrium conditions are satisfied with spherical films.

In the double bubble, the films and the bounding surfaces of the decoration are surfaces of revolution around the axis of symmetry [see Figs. 1(a) and 1(b)], which we take as the z-axis: it is perpendicular to the planar film 0 and has its origin at this film's center. These surfaces all have constant mean curvatures: $1/R$ for the films and b_1 and b_2 for the decoration surfaces, where subscript 1 refers to the two identical surfaces (between the decoration and either bubble) and subscript 2 refers to the remaining surface (between the decoration and the outside gas) (see Fig. 1). Each decoration surface has equation $x \equiv x(z)$, where x is the distance to the z-axis; it is a solution of the Laplace equation for axially symmetric interfaces:

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

where the dots denote differentiation with respect to z and Δp_i is the pressure difference across surface i, positive if the pressure is higher on the side of the z-axis. For a Plateau border, $b_1 > 0$ and b_2 can have either sign; for a decoration bubble, $b_1 < 0$ and $b_2 > 0$.

Let p_0, p_D, and p_B be the pressures of the outside gas, in the decoration, and in the twin bubbles, respectively. Equilibrium of pressures requires that

$$p_B - p_D = 2\gamma_D b_1, \qquad (4)$$

$$p_D - p_0 = 2\gamma_D b_2, \qquad (5)$$

$$p_B - p_0 = \frac{2\gamma}{R}, \qquad (6)$$

whence

$$b_1 + b_2 = \frac{\gamma}{\gamma_D}\frac{1}{R}. \qquad (7)$$

In addition to equilibrium of pressures, there must be equilibrium of the decoration surface and film tensions, $\boldsymbol{\gamma_D}$ and $\boldsymbol{\gamma}$, respectively, at the decoration triple lines. At the 011 triple line (i.e., where films 0, 1, and 1 meet) this implies that

$$\cos\alpha_1 = \frac{\gamma}{2\gamma_D}, \qquad (8)$$

where α_1 is the angle between films 0 and 1 [see Fig. 1(c)]: equilibrium thus requires $\gamma_D \geqslant \gamma/2$. At the $0'12$ triple junctions, $\boldsymbol{\gamma}$ must bisect the angle between the two $\boldsymbol{\gamma_D}$. Introduc-

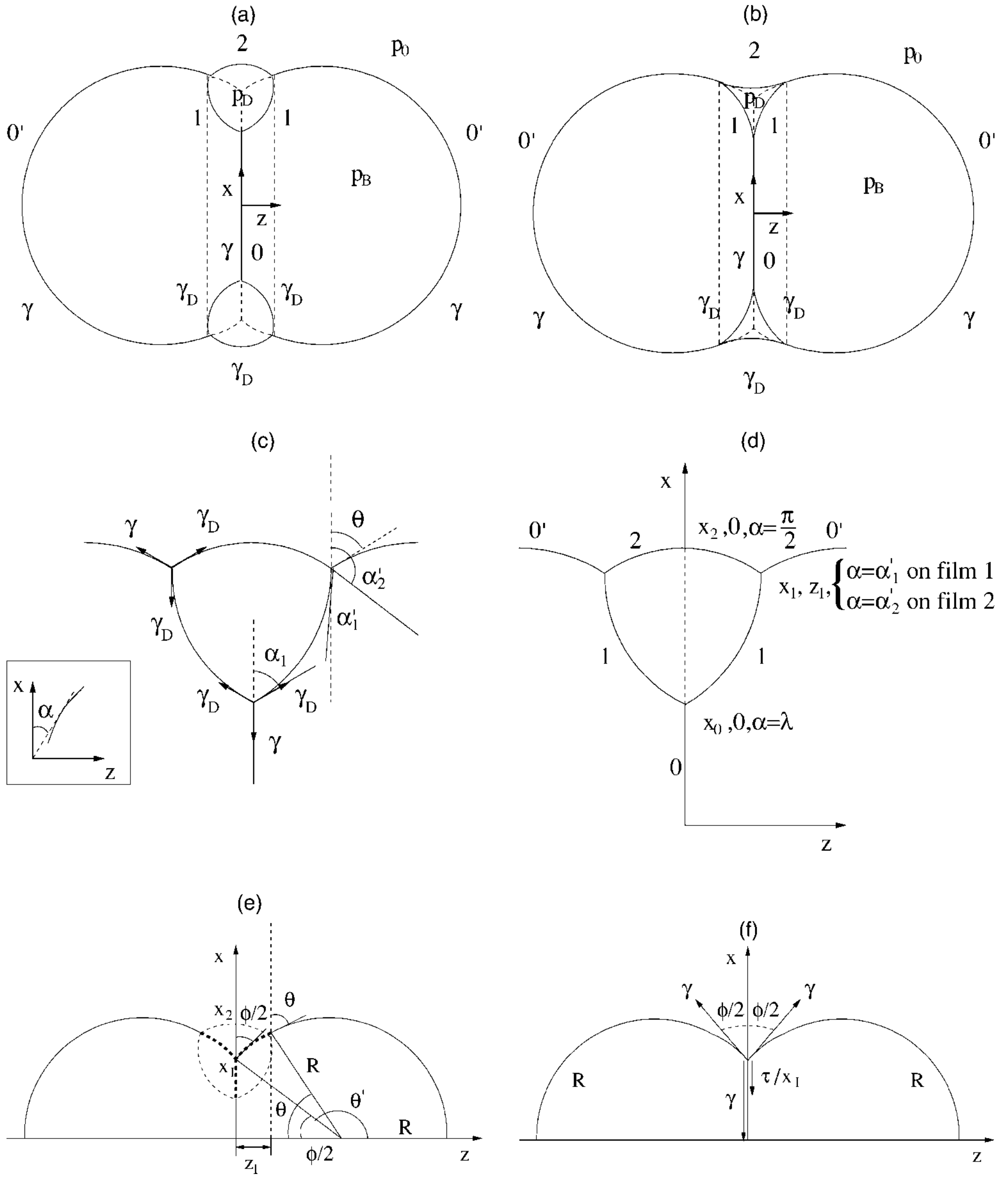

FIG. 1. The decorated double bubble. (a) With a decoration bubble. (b) With a decoration PB. (c) Geometrical quantities pertaining to the decoration. (d) Boundary conditions for integration of Eqs. (15)–(17). (e) Geometrical quantities for calculating the angle between prolongations and the surface energy of the decoration: the prolongations intersect at $(0,x_I)$. (f) The undecorated double bubble with a (positive) triple-line tension τ.

ing θ, the angle between $\boldsymbol{\gamma}$ at this triple line and the x-axis [again, see Fig. 1(c)], we must have

$$\alpha_1' + \alpha_2' = 2\theta, \tag{9}$$

where α_1' and α_2' are the angles between surfaces 1 and 2, respectively, and the x-axis at this triple line. Equilibrium of tensions at the $0'12$ triple line further requires that

$$\cos(\theta - \alpha_1') = \frac{\gamma}{2\gamma_D}. \tag{10}$$

If we now define an angle λ $(0 \leqslant \lambda \leqslant \pi/2)$ such that

$$\cos\lambda = \frac{\gamma}{2\gamma_D}, \tag{11}$$

then the equilibrium conditions for the surface tensions [Eqs. (8)–(10)] can be expressed more concisely as

$$\alpha_1 = \lambda, \tag{12}$$

$$\alpha_2' - \alpha_1' = 2\lambda, \tag{13}$$

$$\theta - \alpha_1' = \lambda. \tag{14}$$

In order to integrate Eq. (3), we introduce the arc length s along $x(z)$ from a chosen origin. Equation (3) for $x(z)$ is then

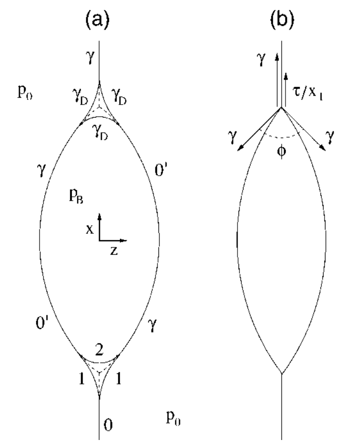

FIG. 2. Decorated lens bubble on a flat film. (a) Definition of key quantities. (b) The undecorated lens bubble with a (negative) triple-line tension τ.

equivalent to the following set of first-order differential equations:

$$\frac{dx}{ds} = \cos \alpha, \tag{15}$$

$$\frac{dz}{ds} = \sin \alpha, \tag{16}$$

$$\frac{d\alpha}{ds} = 2b_i - \frac{\sin \alpha}{x}, \tag{17}$$

where α $(0 \leqslant \alpha \leqslant \pi)$ is the angle between the tangent to the $x=x(z)$ curve and the positive x-axis [see inset in Fig. 1(c)]: $\tan \alpha = dz/dx$.

For a given λ [i.e., a given γ/γ_D ratio, see Eq. (11)], and once the boundary condition has been set (e.g., by fixing $x_0=1$), Eqs. (15)–(17) define a one-parameter family of solutions for the decoration surfaces. We choose b_1 as the parameter and start by integrating Eqs. (15)–(17) for decoration surface 1, starting at $x=x_0=1$, $z=0$, $\alpha=\alpha_1$ [from Eq. (8)], up to a tentative $x=x_1$, $z=z_1$, $\alpha=\alpha_1'$. For this x_1, we then find α_2' from Eq. (13) and θ from Eq. (14). Using x_1 and θ, the radius R of the spherical films can be calculated from [see Fig. 1(e)]

$$R = \frac{x_1}{\sin \theta}, \tag{18}$$

and b_2 from Eq. (7). With this b_2 we integrate Eqs. (15)–(17) for decoration surface 2, with initial conditions $x=x_1$, $z=z_1$, $\alpha=\alpha_2'$. The resulting profile must reach $\alpha=\pi/2$ for $z=0$. This will happen *only* for a particular x_1 that has to be found by trial and error. Figure 3 shows examples of calculated decorations of a double bubble for $\gamma_D=\gamma$ (decoration bubble) and $\gamma_D=\gamma/2$ (Plateau border), for different b_1. In the former case the decoration surfaces meet the films at $2\pi/3$ angles, whereas in the latter they do so tangentially. The corresponding geometrical parameters are collected in Tables I and II. All lengths are in units of x_0, the radius of the planar film 0 (which equals the radius of the 011 triple line).

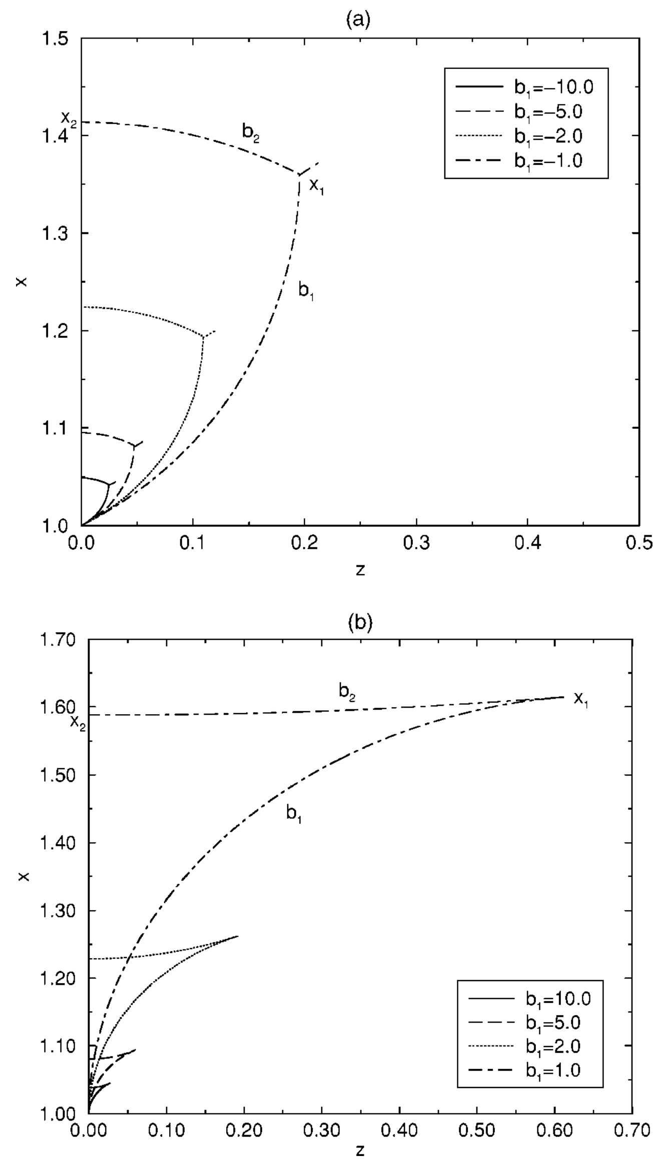

FIG. 3. Calculated shapes of (a) decoration bubbles and (b) PBs around a double bubble oriented as in Fig. 1, for b_1 as given (see also Tables I and II). The origin of coordinates is at the center of the planar interbubble film.

The prolongations of the planar and spherical films, P and P', respectively [dashed in Figs. 1(a), 1(b), and 1(c)], meet at a geometrical line—a circle of radius x_I. As pointed out above, this is a special situation: in general, it is uncertain whether the prolongations of these surfaces of constant mean curvature into a decoration will all intersect at a single line.

The angle ϕ between the prolongations of the two spherical films $0'$ [see Fig. 1(e)] can be obtained from

$$z_1 = R\left(\cos\frac{\phi}{2} - \cos \theta\right). \tag{19}$$

For each solution, we also found the radius x_I of the line where the film prolongations intersect:

TABLE I. Geometrical parameters pertaining to the double bubble with decoration bubble of Fig. 3(a): $\gamma_D/\gamma=1$, $x_0=1.0$. We fix b_1.

b_1	b_2	x_1	x_2	x_I	R
−10.0	10.8345	1.042	1.0487	1.0279	1.1983
−5.0	5.8055	1.082	1.0950	1.0541	1.2420
−2.0	2.7303	1.194	1.2239	1.1259	1.3693
−1.0	1.6412	1.360	1.4136	1.2300	1.5597

$$x_I = R \sin\frac{\phi}{2}, \tag{20}$$

as well as the area A_D of the decoration cross section, which is given by

$$A_D = 2\left(\int_{x_0}^{x_1} z\,dx + \int_{x_1}^{x_2} z\,dx\right). \tag{21}$$

[Note that the second integral in the above equation is positive in the case of a decoration bubble ($x_2 > x_1$) and negative in the case of a PB ($x_2 < x_1$). The factor 2 comes from the fact that because of symmetry we only actually calculate half the decoration.] $A_D^{1/2}/x_I$ is a measure of the size of the decoration relative to that of the bubbles (in the case of a PB, it is a measure of the liquid fraction). In Fig. 4 we plot the deviation $\Delta\phi$ of ϕ in a double bubble from its value in the absence of a decoration, $2\pi/3$, vs $A_D^{1/2}/x_I$. It is negative (and larger) for decoration bubbles, and positive (and smaller) for PBs.

Similar results are obtained for the lens bubble, to which Eq. (7) for the equilibrium of pressures still applies. In this equation, b_1 and b_2 are the (constant) mean curvatures of decoration surfaces 1 and 2, respectively [see Figs. 1(a) and 2(a)], and R (>0) is the radius of the spherical films making up the bubble. As in the case of the double bubble, films 0′ and the decoration surfaces are surfaces of revolution around the axis of symmetry [see Fig. 2(a)], which we again take as the z-axis: it is perpendicular to the planar film 0 and has its origin at the center of the circular hole in this film, which is occupied by the lens bubble. Notice that the roles of surfaces 1 and 2 are reversed: now subscript 1 refers to the two identical surfaces (between the decoration and the outside gas) and subscript 2 refers to the remaining surface (between the decoration and the bubble). Figure 5 shows the calculated

TABLE II. Geometrical parameters pertaining to the dubble bubble with decoration PB of Fig. 3(b): $\gamma_D/\gamma=0.5$, $x_0=1.0$. We fix b_1.

b_1	b_2	x_1	x_2	x_I	R
10.0	−8.3142	1.045	1.0382	1.0300	1.1864
5.0	−3.3548	1.094	1.0809	1.0620	1.2156
2.0	−0.5115	1.262	1.2283	1.1743	1.3437
1.0	0.2332	1.615	1.5884	1.4314	1.6218

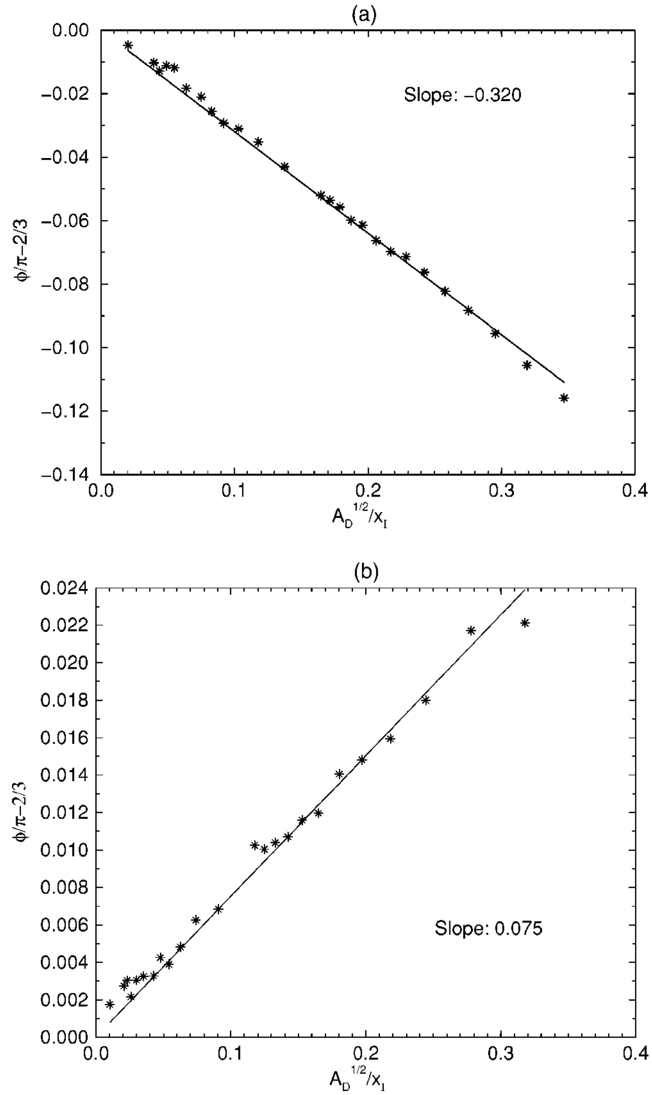

FIG. 4. Deviation of ϕ, the angle between spherical film prolongations into the decoration of a double bubble, from its value in the absence of a decoration, $2\pi/3$, vs decoration size $A_D^{1/2}/x_I$, for (a) decoration bubbles and (b) PBs. The solid lines are linear fits going through the origin; slopes are given in each case.

shape of the decoration bubble and PB around a lens bubble; the geometrical parameters pertaining to these curves are collected in Tables III and IV, respectively. In Fig. 6 we plot the deviation $\Delta\phi$ of ϕ, the angle between the two spherical films [see Fig. 2(b)], from its value in the absence of a decoration, $2\pi/3$, vs $A_D^{1/2}/x_I$. Note that $\Delta\phi$ has opposite signs for the double and lens bubbles. Experimentally, $\Delta\phi$ for the PB decorating the triple line of a flat circular film suspended by two catenoidal films can be as large as 2.5° [8], giving $\phi/\pi-2/3\sim 0.014$; this is of the order of what we predict [see Figs. 4(b) and 6].

IV. EXCESS ENERGY OF DECORATION: DEFINITION AND DERIVATION

We next proceed to calculate the excess energy of a decoration, defined as the excess surface energy (per unit length

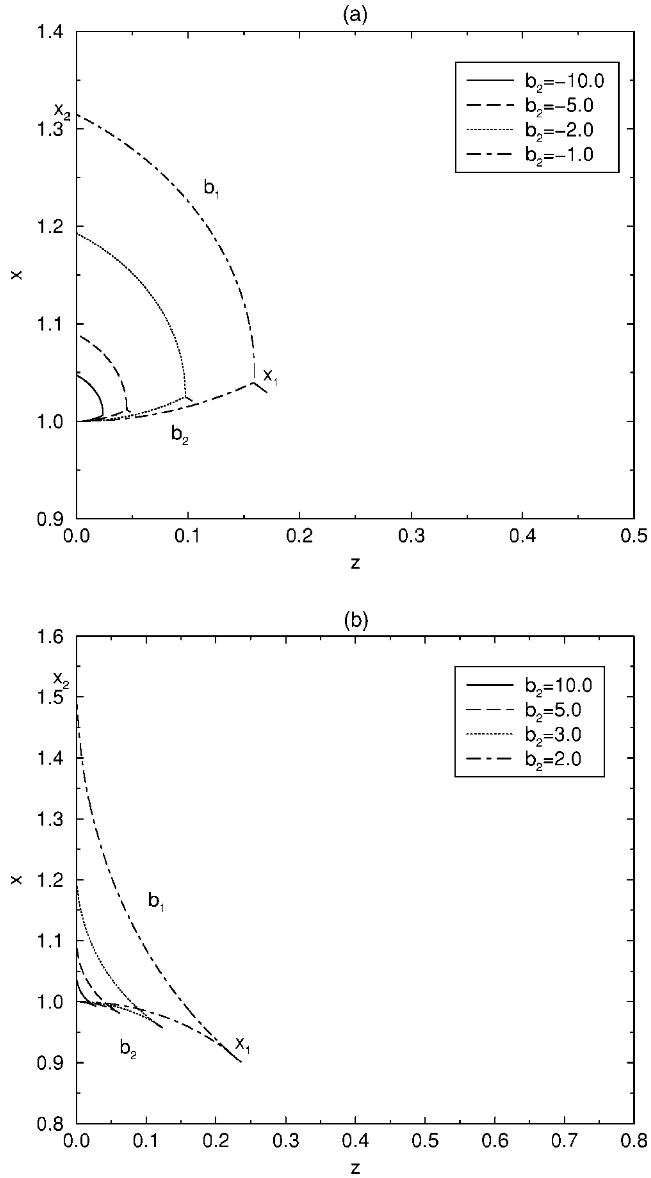

FIG. 5. Calculated shapes of (a) decoration bubbles and (b) PBs around a lens bubble oriented as in Fig. 2, for b_2 as given (see also Tables III and IV). The origin of coordinates is at the center of the lens bubble.

of the line of radius x_I) of the decoration relative to the surface energy of the film prolongations. A detailed derivation is presented for the double bubble. The total area of the decoration surfaces is $2(S_1+S_2)$, where S_1 is the area of each of decoration surfaces 1 and S_2 is half the area of decoration surface 2 [see Fig. 1(d)]:

$$S_i = 2\pi\int_0^{z_1} x\sqrt{1+\left(\frac{dx_i}{dz}\right)^2}dz, \quad (i=1,2). \tag{22}$$

The prolongation P of the planar interbubble film is a circular "crown" [i.e., the region between the two concentric circles of radii x_I, given by Eq. (20), and x_0] of area

TABLE III. Geometrical parameters pertaining to the lens bubble with decoration bubble of Fig. 5(a): $\gamma_D/\gamma=1$, $x_0=1.0$. Note that now we fix b_2.

b_2	b_1	x_1	x_2	x_I	R
−10.0	10.8586	1.0063	1.0472	1.0197	1.1647
−5.0	5.8510	1.0118	1.0893	1.0370	1.1751
−2.0	2.8343	1.0251	1.1929	1.0780	1.1986
−1.0	1.8154	1.0401	1.3148	1.1239	1.2264

$$S_P = \pi\left(R^2\sin^2\frac{\phi}{2} - x_0^2\right). \tag{23}$$

Finally, each spherical film prolongation P' is a slice of height z_1 of a sphere of radius R; its area is $2\pi R z_1$ or, using Eq. (19),

$$S_{P'} = 2\pi R^2\left(\cos\frac{\phi}{2} - \cos\theta\right). \tag{24}$$

ϵ, the excess energy per unit length of the decoration of total length $2\pi x_I$, is thus

$$\frac{\epsilon}{\gamma} = \frac{1}{2\pi x_I}\left[\frac{2\gamma_D}{\gamma}(S_1+S_2) - (S_P + 2S_{P'})\right]. \tag{25}$$

In Fig. 7 we plot the dimensionless quantity $\epsilon/(\gamma x_I)$ versus $A_D^{1/2}/x_I$ for the double bubble decorated with a bubble [Fig. 7(a)] or a PB [Fig. 7(b)] of cross-sectional area A_D. As for 2D decorations, the excess energy of a decoration bubble is positive, whereas that of a PB is negative. Fitting straight lines through the origin to the data in Figs. 7(a) and 7(b) gives

$$\frac{\epsilon}{\gamma} = 1.693 A_D^{1/2}, \quad \text{(decoration bubble)}, \tag{26}$$

$$\frac{\epsilon}{\gamma} = -0.393 A_D^{1/2}, \quad \text{(PB)}, \tag{27}$$

whose prefactors closely approximate those for 2D foams [see Eqs. (1) and (2)]. For a lens bubble we likewise have, from Fig. 8,

$$\frac{\epsilon}{\gamma} = 1.595 A_D^{1/2}, \quad \text{(decoration bubble)}, \tag{28}$$

TABLE IV. Geometrical parameters pertaining to the lens bubble with decoration PB of Fig. 5(b): $\gamma_D/\gamma=0.5$, $x_0=1.0$. Note that now we fix b_2.

b_2	b_1	x_1	x_2	x_I	R
10.0	−8.2841	0.9922	1.0383	1.0087	1.1655
5.0	−3.3072	0.9813	1.0943	1.0199	1.1815
3.0	−1.3465	0.9593	1.1980	1.0408	1.2304
2.0	−0.4277	0.9076	1.5152	1.0859	1.2721

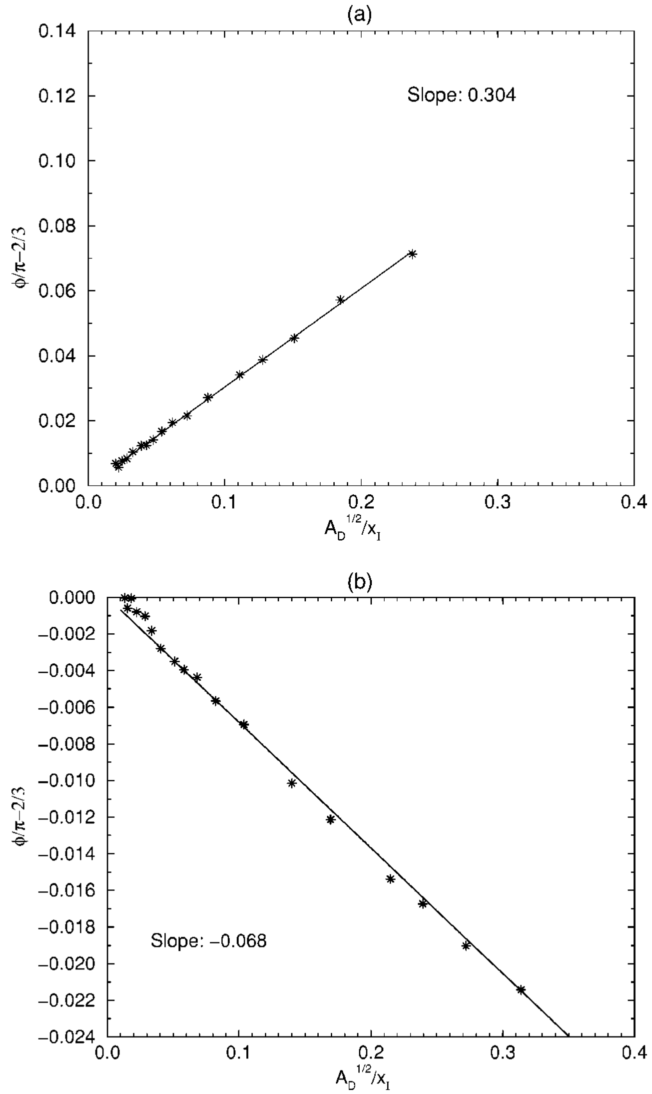

FIG. 6. Deviation of ϕ, the angle between film prolongations into the decoration of a lens bubble, from its value in the absence of a decoration, $2\pi/3$, vs decoration size $A_D^{1/2}/x_I$, for (a) decoration bubbles and (b) PBs. The solid lines are linear fits going through the origin; slopes are given in each case.

$$\frac{\epsilon}{\gamma} = -0.386 A_D^{1/2}, \quad \text{(PB)}, \tag{29}$$

whose agreement with the 2D result is somewhat less good than for the double bubble. Note that Eqs. (26)–(29) hold even for decorations whose linear size is of the order of the triple-line radius x_I.

V. DIRECT MINIMIZATION OF THE SURFACE ENERGY OF A DOUBLE BUBBLE WITH TRIPLE-LINE TENSION

We assign a line tension τ to the triple line (of radius x_I) of a *dry* (i.e., undecorated) double bubble or lens bubble. This is defined as the contribution of the decoration to the total energy of a unit length of triple line in the *undecorated* cluster. The energy E of the *decorated* double bubble or lens bubble is then the sum of the surface energy γS of the dry films meeting at the triple line of length L, plus the energy τL of that triple line:

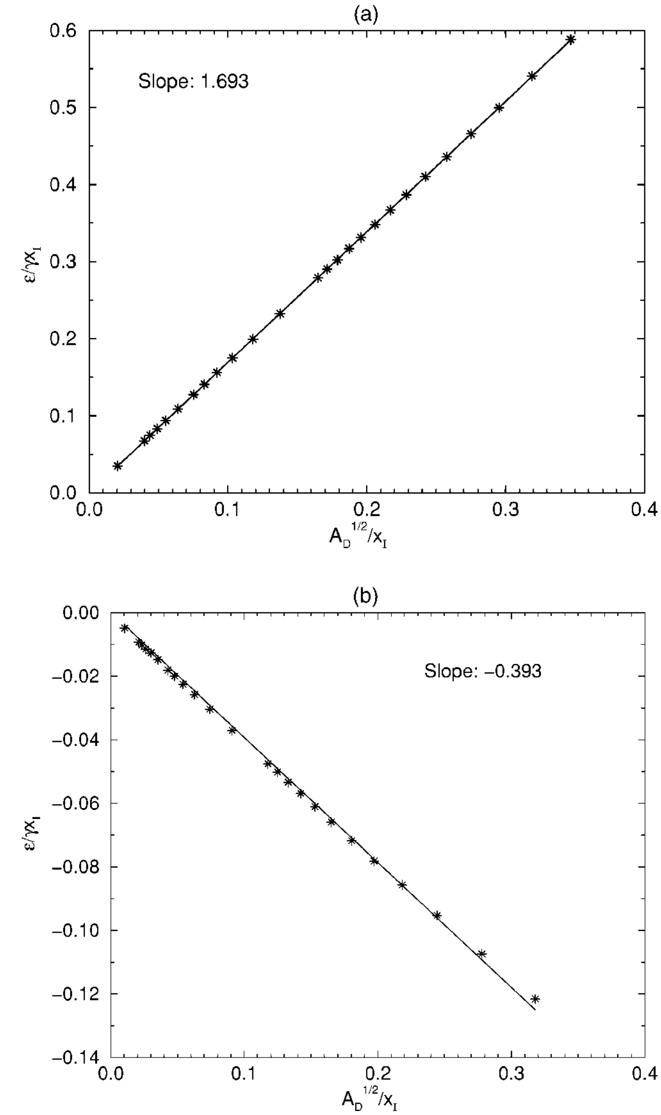

FIG. 7. Dimensionless excess energy $\epsilon/(\gamma x_I)$ of a double bubble vs $A_D^{1/2}/x_I$ for (a) decoration bubble and (b) PB. The solid lines are linear fits going through the origin; slopes are given in each case.

$$E = \gamma S + \tau L. \tag{30}$$

We shall relate τ to ϵ in the next section. In the case of a double bubble, S comprises the areas of the two spherical films of radius R and subtended angle $2\theta' = 2\pi - \phi$, and that of the circular planar film of radius $x_I = R \sin\theta'$ [cf. Eq. (20), see Fig. 1(e)]:

$$\frac{E}{\gamma} = \pi R^2 (5 - 4\cos\theta' - \cos^2\theta') + 2\pi R \sin\theta' \frac{\tau}{\gamma}. \tag{31}$$

The volume of each bubble is

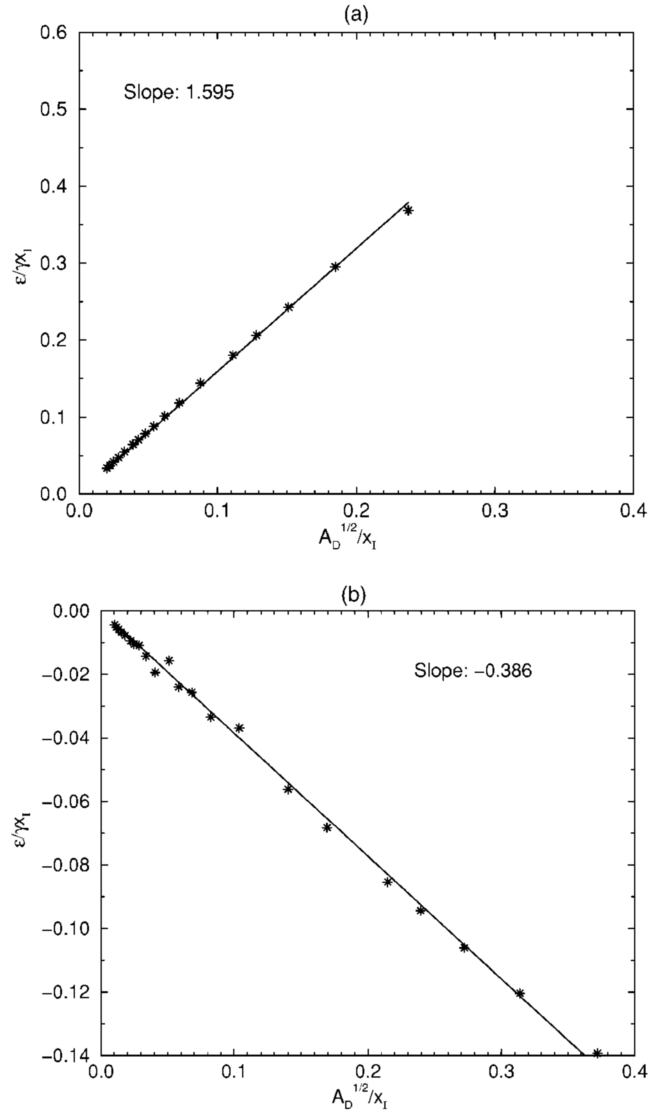

FIG. 8. Dimensionless excess energy $\epsilon/(\gamma x_I)$ of a lens bubble vs $A_D^{1/2}/x_I$ for (a) decoration bubble and (b) PB. The solid lines are linear fits going through the origin; slopes are given in each case.

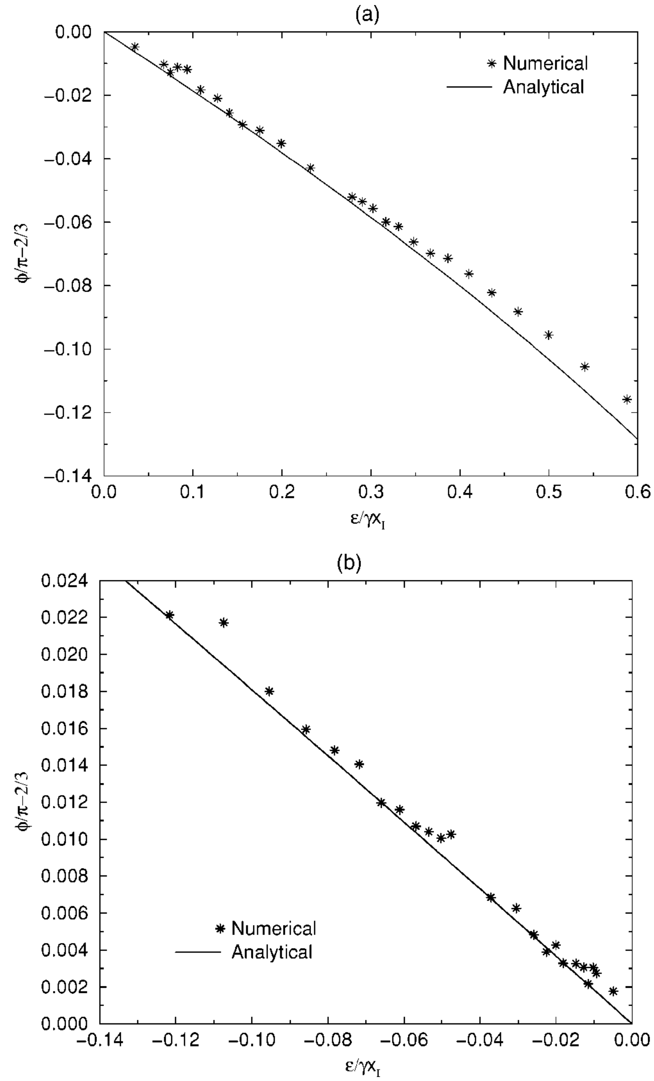

FIG. 9. Deviation of ϕ, the angle between film prolongations into the decoration of a double bubble, from its value in the the absence of a decoration, $2\pi/3$, vs dimensionless excess energy $\epsilon/(\gamma x_I)$, for (a) decoration bubbles and (b) PBs. The solid lines are the analytical result for $\tau/(\gamma x_I)$, Eq. (34), with $\tau = \epsilon/2$.

$$V = \frac{\pi R^3}{3}(2 - 3\cos\theta' + \cos^3\theta'). \tag{32}$$

Minimizing E at fixed V yields

$$-\sin\theta'(1 + 2\cos\theta') = \frac{\tau}{\gamma R}. \tag{33}$$

The equilibrium condition (33) can be derived directly from balancing the $\boldsymbol{\gamma}$ and $\tau\hat{\mathbf{n}}/x_I$ forces acting on the (undecorated) triple line, where $\hat{\mathbf{n}}$ is the principal normal to the (circular) triple line, pointing toward its center. The line tension force acts to contract the triple line if positive, and to dilate it if negative. From Fig. 1(f) we get

$$\left(2\cos\frac{\phi}{2} - 1\right)\gamma = \frac{\tau}{x_I}, \tag{34}$$

which is identical with Eq. (33) since $\theta' = \pi - \phi/2$. Either of these equations defines ϕ as a function of $\tau/(\gamma x_I)$; for small $\tau/(\gamma x_I)$, this is

$$\phi - \frac{2\pi}{3} = -\frac{2}{\sqrt{3}}\frac{\tau}{\gamma x_I}. \tag{35}$$

Similar considerations apply to the lens bubble, for which Eq. (34) is replaced by

$$\left(2\cos\frac{\phi}{2} - 1\right)\gamma = -\frac{\tau}{x_I}, \tag{36}$$

where ϕ is defined in Fig. 2(b).

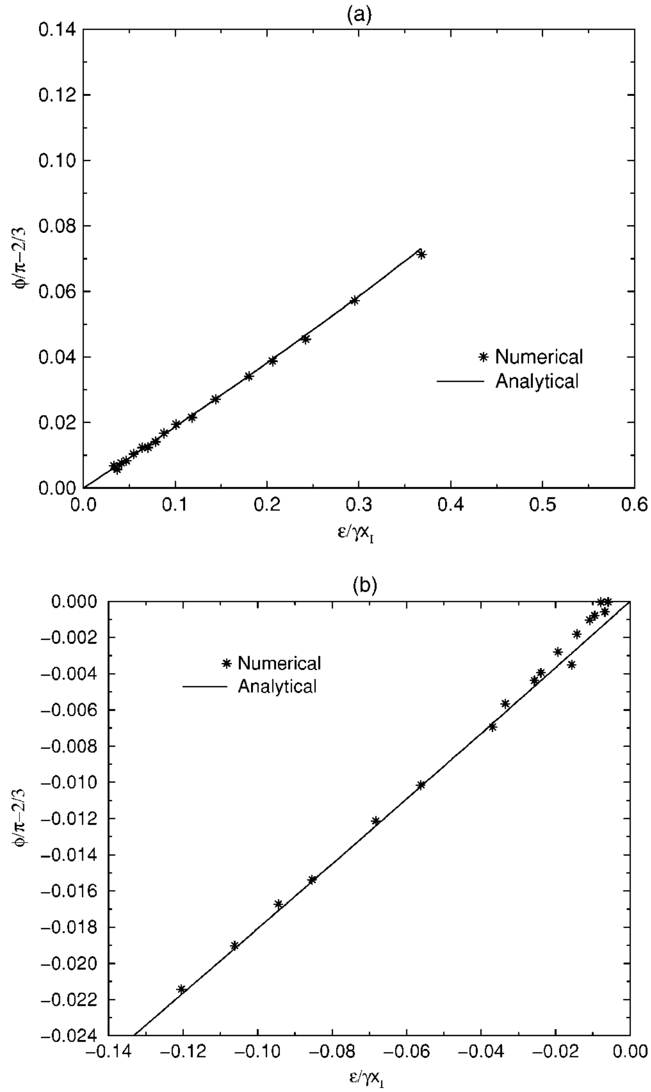

FIG. 10. Deviation of ϕ, the angle between film prolongations into the decoration of a lens bubble, from its value in the the absence of a decoration, $2\pi/3$, vs dimensionless excess energy $\epsilon/(\gamma x_I)$, for (a) decoration bubbles and (b) PBs. The solid lines are the analytical result for $\tau/(\gamma x_I)$, Eq. (36), with $\tau = \epsilon/2$.

VI. EXCESS ENERGY AND LINE TENSION

In a recent paper, Géminard and co-workers [8] obtained a relation between ϵ and τ:

$$\tau = \frac{\epsilon}{2}. \tag{37}$$

Recall that ϵ is the difference between the energy of the actual decorated cluster and that of an undecorated reference cluster with the same radius R of the spherical films and the same radius x_I of the triple line, to which we may assign a line tension τ. To derive this, start by noting that $\epsilon \propto A_D^{1/2}$, where A_D is the PB cross-sectional area. Now consider a length l of PB: it has energy $l\epsilon$. The line tension is, by definition,

$$\tau = \frac{d(l\epsilon)}{dl}, \tag{38}$$

i.e., the work τdl performed by the line tension force equals the change in PB energy, $d(l\epsilon)$. The length l of PB has volume lA_D, which from Eq. (1) is proportional to $l\epsilon^2$. If the PB volume is kept constant, then $\epsilon \propto l^{-1/2}$ and Eq. (37) follows from Eq. (38).

In our theory, the functional dependence of the excess energy ϵ of decorated double or lens bubbles on the cross-sectional area of their decorations is given by Eqs. (26)–(29). Moreover, the film prolongations into the decorations in either cluster meet at a single line at an angle ϕ that deviates from $2\pi/3$. Our numerical calculations yield (see Figs. 9 and 10)

$$2\cos\frac{\phi}{2} - 1 \approx \frac{2}{\sqrt{3}}\left(\phi - \frac{2\pi}{3}\right) \approx \frac{1}{2}\frac{\epsilon}{\gamma x_I}, \tag{39}$$

which combined with Eq. (36) recovers Eq. (37).

VII. CONCLUDING REMARKS

We have discussed two 3D bubble clusters—the double bubble and the lens bubble—which contain a single, closed, triple line. This line can be decorated with a PB of triangular cross section or, alternatively, with a tubular bubble, in such a way that the prolongations of the two spherical films and of the planar film meet at a single line (a circle), albeit not in general at the equilibrium $2\pi/3$ angles as in 2D. Still, this is the 3D equivalent of the decoration property of triangular PBs in 2D, and it allows one to define an excess energy per unit length of the triple line ϵ as the difference between the energy of the decoration surfaces and that of the film prolongations. The decorated cluster shapes and energies have been found by numerical integration of Laplace's equation.

The deviation of the angles from their equilibrium values in a dry foam can be accounted for by introducing a line tension τ associated with the triple line of the undecorated bubble and requiring that the film tension forces $\boldsymbol{\gamma}$, and that due to the line tension, $(\tau/\rho)\hat{\mathbf{n}}$, balance at the triple line. We have numerically verified that this line tension equals half the excess energy per unit length associated with the decoration, as follows from the work of Géminard *et al.* [8].

The excess energy ϵ is a function of the cross-sectional area of the decoration, A_D. For both bubble and PB decorations, the ratio $\epsilon/(\gamma A_D^{1/2})$ is approximately the same for both double and lens bubbles and close to the values for the corresponding 2D decorations.

The two 3D clusters studied are special in that a decoration excess energy can be defined in the same manner as for 2D clusters with triangular PBs. Generalization to arbitrary 3D triple junctions is, however, not straightforward. In particular, it is not even known whether the film prolongations into a 3D decoration, if they can be unambiguously defined, always meet at a single line; this could be investigated using, e.g., the Surface Evolver program [12]. Still, for the purpose of estimating the energy of a 3D wet foam with PBs of triangular cross-section, we may make use of an excess energy ϵ, related to the PB cross-sectional area by $\epsilon/\gamma \simeq -0.4A_D^{1/2}$.

[1] D. Weaire and S. Hutzler, *Physics of Foams* (Oxford University Press, Oxford, 1999).
[2] J. A. F. Plateau, *Statique Expérimentale et Théorique des Liquides Soumis aux Seules Forces Moléculaires* (Gauthier Villars, Paris, 1873).
[3] V. V. Krotov and A. I. Rusanov, Mendeleev Commun. **8**, 177 (1998).
[4] S. G. Srinivasan, J. W. Cahn, H. Jónsson, and G. Kalonji, Acta Mater. **49**, 2821 (1999).
[5] P. I. C. Teixeira and M. A. Fortes, Philos. Mag. **85**, 1303 (2005).
[6] J. E. Taylor, Interface Sci. **7**, 243 (1999).
[7] N. Kern and D. Weaire, Philos. Mag. **83**, 2973 (2003).
[8] J.-C. Géminard, A. Żywociński, F. Caillier, and P. Oswald, Philos. Mag. Lett. **84**, 199 (2004).
[9] J. F. Rodrigues, B. Saramago, and M. A. Fortes, J. Colloid Interface Sci. **239**, 577 (2001).
[10] F. Bolton and D. Weaire, Philos. Mag. B **63**, 795 (1991).
[11] D. Weaire, Philos. Mag. Lett. **79**, 491 (1999).
[12] K. Brakke, Exp. Math. **1**, 141 (1992); see also http://www.susqu.edu/facstaff/b/brakke/evolver