Generalizations of the Young–Laplace equation for the pressure of a mechanically stable gas bubble in a soft elastic material

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The Young–Laplace equation for the pressure of a mechanically stable gas bubble is generalized to include the effects of both surface tension and elastic forces of its surroundings. The latter are taken to be comprised of a soft isotropic material. Generalizations are derived for conditions of constant external pressure and constant system volume. The derived equations are formally exact for a spherical bubble surrounded by a spherical shell of isotropic material, provided that the bubble is sufficiently large for the surface tension to be treated macroscopically, and that the bubble radius is much larger than the thickness of the bubble/soft material interface. The underlying equations are also used to derive a simple expression for the Gibbs free energy of deformation of an elastic medium that surrounds a gas bubble. The possible relevance of this expression to some recently published ideas on decompression sickness ("the bends") is discussed. © *2009 American Institute of Physics*. [doi:10.1063/1.3259973]

I. INTRODUCTION

The Young–Laplace equation for the pressure of a mechanically stable gas bubble surrounded by a fluid medium to which a constant external pressure is applied is[1]

$$P_B = P_0 + 2\gamma/R_B. \quad (1)$$

In Eq. (1), P_B, P_0, γ, and R_B are, respectively, the gas pressure in the bubble, the external pressure applied to the medium, the surface tension, and the bubble radius. Equation (1) is formally exact, provided three conditions are satisfied. Two are well known,[1] but the third is not. The well-known conditions are that the bubble must be large enough for γ to be treated macroscopically, and that the thickness of the interface be much smaller than the radius of the bubble.[1] The third condition is that the medium surrounding the bubble has no rigidity (or shear resistance). More precisely, its shear modulus (below) must be zero. The main purpose of this article is to generalize Eq. (1) to render it applicable to a material with a positive shear modulus, i.e., that one that manifests at least some degree of rigidity.

The need for a generalization of this kind stems from current and recent work on two ostensibly different, but in some ways similar problems: volcanic eruptions and decompression sickness (DCS).

Both phenomena are believed to occur because of gas bubble formation and/or growth that accompanies rapid depressurization of a gaseous solution. The explosive force in volcanic eruptions is believed to occur because of the sudden release of water vapor bubbles formerly dissolved in the magmatic melt.[2–6] The large reduction in external pressure on the melt (e.g., from ≥1000 to 1 atm), as it rises to the earth's surface, is believed sufficient to cause both homogeneous bubble nucleation from the melt, and rapid bubble growth of water vapor bubbles in it.[6]

DCS is also believed to be initiated by the formation and/or growth of gas bubbles in blood and tissues due to overly rapid decompression.[7–10] Here the bubbles consist mostly of an inert gas or gases (e.g., N_2 and He) that entered the lungs while breathing compressed air or a compressed mixed gas breathing mixture. These inert gases subsequently dissolve in the blood and tissues.

Another link between these problems is that, in both, the material that surrounds the gas bubble is not an ordinary liquid. By "ordinary liquid" we mean a liquid (such as liquid water at 1 atm between its normal melting and boiling points), which—because it has no shear resistance—compresses the bubble only by the unmodulated transmission of the external pressure and by surface tension [i.e., as described by Eq. (1)]. However both magma and tissues in the body have some rigidity (or "stiffness"). Magma, at least in the vicinity of its solidification point, has some solidlike structure, and tissues in the body (unlike ordinary liquids) have characteristic preferred shapes. In other words, both these materials manifest elastic behavior characterized by resistance to both shear and compression forces.

Most previous work on both of these problems simply used Eq. (1) to estimate the pressure of a gas bubble in an elastic medium,[6–10] but some work on DCS[11–14] used an approximate extension of Eq. (1) in an attempt to include elastic effects [Eq. (26) below]. We will show, however (results and Fig. 1), that Eq. (26) is physically inconsistent, and in general provides a poor representation of the correct result.

II. THEORY

We use boldface letters for vectors and the usual convention for representing tensors (i.e., the summation sign over

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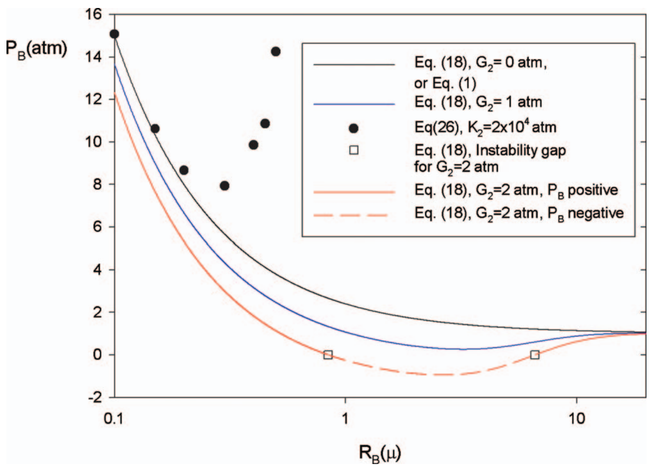

FIG. 1. The pressure of a gas bubble in an elastic material as determined from Eqs. (18) and (26) for various values of the bubble radius (R_B), shear modulus (G_2), and modulus of compression (K_2). Here the elastic material/gas bubble interface has a waterlike surface tension γ of 70 dyn/cm (0.70 μatm). Also here, and in Figs. 2–5, $a_1=-1/3$, the initial volume of the elastic material $V_0^{(2)}=10^3\mu^3$, the external pressure $P_0=1$ atm, and λ_2 (Lamé's first parameter) $=2\times 10^4$ atm. See text and note (17) for the equations that connect λ_2, K_2, and G_2.

tensor suffixes is omitted, and the suffix ll in a given term means summation over the spherical coordinates $rr, \theta\theta, \phi\phi$). Our starting point is Eq. (2), which is derived from Ref. 15,

$$2(1-\chi)\mathbf{grad}\ \mathrm{div}\ \mathbf{u} - (1-2\chi)\mathbf{curl\ curl\ u} = 0. \tag{2}$$

This is a general condition for mechanical equilibrium of an isotropic elastic material that is deformed by surface forces, i.e., its volume and/or shape is changed because of forces applied to its surface(s). χ and $\mathbf{u}$ are, respectively, Poisson's ratio for the material and the displacement vector in the material.[15–17] The former, defined as the ratio of transverse compression to longitudinal extension, is one of several measures of rigidity, and the latter gives the relative displacement of a point in the material due to its deformation.

The problem we solve is for a spherical shell of isotropic elastic material of arbitrary thickness that surrounds a spherical gas bubble at its center. We use spherical coordinates with the origin at the center of the bubble, and the labels "1" and "2" for the bubble and the elastic shell, respectively. Because of spherical symmetry, the displacement vectors $\mathbf{u}^{(i)}$, $i=1,2$ are purely radial. Hence $\mathbf{curl\ u}^{(i)}=0$, $i=1,2$, and Eq. (2) reduces to

$$\mathbf{grad}\ \mathrm{div}\ \mathbf{u}^{(i)} = 0; \quad i=1,2$$

or

$$\mathrm{div}\ \mathbf{u}^{(i)} = r^{-2}d(r^2u_r^{(i)})/dr = \mathrm{const} \equiv 3a_i; \quad i=1,2. \tag{3}$$

The solution of Eq. (3) is

$$u_r^{(i)} = a_i r + b_i r^{-2} \quad i=1,2. \tag{4}$$

In the above, $u_r^{(i)}$ is the radial component of $\mathbf{u}$ in phase (i).

There are five unknowns: a_1, b_1, a_2, b_2, and the bubble pressure P_B. The constant a_1 will be determined from the properties of the gas in the bubble. The remaining four constants will be determined from four independent conditions, specifically four boundary conditions in the case of constant pressure, and three boundary conditions plus a constant volume constraint in the case of constant volume.

First consider the gas bubble. In order for $u_r^{(1)}$ to remain finite at the bubble center ($r=0$), b_1 must be zero. Therefore for the bubble, Eq. (4) reduces to

$$u_r^{(1)} = a_1 r \quad 0 \le r \le R_B, \tag{5}$$

where R_B is the bubble radius. Under spherical symmetry, the three nonvanishing components of the strain tensor are obtained from[15]

$$u_{rr} \equiv \partial u_r/\partial r; \quad u_{\theta\theta} \equiv r^{-1}\,\partial u_\theta/\partial\theta + u_r/r = u_r/r,$$

$$u_{\phi\phi} \equiv (r \sin\theta)^{-1}\,\partial u_\phi/\partial\phi + (u_\theta/r)\cot\theta + u_r/r = u_r/r,$$

so that for the bubble

$$u_{rr}^{(1)} = u_{\theta\theta}^{(1)} = u_{\phi\phi}^{(1)} = a_1.$$

This result is consistent with the requirement that for a hydrostatic compression—in which the deformation involves a change in the body's volume, but not its shape—the components of the strain tensor are of the form $u_{ik}=\mathrm{const}x\delta_{ik}$, where δ_{ik} is the Kronecker delta.[15]

A value for a_1 is obtained from the fact that for an isotropic material the trace of the strain tensor u_{ll} provides the "relative volumetric strain" for the deformation.[15] Thus

$$u_{ll}^{(1)} \equiv (u_{rr}^{(1)} + u_{\theta\theta}^{(1)} + u_{\phi\phi}^{(1)}) = 3a_1 = \Delta V^{(1)}/V_0^{(1)},$$

where $\Delta V^{(1)}/V_0^{(1)}$ is the relative volumetric strain. By definition, the relative volumetric strain is the fractional change in the volume of a material, relative to its initial volume (i.e., its volume at zero pressure), as a consequence of a positive pressure applied to its surface(s). For an arbitrary positive pressure P_B applied to an ideal gas,

$$\Delta V^{(1)}/V_0^{(1)} \equiv (V^{(1)} - V_0^{(1)})/V_0^{(1)} = (P_0/P_B) - 1, \tag{6}$$

so that for $P_B > 0$, as $P_0 \to 0$,

$$\Delta V^{(1)}/V_0^{(1)} \to -1, \quad \text{and} \quad a_1 \to -1/3. \tag{7}$$

The identical result is obtained by repeating this calculation for a real gas in a pressure range for which its compressibility factor[18] remains finite, or equivalently, wherein its volume is given reliably by a virial equation of state.[18,19]

In all our calculations P_B will never exceed about 20 atm. Consequently, the above value for $a_1(-1/3)$ will be essentially exact here. For conditions under which the compressibility factor diverges (or the virial expansion breaks down), Eq. (7) may be invalid. But this is irrelevant since we will not consider such extreme conditions.

The remaining three unknowns P_B, a_2, b_2 are determined from conditions that are fixed by the specific problem being addressed. We provide solutions for two problems: (1) constant external pressure and (2) constant total volume. An expression for the Gibbs free energy of elastic deformation is also derived.

A. Constant external pressure

Here the three independent equations needed stem from three boundary conditions,

$$u_r^{(1)}(R_B) = u_r^{(2)}(R_B), \tag{8}$$

$$P_B = -\sigma_{rr}^{(2)}(R_B) + 2\gamma/R_B, \tag{9}$$

$$P_0 = -\sigma_{rr}^{(2)}(R_0). \tag{10}$$

In the above, P_0 is the constant external pressure applied at R_0, R_0 is the outer radius of the elastic shell, γ (which is presumed constant with R_B) is the surface tension of the elastic material at the gas bubble/elastic shell interface, and $\sigma_{rr}^{(2)}(r)$ is the radial component of the stress tensor in the elastic shell at r. Equation (8) satisfies the requirement of continuity of the displacement vector across the gas bubble/elastic shell interface, and Eqs. (9) and (10) are expressions of the balance of forces normal to the surface at the inner and outer radii of the elastic shell, respectively. The two terms on the right-hand side of Eq. (9) give, respectively, the elastic and surface tension contributions to the total pressure acting on the bubble. The external pressure is subsumed in the elastic term.

Provided the stresses and strains in the elastic material are sufficiently small for the linear regime (or Hooke's law) to apply, the nine components of the stress and strain tensors are linearly related, so that the components of one are readily obtained from those of the other. The general relation for the stress tensor components in terms of the corresponding strain tensor components is

$$\sigma_{ik} = E(u_{ik} + (\chi/(1-2\chi))u_{ll}\delta_{ik})/(1+\chi), \tag{11}$$

where E is Young's modulus.[15–17] The three nonvanishing components of the strain tensor in the elastic shell are again obtained using Eq. (4),

$$u_{rr}^{(2)} = \partial u_r^{(2)}/\partial r = a_2 - 2b_2 r^{-3}, \quad R_B \le r \le R_0, \tag{12}$$

$$u_{\theta\theta}^{(2)} = u_{\phi\phi}^{(2)} = u_r^{(2)}/r = a_2 + b_2 r^{-3}, \quad R_B \le r \le R_0. \tag{13}$$

Combining Eqs. (11)–(13) gives

$$\sigma_{rr}^{(2)} = 3a_2K_2 - (4b_2G_2/r^3), \quad R_B \le r \le R_0. \tag{14}$$

In Eq. (14), K_2 and G_2 are, respectively, the moduli of compression and rigidity of the elastic shell.[15–17] Substituting Eqs. (4), (5), and (14) into Eqs. (8)–(10) gives

$$a_1R_B = a_2R_B + b_2R_B^{-2}, \tag{15}$$

$$P_B = -3a_2K_2 + 4b_2G_2/R_B^3 + 2\gamma/R_B, \tag{16}$$

$$P_0 = -3a_2K_2 + 4b_2G_2/R_0^3. \tag{17}$$

Equations (15)–(17) are independent, so that they can be combined and solved simultaneously for a_2, b_2, and P_B. The result is

$$P_B = P_0 f(\nu) + 4a_1G_2(1-\nu f(\nu)) + 2\gamma/R_B,$$

$$f(\nu) \equiv (1+\alpha_2)/(1+\alpha_2\nu), \quad \alpha_2 \equiv 4G_2/3K_2,$$

$$\nu = (R_B/R_0)^3, \quad R_0^3 = R_B^3 + (3/4\pi)V_0^{(2)}(1+3a_2),$$

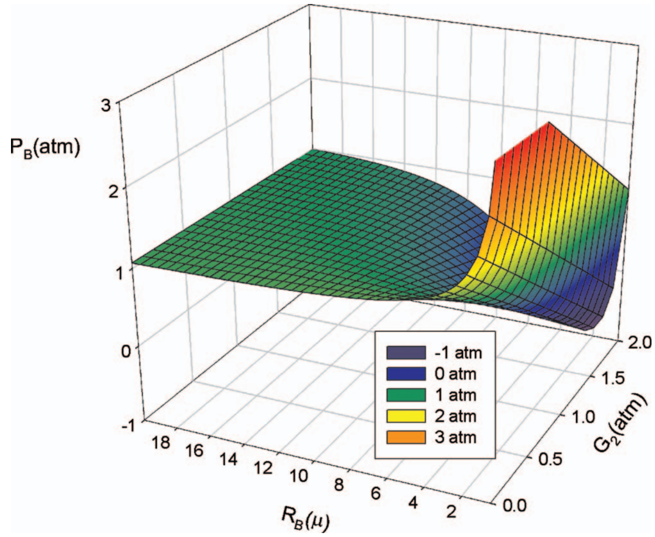

FIG. 2. The pressure of a gas bubble in an elastic material expressed as a P_B–R_B–G_2 surface determined from Eq. (18). γ and all the other parameters (other than G_2) are fixed at the values given with Fig. 1. The black, blue, and red curves in Fig. 1 are cuts through this surface in the G_2=0, 1, and 2 atm planes, respectively.

$$a_2 = (4G_2a_1\nu - P_0)/(3K_2 + 4\nu G_2); \quad b_2 = R_B^3(a_1 - a_2). \tag{18}$$

In Eq. (18), ν is the volume fraction occupied by the bubble in the system, and $V_0^{(2)}$ is the volume of the elastic material before the deformation. From their definitions, as $\alpha_2 \to 0$, $f(\nu) \to 1$. Clearly, $\alpha_2 \to 0$ both for $G_2 > 0, K_2 \to \infty$, and for $G_2 \to 0$, $0 < K_2 < \infty$, i.e., for a totally incompressible material with shear resistance, and for a material with nonzero, finite compressibility, without shear resistance, respectively. In the second case, which applies to real nonrigid materials, Eq. (18) reduces to Eq. (1) for all values of K_2. In other words, it is nonzero values of the shear modulus G_2 *only*, irrespective of the value of the modulus of compression K_2, which creates deviations from Eq. (1) due to elasticity of the medium. This was not appreciated in some earlier work [Refs. 11–14 and Eq. (26) below] where K_2, which was taken to be an effective (or "lumped") constant, was the only constant used to account for elastic effects in the medium on P_B. In materials for which G_2=0 (or equivalently, χ_2=1/2 or E_2=0) as is the case for ordinary liquids, or any material with no rigidity or stiffness, Eq. (1) provides essentially exact values of P_B, irrespective of the value of K_2.[1]

Equation (18), which is new, is our main result. Its properties are illustrated in Figs. 1–4 and will be discussed further below.

B. Constant total volume

We again use continuity of the displacement vector and equality of forces normal to the gas bubble/elastic material interface, i.e., Eqs. (15) and (16). But here Eq. (17) does not apply. It is replaced by an exact relation between a_2 and ν (the volume fraction of the bubble), which follows from the constant volume constraint. Specifically, using $u_{ll}^{(2)}$ for the trace of the strain tensor in the elastic medium, together with Eqs. (12) and (13), gives

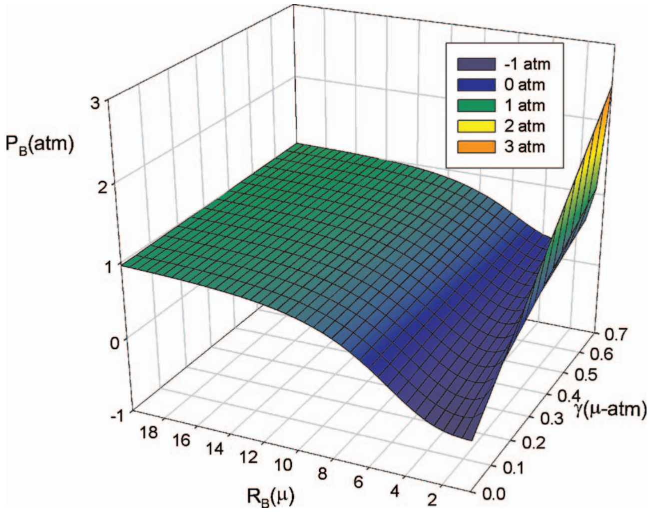

FIG. 3. The pressure of a gas bubble in an elastic material expressed as a $P_B - R_B - \gamma$ surface determined from Eq. (18). $G_2 = 1$ atm, and all the other parameters (other than γ) are fixed at the values given with Fig. 1. The blue, red, and black curves in Fig. 4 are cuts through this surface in the $\gamma = 0.70$, 0.25, and 0.0 μatm planes, respectively.

$$u_{ll}^{(2)} \equiv u_{rr}^{(2)} + u_{\theta\theta}^{(2)} + u_{\phi\phi}^{(2)}$$
$$= 3a_2 = \Delta V^{(2)}/V_0^{(2)} = -V^{(1)}/V_0^{(2)} = -(4\pi/3)R_B^3/V_0^{(2)} = -\nu$$

or

$$a_2 = -\nu/3. \tag{19}$$

In the above, the constant volume constraint $V^{(1)}(R_B) + V^{(2)}(R_B) = V_0^{(2)}$, where $V_0^{(2)}$ is the constant system volume (i.e., the volume of the elastic material at zero pressure, and in the absence of the bubble), was used to equate the volumetric strain of the elastic material ($\Delta V^{(2)}(R_B) \equiv V^{(2)}(R_B) - V_0^{(2)}$) to the negative of the bubble volume ($-V^{(1)}(R_B)$).

Combining Eqs. (15), (16), and (19) gives

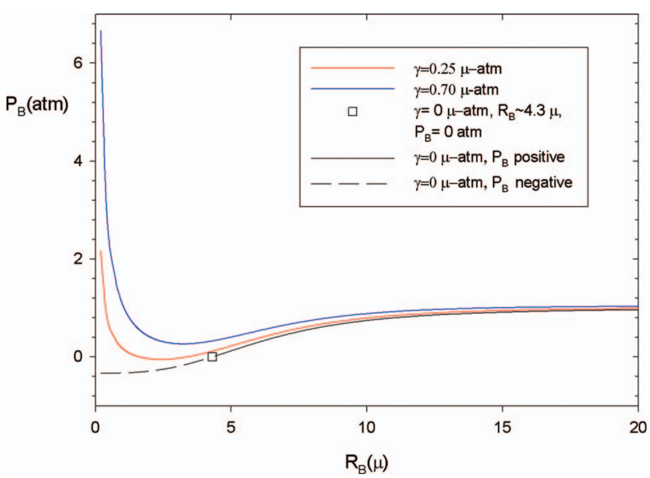

FIG. 4. The pressure of a gas bubble in an elastic material determined from Eq. (18). $G_2 = 1$ atm, and all other parameters (other than γ) are fixed at the values given with Fig. 1. For materials at these conditions, and with no surface tension (the black curve), a bubble with radius less than about 4.3μ cannot exist.

$$P_B = \nu K_2(1 + \alpha_2) + 4G_2 a_1 + 2\gamma/R_B, \tag{20}$$

where α_2 and a_1 have been given above. Equation (20) is the generalized Young–Laplace equation for the system maintained at a constant volume. As $G_2 \to 0$, $P_B \to \nu K_2 + 2\gamma/R_B$, which is the constant volume analog of the Young–Laplace equation. This correctly reduces to $P_B \to \nu K_2$ ($= \nu\lambda_2$) in the absence of a surface tension [λ_2, "Lamé's first parameter," is equal to K_2 if $G_2 = 0$ (Refs. 15–17)]. The function νK, which gives the pressure in a slightly compressed isotropic homogeneous material, has been known and used for decades.[20]

While formally exact in the sense that Eq. (18) is formally exact, Eq. (20) will be more difficult to apply than Eq. (18) for the applications considered here. This is because for a condensed phase G_2 and K_2 are harshly density dependent, and these dependencies are mostly not known.

C. The Gibbs free energy of elastic deformation

For many applications, such as estimating activation barriers to bubble formation and identifying stable or metastable bubble states,[21] and others,[22] nonmechanical or thermodynamic functions that include the entropy (S) are needed. In this section we use some of the above results to derive a simple expression for the Gibbs free energy for the deformation of an elastic shell that is maintained at a constant external pressure, and encloses a small gas bubble at its center. In Sec. IV we will point out a possible connection between this expression and a recently published idea on the origin of a certain form of DCS.

Provided the pressure and density of a material are homogeneous, i.e., constant throughout the material, the Gibbs free energy of the material (here given the symbol Φ, so as not to confuse it with the modulus of rigidity G) varies with temperature and pressure according to the well-known expression[18]

$$d\Phi = -SdT + VdP,$$

which, for isothermal changes, becomes

$$d\Phi_T = VdP.$$

As shown in Ref. 15, the generalization or tensor form of this expression for elastic materials with position-dependent stress and strain tensors is

$$d\Phi_T = -V_0 u_{ik} d\sigma_{ik},$$

where V_0 is the volume of the undeformed material. Therefore the isothermal Gibbs free energy of deformation of an elastic shell around a gas bubble at its center can be obtained from

$$\Delta\Phi_T(\text{elas}) = -V_0^{(2)} \int_{\sigma_{ik}(R_B)}^{\sigma_{ik}(R_0)} u_{ik}^{(2)} d\sigma_{ik}^{(2)}. \tag{21}$$

The right-hand side of Eq. (21), which is a sum over nine terms, reduces to a sum over three terms for isotropic materials and spherical symmetry. The converse of Eq. (11), which is needed for the integrand in Eq. (21), is

$$u_{ik}^{(2)} = [\delta_{ik}\sigma_{ll}^{(2)}/9K_2] + [(\sigma_{ik}^{(2)} - (\delta_{ik}\sigma_{ll}^{(2)}/3))/2G_2], \tag{22}$$

where

$$\sigma_{ll}^{(2)} \equiv (\sigma_{rr}^{(2)} + \sigma_{\theta\theta}^{(2)} + \sigma_{\phi\phi}^{(2)}) = 9a_2K_2.$$

In arriving at the above, we used Eq. (14) for $\sigma_{rr}^{(2)}$, and

$$\sigma_{\theta\theta}^{(2)} = \sigma_{\phi\phi}^{(2)} = 3a_2K_2 + (2b_2G_2/r^3), \quad R_B \le r \le R_0,$$

which came from Eqs. (11) and (13). Substituting Eq. (22) into Eq. (21), contracting the result, and integrating gives

$$\Delta\Phi_T(\text{elas}) = 6V_0^{(2)}G_2(a_1 - a_2)^2(1 - \nu^2). \tag{23}$$

On using Eqs. (15)–(17), Eq. (23) can be rewritten as

$$\Delta\Phi_T(\text{elas}) = 3V_0^{(2)}R_0^6(P_B - P_0 - (2\gamma/R_B))^2 \times(1 - \nu^2)/8G_2(R_0^3 - R_B^3)^2. \tag{24}$$

For a bubble that is small relative to its surrounding elastic shell [i.e., when $(R_B/R_0)\to 0$] Eq. (24) becomes

$$\Delta\Phi_T(\text{elas}) \cong C(\Delta P - (2\gamma/R_B))^2 \cong C\Delta P^2, \tag{25}$$

where $\Delta P \equiv (P_B - P_0)$ and $C(=3V_0^{(2)}/8G_2)$ is a constant. The right-most approximation can be used when surface tension effects are small, relative to elastic effects.

III. RESULTS

We focus on the predictions of Eq. (18). As indicated above, while this equation is formally exact, its numerical implementation requires that an estimate be used for one of its parameters (a_1). This estimate ($-1/3$) will be essentially exact for real gases at low-to-moderate pressures, but may be inapplicable at extreme pressures. Partly because of this, we avoid the very high pressure regime and limit our applications to bubbles for which $(0 < P_B < 20)$ atm.

From Eq. (18), P_B is seen to be a function of six variables: $(K_2, G_2, \gamma, R_B, P_0, V_0^{(2)})$. Our main interest is in the effect of R_B, G_2, and γ on P_B at ordinary external pressures, for low but nonzero values of G_2, and for typical condensed phase values of the modulus of compression K_2. Consequently, we fix the values $P_0=1$ atm, $V_0^{(2)}=10^3\mu^3$, and $\lambda_2 = 2\times 10^4$ atm (which is approximately representative of λ_2 values for ordinary liquids) in all our calculations.

Calculations

The evaluation of P_B from Eq. (18) must be done iteratively. There are a number of ways of doing this; the following is straightforward and rapidly convergent. Since a_2 is small ($\approx -10^{-5}$), it is initially set to zero to provide initial estimates for ν, R_0, P_B. The estimate of ν is used to improve the estimate of a_2 [using the expression given for it with Eq. (18)], which is used to provide new values of ν, R_0, P_B, and the equations are iterated. Convergence is rapid. Here four iterations provided convergence of P_B to within at least 1 part in 10^6. We note in passing, that by using the approximation $f(\nu)=1$ (which is exact for a totally incompressible material with finite shear resistance), Eq. (18) reduces to a simpler form, from which an approximate value of P_B can be obtained without iteration. As indicated previously, a_1 was set equal to $-1/3$ in all the calculations.

Figures 2 and 3, respectively, show a $P_B - R_B - G_2$ surface at fixed γ, and a $P_B - R_B - \gamma$ surface at fixed G_2, both obtained from Eq. (18). Figures 1 and 4 show several cuts through the surfaces in Figs. 2 and 3, respectively.

Figure 1 also includes a plot of P_B versus R_B, as predicted by

$$P_B = P_0 + K_2\nu + 2\gamma/R_B. \tag{26}$$

This is the approximate generalization of Eq. (1) for elastic effects used in Refs. 11–14.[23] Equation (26) is internally inconsistent. It consists of a sum of the unmodulated external pressure P_0 (that is applicable to a homogeneous medium containing a bubble, maintained at a fixed external pressure), a compression term $K_2\nu$ (that is applicable to a homogeneous medium containing a bubble, maintained at fixed total volume), and the surface tension term $2\gamma/R_B$. Equation (26) is also inconsistent with the correct solution of Eq. (2) for the gas bubble-elastic medium system. As indicated in the discussion under Eq. (18), the key error in Eq. (26) is the assumption that K_2 (as opposed to G_2) is the salient variable that accounts for deviations from Eq. (1) due to elastic effects in the medium. Also, Fig. 1 shows that except for bubbles small enough for the surface tension term to make the dominant contribution to P_B, Eq. (26) provides a poor numerical approximation of the correct result. It predicts the wrong sign for elastic effects on P_B for the conditions in Fig. 1. It is also asymptotically incorrect.

It is seen from Figs. 1–4, that for the conditions in these figures, which represent materials with low shear resistances, and high condensed phaselike resistances to compression, the effect of shear resistance is to lower the values of P_B, relative to Eq. (1). As shown in Figs. 1 and 2, when G_2 is increased from zero, with γ held fixed, the hyperbolic form of Eq. (1) is changed, so that (depending on the values of the other parameters) a minimum in P_B can appear at intermediate R_B values. This is illustrated by the tilted gulley shown on the surface plotted in Fig. 2. The gulley tilts downward with both increasing G_2 at fixed γ [Fig. 2] and with decreasing γ at fixed G_2 [Fig. 3]. Moreover, as G_2 increases while γ is held fixed, P_B can become negative, indicating a region of mechanical instability. For example, for $G_2=2$ atm and the other conditions in Fig. 1, a mechanically stable gas bubble with a radius in the approximate range $(0.84-6.6)\mu$ cannot exist, because within this range, the gas pressure in it would have to be negative.

As far as the author is aware, this oddity, namely, that small and large gas bubbles can exist, while bubbles of intermediate size cannot, is new. It stems from the opposing effects on the bubble pressure of surface tension and shear resistance, which dominate P_B at low and intermediate R_B values, respectively.

These figures also show how the location of the region of instability depends on the values of G_2 and γ. Figures 3 and 4 show, for example, that in the absence of a surface tension, only relatively large bubbles will be mechanically stable. For the conditions in Fig. 4, and for $\gamma=0$, only a bubble with radius greater than $\approx 4.3\mu$ will exist. It is also noteworthy that for $\gamma=0$, and the other conditions in Fig. 4, $P_B < P_0$ for all finite bubble radii.

It is worth briefly describing the properties of Eq. (18) in the asymptotic double limit ($R_B \to R_0$, $R_0 \to \infty$). For the center of mass of the soft material to remain stationary, P_B must approach P_0 in this limit. As demonstrated in Figs. 1–4, Eq. (18) satisfies this requirement for arbitrary values of G_2 and K_2. This can also be shown analytically. In this double limit, by using Eq. (18) and the equations under it, $\nu \to 1$, $f(\nu) \to 1$, and $P_B \to P_0$. However the approach to the asymptotic limit is not simple. We discuss this in terms of the plots in Fig. 4.

While it is not apparent (because of the scale of P_B and range of R_B in this figure), the limit is approached monotonically from below only for the $\gamma=0$ μatm plot. For the $\gamma=.70$ μatm plot, there is a low maximum beyond the minimum at ($P_B \cong 1.036$ atm; $R_B \cong 26\mu$). This plot subsequently approaches P_0 (1 atm) monotonically from above. The first term in Eq. (18) is essentially constant and equal to P_0 for these conditions at all radii. Therefore, for γ and G_2 both positive, the second and third terms in Eq. (18) are the source of the nonmonotonic approach to the limit. With increasing R_B, the second term (for $R_B \geq .1\mu$) monotonically increases (becoming less negative), while the third term monotonically decreases (becoming less positive).

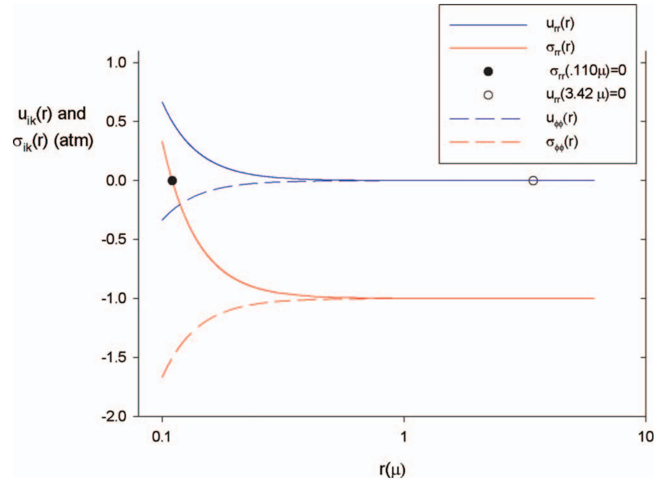

FIG. 5. The radial and tangential components of the stress and strain tensors in an elastic shell surrounding a gas bubble at its center. Only the $\phi\phi$ tangential components are shown; they are equal to the corresponding $\theta\theta$ components. Here $G_2=1$ atm, and (a_1, γ, $V_0^{(2)}$, P_0, and λ_2) have the values given in the legend for Fig. 1. r is the radial distance in the elastic shell measured from the center of the bubble. The radius of the gas bubble (R_B) is 0.10μ. Using these parameters, Eq. (18), and the equations under it, $P_B = 13.67$ atm, $a_2=-0.1667 \times 10^{-4}$, $b_2=-.3333 \times 10^{-3}\mu^3$, and $R_0=6.203\mu$. The curves start at the surface of the bubble ($r=R_B$) and end at the outer radius of the elastic shell ($r=R_0$).

IV. SUMMARY AND DISCUSSION

The generalized Young–Laplace equation, Eq. (18), which is applicable to a gas bubble in an elastic material that has a surface tension, and can also resist both compression and shear forces, predicts behavior that differs markedly from the original Young–Laplace equation, Eq. (1). The latter is inapplicable to materials that resist shear (i.e., have some rigidity or stiffness). For example, unlike Eq. (1), Eq. (18) can have a minimum in its P_B versus R_B plot at finite values of R_B. Also, on the basis of Eq. (18), a bubble may be mechanically unstable for a finite range of R_B values at intermediate R_B, but be mechanically stable outside this range. In other words, depending on the relative magnitude of the shear modulus to the other parameters, there may be elastic materials for which small and large, but not intermediate-sized gas bubbles are mechanically stable. This unusual behavior results from the opposing effects of shear resistance and surface tension on the bubble pressure. Surface tension and shear resistance, respectively, exert positive and (for the conditions considered here) negative effects on P_B, with the former and latter dominant at small and intermediate R_B values, respectively.

Mechanical instability gaps of the kind illustrated by the bottom plot in Fig. 1, if they exist in real (as opposed to "model") elastic materials, have an interesting and important practical implication. For an elastic material with such an instability gap, large gas bubbles, although mechanically stable once formed, are unlikely to form from small gas bubbles. This is because using the conditions for the bottom plot in Fig. 1 as an example, a growing small bubble, on reaching the lower instability bound ($\approx .84\mu$), will not be able to traverse the rather broad mechanical instability gap ($\approx 6\mu$). It can survive only by acquiring some dissolved gas from the surrounding elastic material, thereby increasing its pressure, and shrinking back to a smaller mechanically stable radius. For this reason, it may be unlikely to find large gas bubbles in some elastic materials. Put another way, the bubbles found in these materials are likely to be small.

The effect of shear strain in the elastic shell on the bubble pressure P_B can be understood from a simple physical picture. As will be shown below, it is the product of $2G_2$ and the radial component of the strain tensor at the bubble surface ($u_{rr}^{(2)}(R_B)$), which (to an excellent approximation) accounts for the effect of G_2 on $\sigma_{rr}^{(2)}(R_B)$, and thereby on P_B [see Eq. (9)]. This is illustrated by Eq. (29) below and the plots in Fig. 5. The latter shows the radial and tangential components of the stress and strain tensors across the elastic shell under conditions typical of those considered here. These plots were obtained using Eqs. (12)–(14), the equations given above Eq. (23), and the parameters given with Fig. 5. The exact general relations between the stress and strain tensor components are given by Eq. (11). To illustrate the underlying physics, the equation for $\sigma_{rr}^{(2)}(r)$ given by Eq. (11) is first recast explicitly in terms of G_2, giving Eq. (27), which (given linear response) is exact. Subsequently, χ is set to 1/2 (χ is here 0.499 975), giving Eq. (28). Equation (29) is obtained from Eq. (28) by using the approximation $P_0 \cong -3a_2K_2$, which is accurate, provided $\nu G_2 \ll P_0$ and $\nu G_2 \ll K_2$ [see the expression for a_2 under Eq. (18)]. This last approximation is also an excellent one for the conditions used in Fig. 5, where $\nu G_2 \cong 4.2 \times 10^{-6}$,

$$\sigma_{rr}^{(2)}(r) = 2G_2 u_{rr}^{(2)}(r) + 9a_2K_2(\chi/(1+\chi)), \tag{27}$$

$$\sigma_{rr}^{(2)}(r) \cong 2G_2 u_{rr}^{(2)}(r) + 3a_2K_2, \tag{28}$$

$$\sigma_{rr}^{(2)}(r) \cong 2G_2 u_{rr}^{(2)}(r) - P_0. \quad (29)$$

The signs of $u_{rr}(r)$ and $\sigma_{rr}(r)$ are both physically significant. For $u_{rr}(r)>0$ and $u_{rr}(r)<0$, the material in the shell is radially stretched and radially compressed, respectively, relative to the initial undeformed state.[15] From Fig. 5 it is seen that the material in this example is radially stretched in the vicinity of the bubble surface $(0.10 \le r < 3.42)\mu$. It is radially compressed in the vicinity of the applied pressure $(3.42 < r \le 6.20)\mu$, but this compression is very slight [e.g., $u_{rr}(6\mu) \cong -1.4\times 10^{-5}$]. All this makes physical sense because the bubble is here about 1500 times more compressible than the elastic material, so the elastic material near the bubble will radially stretch into it, rather than be radially compressed by it. Since the trace of the strain tensor is invariant with r (here $u_{ll}^{(2)}=3a_2\cong -5\times 10^{-5}$), radial stretching is accompanied by tangential compressions. These compressions are illustrated by the dashed blue curve in Fig. 5. $u_{\phi\phi}^{(2)}(r)$ and $u_{\theta\theta}^{(2)}(r)$, which are equal, are negative over the entire shell.

Also, for $\sigma_{rr}(r)>0$ and $\sigma_{rr}(r)<0$, the radial component of the stress tensor points away from the bubble and toward the bubble, respectively. Thus, a positive $\sigma_{rr}(R_B)$ contributes negatively to the bubble pressure [see Eq. (9)]. From Fig. 5 it is seen (moving radially away from the bubble through the elastic shell) that $\sigma_{rr}^{(2)}(r)$ decreases with r and switches from being positive to negative at $r\cong 0.110\mu$. As with the strain tensor, the trace of the stress tensor is invariant with r. Here $\sigma_{ll}^{(2)}=9a_2K_2\cong -3P_0$. This invariance ensures that the tangential stresses, $\sigma_{\theta\theta}^{(2)}(r)$ and $\sigma_{\phi\phi}^{(2)}(r)$, which are equal, increase as the radial stress decreases.

Returning to Eq. (29), we see that this equation, without the $-P_0$ term, is Hooke's law for radially stretching an inhomogeneous material, expressed in units of pressure (rather than force). Thus, $2G_2$, $u_{rr}^{(2)}(R_B)$, and $\sigma_{rr}^{(2)}(R_B)$ are, respectively, the Hooke's law spring constant for the material, the degree of radial stretching of the material at the bubble surface, and the radial stress in the material at the bubble surface, respectively. The $-P_0$ term, which represents the contribution of the unmodulated external pressure to $\sigma_{rr}^{(2)}(R_B)$, is transmitted by λ_2, the pure compression part of K_2.[17] To summarize, Eq. (29) shows that (i) for $u_{rr}^{(2)}(R_B)>0$ and $u_{rr}^{(2)}(R_B)<0$, G_2, respectively, contributes negatively and positively to P_B, and (ii) provided $P_0>0$, λ_2 always contributes positively to P_B.

With respect to applications, this work may be relevant to a recently published idea on the origin of a certain form of DCS. Specifically, Strauss *et al.*[24] recently suggested that the relatively common "pain-only" DCS (colloquially, "the bends," which is manifested by joint pain) may be explained by a purely physical mechanism. The suggestion is that in this form of DCS, gas bubble growth within an enclosed pain-sensing organelle (the *Ruffini* type 2 corpuscule) is the cause of pain-only DCS. This organelle, which is embedded in joint capsules, generates orthopedic joint pain on injury to the joint by the stretching of its nerve-rich outer elastic membrane (the *perineurium*). Strauss *et al.*[24] suggested that pain-only DCS is caused by the stretching of this membrane due to gas bubble growth within the pain-sensing organelle.

Equation (25), for the Gibbs free energy of a stretched elastic shell around a small gas bubble ($\Delta\Phi_T$(elas)), would seem to be relevant to this. The function $\Delta\Phi_T$(elas) is a simple scalar measure of the extent to which an elastic shell is stretched. Also, it has long been known from empirical studies that functions (called "risk functions" in probabilistic DCS theories[7–10,25,26]) that increase with the relative pressure ΔP are useful practical measures of the risk of incurring DCS. Since $\Delta\Phi_T$(elas) was here shown to be quadratic in ΔP for a small gas bubble trapped inside an elastic shell, the novel idea of Strauss *et al.* is consistent both with Eq. (25) and with earlier empirical work. Also, it should be possible to develop new risk functions based on an explicit bubble trapped in an elastic medium, i.e., from the basis of Eq. (25).

In this work the comparatively simple problem of a single bubble trapped in the center of an elastic spherical shell was solved for the bubble pressure and the Gibbs free energy of the shell. Future applications to DCS, volcanic eruptions, and other areas may require solutions to problems involving many gas bubbles in an elastic medium. While this is a difficult problem, some progress has been made in related work on the effect of elastic strain on the thermodynamics[22] and kinetics[27] of phase transitions. A possible future direction for this work would be to extend it to the effect of medium elasticity on the thermodynamics and kinetics of a many-bubble system, particularly as it relates to the DCS problem.

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[16] I. S. Sokolnikoff, *Mathematical Theory of Elasticity*, 2nd ed. (Krieger, Malabar, FL, 1983).

[17] The modulus of hydrostatic compression (or the modulus of compression) K, the modulus of rigidity (or the shear modulus) G, Young's modulus E, and Poisson's ratio χ are related as follows (Refs. 15 and 16): $E = 2G(1+\chi) = 3K(1-2\chi)$, where E is a measure of stiffness of an isotropic elastic material, and K, G, and λ are related by $K = \lambda + (2G/3)$, which can be taken as the definition of λ. Also, λ and G are called Lamé's first and second parameters, respectively. Physically, λ and G, respectively, provide the pure compression and the pure shear contributions to K, and K is simply the reciprocal of the familiar coefficient of isothermal compressibility κ, where $\kappa \equiv -(1/V)(\partial V/\partial P)_T$. For materials with $G=0$, the elastic characteristics of ordinary fluids (that resist compression but not shear) are recovered. This limit, in which $\chi = 0.5$ (exactly), is also known as the "isotropic upper limit of χ" (Ref. 16). Our interest here is in materials for which $G/K \approx 10^{-4}$, or equivalently, $G \cong E/3$. These are also materials for which χ is very slightly less than 0.5. Soft rubber and gelatin (e.g., "jello") are examples.

[18] D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976), Chap. 12.

[19] Most determinations of the relative volumetric strain $(\Delta V/V_0)$ are for highly incompressible condensed phase materials for which the full equation of state is not known. Here the value of V_0, the (extrapolated) zero-pressure volume, is usually unknown, so that $\Delta V/V_0 (\equiv (V-V_0)/V_0)$ cannot be determined directly. For these cases, which are the norm, $(\Delta V/V_0)$ is estimated from a truncated first-order expansion of the volume in terms of the applied pressure under the assumption that both the applied pressure and the resultant volume change are small (Ref. 15). Thus, $\Delta V/V_0 \cong (P/V_0)(\partial V/\partial P)_T \cong (P/V)(\partial V/\partial P)_T \equiv -P\kappa \equiv -PK^{-1}$. The compressibility functions are presumed known at the required pressure and temperature (T). It turns out that the effect of the two approximations made above—first-order truncation (since P is small) and subsequently replacing V_0 by V (since ΔV is small) exactly cancel one another for an ideal gas. Thus, if $-P\kappa$ is evaluated for an ideal gas, it gives exactly the same value (-1) as is obtained directly for $(\Delta V/V_0)$. This is a consequence of the functional form of the ideal gas equation of state $(P_T V = C)$.

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