Free energy wells for small gas bubbles in soft deformable materials

Saul Goldman[a)]

Department of Chemistry, The Guelph-Waterloo Physics Institute, and The Guelph-Waterloo Center for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

Thermodynamic expressions are derived for the system relative Gibbs free energy, and the relative Gibbs free energy per bubble, for all possible equilibrium bubble states that can form in a soft slightly rigid material, initially supersaturated with a dissolved inert gas (N_2). While the thermodynamic manipulations are exact, the final expressions are approximate, due to an approximation made in deriving the expression for the elastic free energy of a soft material containing more than a single bubble. The expressions predict that provided the shear modulus of the soft material is not negligibly small, free energy wells which stabilize small gas bubbles for finite periods of time exist in such materials. This is consistent with a previous calculation, based solely on the bubble pressure equation, which resulted in the conjecture that bubbles found in soft materials with some rigidity (or shear resistance) are likely to be small. The possible relevance of this to the field of decompression sickness is outlined. © *2010 American Institute of Physics.* [doi:10.1063/1.3394940]

I. INTRODUCTION

This is the second of two articles about the effect of elasticity on the pressure and stability of gas bubbles suspended in a soft elastic material. In the first article,[1] an essentially exact equation was derived for the pressure of a single gas bubble suspended in a soft elastic material. From the basis of that equation, the conjecture was made that soft elastic materials with a non-negligible shear modulus (below) may stabilize small gas bubbles. Moreover, for materials in which both shear resistance and surface tension forces exist, it was found that both small and large gas bubbles can be expected to form, albeit on different timescales. This differs from the behavior of bubbles in ordinary liquids, where minimization of the effect of surface tension, in the absence of shear resistance, acts to stabilize large gas bubbles only.[2]

A simple physical mechanism, if it exists, that acts to stabilize small inert gas bubbles in the body, would be highly relevant to understanding the physical basis of "decompression sickness" (DCS). DCS sometimes arises in people and animals, following a rapid decompression (i.e., a reduction in external pressure) from an initially stable higher pressure state. The greater the pressure drop, the greater is the probability that DCS will occur. DCS can be either "hyperbaric DCS" (as in scuba diving) or "hypobaric DCS" (as in space exploration), depending on whether the initial pressure is, respectively, greater than or equal to 1 atm.

DCS is believed to be initiated by the growth of pre-existing gas bubbles in specific tissues of the body, with the manifest form of DCS dependent on the tissue involved. For example, two mild forms of DCS are "skin bends" (which involves itching and/or a rash), and "pain-only DCS"—more generally "the bends," which involves joint pain only. In these manifestations, the expanding gas bubbles are believed,

respectively, to be in the skin,[3,4] and (as has been recently postulated) inside enclosed pain-sensing organelles, which are themselves embedded in joint capsules.[5] Severe forms of DCS include "neurological DCS," (or "CNS DCS") which is believed to arise from the growth of gas bubbles in central nervous system tissue.[3,4,6,7] CNS DCS can result in blindness, paralysis, and even death.

It is known from Doppler (ultrasound) measurements that, subsequent to decompression, an increased incidence of gas bubbles is found in the major veins of the circulatory system, relative to their incidence prior to decompression.[8,9] These bubbles can be detected even after very mild decompressions that do not result in DCS.[9] While there exists a weak positive correlation between the numbers and size of bubbles detected by Doppler measurements following decompression, and the likelihood of subsequently developing some form of DCS,[9] venous system bubbles per se are not believed to be causative of DCS. Rather, as indicated above, DCS is believed to result from gas bubble growth within specific tissues, and that the presence of significant numbers of venous system bubbles provides merely a rough indication that some form of DCS may subsequently occur.

In this second article, the work in Ref. 1 is extended to elastic media containing more than a single bubble, and expressions for the Gibbs free energy functions for such a system are derived. The main purpose of this second article is to determine whether the conjecture in Ref. 1—that soft elastic materials have the potential to stabilize small inert gas bubbles—is thermodynamically supported. The underlying motivation for both articles is to try to provide insight into the influence elasticity of the surrounding medium may have, on the physical basis of DCS.

In order to try to understand the physical basis of DCS, it is necessary to know how the pressure and stability of gas bubbles in tissues vary with the external pressure and with the properties of the tissues. We will model tissues in the

---

a)Electronic mail: sgoldman@uoguelph.ca.

body as isotropic elastic materials that have a surface tension and resist both compression and shear forces. Compression forces act to reduce the volume of a material without changing its shape. Shear forces act to change the shape of a material without changing its volume. The elastic behavior of a simple liquid, such as water, involves no resistance to shear forces (its "shear modulus" is zero) but strongly resists compression (its "modulus of compression" is large). It is the shear modulus, which is entirely absent in simple liquids, such as water, that gives materials whatever rigidity and intrinsic shape they may have. Since most tissues in the body do have intrinsic shapes, it is expected that their shear modulus will be germane to the pressure and stability of inert gas bubbles within them.

II. THEORY

The Young–Laplace (YL) equation (often called simply the Laplace equation) for the pressure of a mechanically stable gas bubble suspended in a fluid medium was recently generalized. The generalization rendered the YL equation applicable to elastic materials that have intrinsic shape due to their having a nonzero shear modulus.[1] For materials that have a surface tension but no shear modulus, such as ordinary liquids, the YL equation is[10]

$$P_B = P + 2\gamma/R_B. \tag{1}$$

In Eq. (1), P_B, P, γ, and R_B are the gas pressure in the bubble, the constant external pressure applied to the medium, the surface tension, and the bubble radius, respectively. The generalized-YL (GYL) equation for the pressure of a bubble in a soft elastic material with both a surface tension and a shear modulus, to which a constant external pressure is applied, was found to be

$$P_B = Pf(\nu) + 4a_1\varepsilon_2(1 - \nu f(\nu)) + 2\gamma/R_B \tag{2}$$

where

$$f(\nu) \equiv (1 + \alpha_2)/(1 + \alpha_2\nu), \quad \alpha_2 \equiv 4\varepsilon_2/3K_2,$$

$$\nu = (R_B/R_S)^3, \quad R_S^3 = R_B^3 + (3V_2^0/4\pi)(1 + 3a_2),$$

$$a_2 = (4\varepsilon_2 a_1\nu - P)/(3K_2 + 4\nu\varepsilon_2).$$

In the above, a_1 is a constant ($-1/3$) for gases at ordinary to moderately high pressures, ν, R_S, and V_2^0 are the volume fraction occupied by the bubble, the radius of the system (bubble+medium) measured from the center of the bubble, and the initial (undeformed) volume of the spherical shell of elastic material that surrounds the bubble, respectively. Also ε_2 and K_2 are the shear modulus and the modulus of compression of the medium, respectively.[11–13] Because of accuracy concerns (below), we will restrict out calculations to soft deformable materials that are only very slightly rigid, for which $\alpha_2 \approx O(10^{-6})$. For α_2, in this range, the GYL equation simplifies to

$$P_B \cong P - (4\varepsilon_2/3)(1 - \nu) + 2\gamma/R_B. \tag{3}$$

Since $\varepsilon_2 > 0$, it is seen from Eq. (3) that the effect of a low degree of shear resistance in the medium is to lower the

bubble pressure, relative to that predicted by the YL equation. Also, depending on the values of P, γ, and ε_2, P_B can, from the basis of these equations, be negative for some intermediate values of R_B. In other words, the GYL equation predicts that there may be soft materials in which both small and large, but not intermediate sized gas bubbles are observed. This unusual situation stems from the opposing effects on P_B of surface tension and shear resistance. The former exerts a positive effect on P_B, and is relatively important for small radii. The latter is relatively important for intermediate radii, where it exerts a negative effect on P_B. Also, it was shown in Ref. 1 that the range of radii over which negative P_B values were predicted could be quite large (e.g., $O(10\mu)$ or more). This indicates, intuitively at least, that any bubbles found in such materials would tend to be small, since though mechanically stable once formed, large bubbles may be unlikely to form.

A. Partitioning the medium

We will require expressions for the relative Gibbs free energy, and for the bubble pressure P_B, for a composite system comprised of a number of gas bubbles suspended in, and in equilibrium with an elastic medium. This requires that the medium be partitioned over the bubbles in the system. A straightforward method, taken from solid state physics[14,15] was used for this. Each bubble is associated with, and is at the center of, a spherical shell or "domain" of the elastic medium.[15] We assume that the bubble densities will be low enough so that the bubbles do not directly influence one another. The inner and outer radii of the elastic domain are the bubble radius R_B and R_0, respectively, where the latter, measured from the center of the bubble, is given by[14,15]

$$R_0 = R_B/\nu^{1/3} = R_S/N_B^{1/3}. \tag{4}$$

R_S, the system radius, is given by

$$R_S = [N_B R_B^3 + (3V_2^0/4\pi)(1 + 3a_2)]^{1/3}. \tag{5}$$

The term $3a_2$ will be determined from boundary conditions. It provides the so-called "volumetric strain" in the medium, which is the fractional change in the volume of the medium that accompanies its deformation, due to different pressures acting on its surfaces. Here this arises due to the formation of bubbles of pressure P_B within the medium, while the external or applied pressure is P.[1,11]

Having decomposed the system into N_B spherical subsystems, the bubble pressure and the elastic free energy of the soft material in the subsystems, are determined in the exact same way as was done for the single-bubble case.[1] Therefore, the derivation for these functions that is given below is brief. It is important to bear in mind, however, that while the solution is essentially exact for $N_B = 1$, the solution for $N_B > 1$, is approximate.

B. The bubble pressure

We use boldface letters for vectors, and the usual convention for representing tensors.[11] We use spherical coordinates, summation over the coordinate labels r, θ, and ϕ is

understood with respect to all suffixes that appear twice in a given term, and the summation sign over tensor suffixes is omitted.

The general condition for mechanical stability of an isotropic material that is deformed by forces applied to its surface(s) is[11]

$$2(1 - \chi)\mathbf{grad} \, \text{div} \, \mathbf{u} - (1 - 2\chi)\mathbf{curl} \, \mathbf{curl} \, \mathbf{u} = 0, \quad (6)$$

where $\mathbf{u}$ is the displacement vector[1,11] and χ is Poisson's ratio.[11–13] Because of spherical symmetry of the subsystems, the displacement vectors both in the bubble and in its surrounding elastic shell are purely radial. Consequently the second term in Eq. (6) vanishes, and the radial components of the displacement vectors that satisfy Eq. (6) are obtained from

$$u_r^{(i)}(r) = a_i r + b_i r^{-2} \quad i = 1, 2. \quad (7)$$

In the above $u_r^{(i)}(r)$ is the radial component of $\mathbf{u}$ in phase i and a_i and b_i are constants (i.e., independent of the radial distance r) to be determined from the boundary conditions.

Using $i = 1, 2$ to represent the bubble and its spherical shell, respectively, it is readily shown[1] that $b_1 = 0$, and provided the bubble pressure is in a range for which the compressibility factor of the gas in it remains finite, $a_1 = -1/3$.

The remaining two constants, a_2 and b_2, and the bubble pressure P_B, require three boundary conditions for their determination. Given the subdivision of the full system into N_B spherical subsystems, two of these conditions are exact, and the third is approximate. The exact conditions are

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

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

Equation (8) stems from the requirement of continuity of the displacement vector across the gas bubble/elastic shell interface, and Eq. (9) reflects the balance of forces normal to the surface at this interface. The two terms on the right-hand side of Eq. (9) give the elastic and surface tension contributions to the total pressure acting on the bubble, respectively. In Eq. (9), $\sigma_{rr}^{(2)}(R_B)$, and γ are the radial component of the stress tenor in the soft material, and the surface tension, respectively, both at this interface.

A third boundary condition, applicable at the subsystem's domain radius R_0, is needed, and an approximation is used for it. For $N_B = 1$ (or $R_0 = R_S$), the exact boundary condition which was used previously[1]

$$P = -\sigma_{rr}^{(2)}(R_S). \quad (10)$$

This is an expression of the balance of normal forces at the outer radius of the system where the constant external pressure (P) is applied.

The approximation we will use here for $N_B > 1$ is

$$P \cong -\sigma_{rr}^{(2)}(R_0). \quad (11)$$

This means that the negative of the radial component of the stress tensor at each domain's outer radius R_0, is set equal to the applied external pressure. A desirable property of this approximation, is that it is exact at both extremities of the range of bubble volume fractions ν, where $N_B = 1$. It will be

shown that these extremities correspond to the lower and upper critical bubble radii of the system, $R_{\text{crit},l}$, and $R_{\text{crit},u}$ respectively. Therefore, though approximate, Eq. (11) does not involve the uncontrolled approximation of extrapolating from low to high ν. Eq. (11) is anchored exactly at both extremities of ν.

There are several routes by which this approximation can be obtained. One is based on making the displacement vector stationary at each domain boundary, where the influence of central enclosed bubble is presumed to vanish. Making $u_r^{(2)}(R_0)$ stationary is equivalent to making the radial component of the strain tensor at the domain boundary $(u_{rr}^{(2)}(R_0))$ zero. This approximation is physically sensible, since when $u_{rr}^{(2)}(R_0) = 0$, the material at the domain boundary is radially undeformed.[1] Under linear response, the radial components of the stress and strain tensors are related through[1,11,13]

$$\sigma_{rr}^{(2)}(r) = 2\varepsilon_2 u_{rr}^{(2)}(r) + 9a_2 K_2(\chi/(1 + \chi)), \quad (12)$$

which for the materials of interest here reduces almost exactly to[1]

$$\sigma_{rr}^{(2)}(r) \cong 2\varepsilon_2 u_{rr}^{(2)}(r) - P. \quad (13)$$

Using $u_{rr}^{(2)}(R_0) = 0$ in Eq. (13) gives Eq. (11).

An alternate route to Eq. (11) is outlined in Ref. 16.

Equations (8), (9), and (11) are independent, so that they can be combined and solved simultaneously for a_2, b_2, and P_B. The result is

$$P_B = Pf(\nu) + 4a_1\varepsilon_2(1 - \nu f(\nu)) + 2\gamma/R_B,$$

$$f(\nu) \equiv (1 + \alpha_2)/(1 + \alpha_2\nu); \quad \alpha_2 \equiv 4\varepsilon_2/3K_2;$$

$$\nu = (R_B/R_0)^3, \quad (14)$$

$$R_0^3 = R_B^3 + (3/4\pi)(V_2^0/N_B)(1 + 3a_2);$$

$$a_2 = (4\varepsilon_2 a_1 \nu - P)/(3K_2 + 4\nu\varepsilon_2);$$

$$b_2 = R_B^3(a_1 - a_2); \quad a_1 = -1/3.$$

Equation (14) is isomorphic with Eq. (2), and correctly reduces to it for $N_B = 1$. Equation (14), which generalizes Eq. (2) from $N_B = 1$ to $N_B \geq 1$, will be used for the bubble pressure in the expressions for the free energy for systems in which $N_B > 1$.

C. Gibbs free energy of elastic deformation

The derivation of an expression for the Gibbs free energy of elastic deformation of the soft material associated with each bubble, is done exactly as was done for the single bubble,[1] except that the upper limit of integration is now the domain radius R_0, rather than to the system radius R_S (Ref. 17) $(R_0 = R_S/N_B^{1/3})$. The expressions used for the stress and strain tensor components, $\sigma_{ik}^{(2)}$ and $u_{ik}^{(2)}$, respectively, and the details of the contraction and the integration are as in Ref. 1. Thus, from

$$dg_{elas} = -(V_2^0/N_B)u_{ik}^{(2)}d\sigma_{ik}^{(2)},$$

we get

$$\Delta g_{elas} = -(V_2^0/N_B)\int_{\sigma_{ik}(R_B)}^{\sigma_{ik}(R_0)} u_{ik}^{(2)}d\sigma_{ik}^{(2)}$$

$$= 6(V_2^0/N_B)\varepsilon_2(a_1-a_2)^2(1-\nu^2). \qquad (15)$$

The value of $a_1(-1/3)$ and the expressions for ν, R_0, and a_2, that are given with Eq. (14), are used in Eq. (15). In the above, Δg_{elas} is the elastic Gibbs free energy due to shear resistance, attributed to the elastic domain associated with each bubble. From this, the elastic Gibbs free energy of the medium for the full system is simply

$$\Delta G_{elas} = 6V_2^0\varepsilon_2(a_1-a_2)^2(1-\nu^2). \qquad (16)$$

A key property of Eq. (16) that will be germane to the existence of metastable free energy wells for small gas bubbles in elastic materials, is its prediction of near constancy of ΔG_{elas}, for a given ε_2. Specifically, we will have $a_2/a_1 \approx 10^{-4}$ so that

$$\Delta G_{elas} \cong (2/3)V_2^0\varepsilon_2(1-\nu^2) \qquad (16')$$

$$\cong (2/3)V_2^0\varepsilon_2 \qquad (16'')$$

Eq. (16″) follows from Eq. (16′) since we will have $\nu \leq .03$

D. Gibbs free energy of dissolution

We use the process of dissolution from a supersaturated solution as a means of creating a system with an excess quantity of gas, relative to what is present at saturation in solution. Our interest is in the stable and metastable bubble distributions that arise when excess gas coexists in equilibrium, or conditional equilibrium (below), with a soft elastic material.

Consider the dissolution process from an initial state comprised of a supersaturated solution of N_2 dissolved in a soft elastic medium. We need an expression for the Gibbs free energy of dissolution from this state to all possible two-phase equilibrium composite states that can form when excess gaseous N_2 is released to the medium as gaseous bubbles. The term "equilibrium" here refers to a conditional or partial equilibrium. This means that the bubbles are in mechanical and thermal equilibrium with the surrounding medium, and the chemical potentials of N_2 in the bubbles and the surrounding medium are equal,[2,18,19] but the bubbles are constrained to some specified radius R_B. The global minimum over all possible conditional minima provides the most stable possible state for the system as a whole. A macroscopic system will always be found in this final state, given sufficient time.[18–20]

These states of conditional or partial equilibrium are in the class of extrapolated or interpolated states that arise in statistical kinetics.[21] They are postulated to exist on a short time-scale relative to the long time-scale in Thermodynamics. Frenkel discussed what he called the "extended thermodynamic theory" of these states, and gave several examples of them.[21] The best-known example is transition-state theory[19,22,23] (TST). This theory also deals with a system that traverses a series of states of conditional or partial equilibrium, before reaching the final equilibrium state. Partial or conditional equilibrium in TST refers to the condition wherein each reacting species is at all times assumed to be equilibrated with respect to a Maxwell–Boltzmann distribution,[18,19] but not with respect to its concentration in the thermodynamically most stable state of the system. It is only in the final most stable equilibrium state, that the concentrations reach their respective equilibrium values.

We are looking for the possible presence of free energy wells for small gas bubbles which, if present, would provide them with a degree of longevity. Equations for mass balance, mechanical stability, and equality of chemical potentials of N_2 in the two phases can be written for all the points along a conditional equilibrium path, so that it is possible to fully characterize all the composite states that comprise this path. It is however not possible to simultaneously satisfy the conditions of mass balance, mechanical stability, and equality of chemical potentials, over a continuous range of bubble radii using a single bubble (see Ref. 2 and below). In order to generate a continuous range of bubble radii at which the bubbles are in states of conditional equilibrium, an additional variable—the number of bubbles in the system at each radius $N_B(R_B)$—must be introduced. It will be shown that $N_B(R_B)$ is a single-valued function of R_B.

As a consequence, we need an equation for the relative Gibbs free energy of a composite system comprised of N_B gas bubbles each of radius R_B, suspended in, and in conditional equilibrium with a surrounding elastic medium. This expression will be obtained from the Gibbs free energy change that accompanies the dissolution process in which a super-supersaturated one-phase system gives off some of its excess dissolved gas as bubbles. The process is taken to occur at a fixed temperature T, a fixed external pressure P, and within a closed system. These conditions, together with a further correction discussed below, are required in order that the modified Gibbs free energy function that will be used be a valid measure of the relative stability of the states being generated and compared.

The required relative system Gibbs free energies are obtained by subtracting the Gibbs free energy of the initial super-saturated state from that of the composite states. [The initial supersaturated solution can be created by a step decompression applied to a pre-existing saturated solution that had been maintained at the relatively elevated pressure $P_{in}(P_{in} > P)$]. As originally formulated, the Gibbs free energy function provides an exact measure of the relative stability of states, provided the states being compared have the same number of moles of each component, and are all at the same temperature and pressure as the corresponding external temperature and pressure reservoirs.[2,10,20,21,24–28] More precisely, for the Gibbs free energy function to be a valid measure of the relative stability of a composite system, all the component subsystems of the composite system must have the same pressure as the external reservoir pressure.[2,10,20,21,24–28] In the problem under consideration however, the actual bubble pressure P_B will generally differ from the external pressure P because of surface tension and shear modulus effects [see Eqs. (2), (3), and (14)]. Therefore the N_2 in the bubbles will

not generally be at the required constant external pressure P. As described in more detail elsewhere,[2,24] this complication can be dealt with by a two-part corrective procedure. First, one uses Callen's reformulated postulatory thermodynamics[29] in place of Gibbs' original formulation. This obviates the Gibbs requirement of a reversible path along which the pressure of all the subsystems in the composite state are at the constant reservoir pressure (which is here impossible). Second, for purposes of the composite state free energy evaluation, one corrects (or rescales) the chemical potential of the gas in the bubbles to what it would be if the bubble pressure were P, as opposed to the actual value P_B.[2,21,24] The product of this rescaled chemical potential and the actual number of gas molecules provides the gas phase contribution to the free energy of the full compound system. The actual number of gas molecules is determined from the equality of chemical potentials of N_2 in the two phases, with each phase considered at its actual pressure (below).

This way of calculating the Gibbs free energy of a composite system that contains a subsystem with a pressure that is different from the external pressure, was apparently first used about 70 years ago by Frenkel.[21] Later, Abraham wrote out the method systematically, and called the resultant computational prescription a "postulate" [it is postulate 3′ of Ref. 24], for which the ultimate justification was to be any *a posteriori* success it may have in applications.[24] Here, as in Ref. 2, we assume this postulate to be correct. We will find support for it both in this work (below), and in the relatively recent work on nucleation theory by Debenedetti,[25,26] and by Tester and Modell,[25,27] who use the equivalent of this method in related problems. The result is

$$\Delta G(R_B, P) = G_{fin}(R_B, P) - G_{in}(\{x(in)\}, P),$$

$$G_{in}(\{x(in)\}, P) = \sum_{j=1}^{2} N_j \mu_{j,l}(\{x_j(in)\}, P),$$

$$G_{fin}(R_B, P) = G_{elas}(R_B, P) + G_{surf}(R_B, P) + G_l(R_B, P) + G_g(R_B, P),$$

$$G_{elas}(R_B, P) = 6V_2^0 \varepsilon_2 (a_1 - a_2)^2 (1 - \nu^2),$$

$$G_{surf}(R_B, P) = 4\pi r^2 \gamma N_B(R_B, P),$$

$$G_l(R_B, P) = \sum_{j=1}^{2} N_{j,l}(R_B, P) \mu_{j,l}(x_{j,l}(R_B), P),$$

$$G_g(R_B, P) = N_{2,g}(R_B, P) \mu_{2,g}(R_B, P),$$

$$N_{2,g}(R_B, P) = (4\pi/3) R_B^3 P_B N_B(R_B, P)/kT,$$

$$\mu_{2,g}(R_B, P) = \mu_{2,g}(R_B, P_B) + kT \ln(P/P_B),$$

$$N_B(R_B, P) = N_1 kT([x_2(in)/x_1(in)]$$
$$- [x_{2,l}(R_B)/x_{1,l}(R_B)])/((4/3)\pi R_B^3 P_B). \quad (17)$$

In Eq. (17), $P_B \equiv P_B(R_B, P)$, a dependent variable, is the bubble pressure given by Eq. (14), $G_{in}(\{x(in)\}, P)$ and

$G_{fin}(R_B, P)$ are the Gibbs free energies in the initial state, and the corrected (or rescaled) Gibbs free energy in the final state, respectively, N_j is the total number of molecules of type j in the system, and $\mu_{j,\alpha}(.)$ is the chemical potential of component j in phase α at the conditions defined by the variables in parenthesis.[18,19] Also, $G_{elas}(R_B, P)$ and $G_{surf}(R_B, P)$ are the total elastic and surface free energies in the final state, respectively, $G_l(R_B, P)$ is the total Gibbs free energy of the soft material in the final state in the absence of shear resistance, and $G_g(R_B, P)$ is the total (corrected or rescaled) Gibbs free energy of the gas phase in the final state. As indicated above, it is obtained from

$$G_g(R_B, P) = N_{2,g}(R_B, P) \mu_{2,g}(R_B, P),$$

i.e., from the product of the actual number of gas molecules in all the bubbles, and the re-scaled chemical potential of the gas $[\mu_{2,g}(R_B, P)]$, evaluated at P (not P_B).[2,21,24–27] Thus, both the external pressure and the bubble pressure enter into the evaluation of the gas phase contribution to the total free energy of the composite system. This is consistent with the work in Refs. 21, 24, 26, and 27.

$N_{j,l}(R_B, P)$ is the total number of molecules of type j in the soft material in the final state, and $x_j(in)$, $x_{j,l}(R_B)$ are the mole fractions of j in the initial supersaturated state, and in the soft medium in the composite state, respectively.

The last expression in Eq. (17) for the number of bubbles N_B, was obtained by combining the condition for mass balance for N_2 with the ideal gas law. Additional details are provided in Ref. 2, where its two-component generalization for a nonelastic liquid medium was derived.

Combining the components of Eq. (17) and simplifying gives

$$\Delta G(R_B, P)/NkT = N_B \lfloor 4\pi R_B^2 \gamma$$
$$- (4/3)\pi R_B^3 P \ln(P_B/P) \rfloor/NkT$$
$$+ 6V_2^0 \varepsilon_2 (a_1 - a_2)^2 (1 - \nu^2)/NkT$$
$$+ \sum_{j=1}^{2} x_j(in) \ln[x_{j,l}(R_B)/x_j(in)]. \quad (18)$$

$$\Delta g(R_B, P) \equiv \Delta G(R_B, P)/N_B,$$

$$\Delta g(R_B, P)/kT = \lfloor 6(V_2^0/N_B)\varepsilon_2 (a_1 - a_2)^2 (1 - \nu^2)$$
$$+ 4\pi R_B^2 \gamma - (4/3)\pi R_B^3 P \ln(P_B/P) \rfloor/kT$$
$$+ (N/N_B) \sum_{j=1}^{2} x_j(in) \ln[x_{j,l}(R_B)/x_j(in)].$$
$$(19)$$

In these equations, Eq. (14) is to be used for P_B, ν, a_1, and a_2, the expression for N_B in Eq. (17), together with Eq. (14) for P_B, is to be used for the number of bubbles, Eq. (16) was used for the elastic free energy term in Eq. (18), and $N(=N_1 + N_2)$ is the total number of molecules in the system.

$\Delta G(R_B, P)$ is the (conditional, relative, corrected) Gibbs free energy for the entire compound system of N molecules and N_B bubbles, at external pressure P, given an equilibrium bubble radius R_B. The global minimum over all possible

$\Delta G(R_B, P)$ values provides the most stable state possible for the system. Given sufficient time, the system will end up in this state.

On the other hand, $\Delta g(R_B, P)$ is the (conditional, relative, corrected) Gibbs free energy of the compound system per bubble, at external pressure P, given an equilibrium bubble radius R_B. This function will be used to estimate the radii of small metastable inert gas bubbles in elastic media.

In the derivation of Eqs. (18) and (19), the equality of chemical potentials (which ensures zero net flux of N_2 into or out of the bubbles),[2,21,24–27]

$$\mu_{2,l}(x_{2,l}(R_B), P) = \mu_{2,g}(R_B, P_B),$$

written as

$$\mu_{2,l}(x_{2,l}(R_B), P) = \mu_{2,g}(R_B, P) + kT \ln(P_B/P),$$

was used to obtain the chemical potential difference of the solute in the two phases at P,

$$\Delta \mu_2(R_B, P) \equiv [\mu_{2,g}(R_B, P) - \mu_{2,l}(x_{2,l}(R_B), P)]$$

$$= -kT \ln(P_B/P).$$

The term $\Delta \mu_2(R_B, P)$ arises when the components of Eq. (17) are combined.[2] This is the origin of the $\ln(P_B/P)$ terms in Eqs. (18) and (19), which correct the free energy expressions for the difference between the bubble pressure P_B and the external pressure P (i.e., it is the Frenkel/Abraham correction to these free energy functions). This term lowers the free energy for $P_B > P$, and raises it for $P_B < P$. In the latter case, when $P_B \rightarrow 0$ and $P > 0$, this term raises the free energy boundlessly so that the likelihood of observing such states becomes negligible. Thus, it is solely through this correction term, that negative bubble pressures are thermodynamically precluded. Since negative pressures can arise from the GYL equation, but cannot be sustained in a gas phase, we take this result as a *posteriori* support for the validity of Abraham's postulate 3′. As indicated previously, relatively recent work on nucleation theory[25–27] further supports its validity.

E. Critical bubble radii

The range of possible bubble radii is bounded from below and above, by the lower and upper critical bubble radii, $R_{crit,l}$ and $R_{crit,u}$, respectively. These are the radii of the smallest and largest possible bubbles that can exist, given the system, and the requirements that the bubbles are mechanically stable, and satisfy both mass balance and equality of chemical potentials. They are determined by setting $N_B = 1$ in the expression for N_B in Eq. (17), and numerically finding the two real positive roots of the resulting equation. Additional details are given in Sec. III B.

Both critical radii are system-size-dependent, but for the systems and the range of ε_2's considered here, $R_{crit,l}$ can be estimated conveniently, without iteration, and to about 1 part in 10^4 by using the closed-form infinite-system $R_{crit,l}(\infty)$ in its place an approximation. $R_{crit,l}(\infty)$ is obtained by inverting Eq. (2), and taking the limit $\nu \rightarrow 0$. It is given by

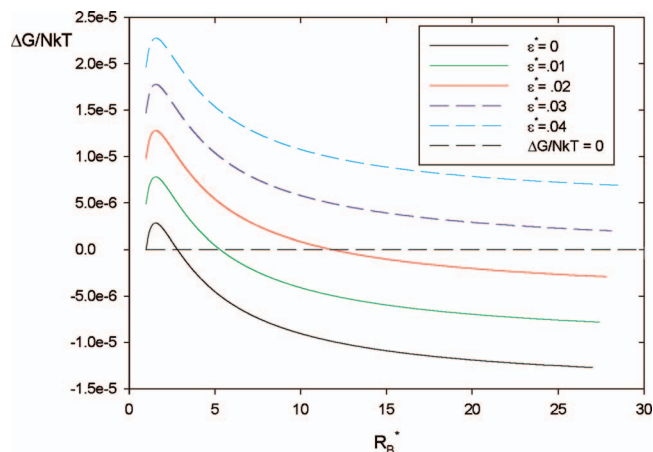$$R_{crit,l}(\infty) = 2\gamma/[P_{in} - P(1 + \alpha_2) + (4\varepsilon_2/3)] \quad (20)$$

or

FIG. 1. Reduced relative system Gibbs free energy as determined from Eq. (18), as a function of the reduced bubble radii ($R_B^* \equiv R_B/R_{crit,l}$), and the reduced shear resistances ($\varepsilon_2^* = \varepsilon_2/P$). All the other parameters and conditions are given in Sec. III A. The curves begin at $R_B^* = 1$, and end at $R_B^* = R_{crti,u}/R_{crit,l}$. See Table I for the values of the critical radii.

$$R_{crit,l}(\infty) \cong 2\gamma/[P_{in} - P + (4\varepsilon_2/3)]. \quad (20')$$

Equation (20′) follows from Eq. (20) since we will have $\alpha_2 < 10^{-4}$.

III. RESULTS

Our results are given graphically in Figs. 1–7, supplemented by Table I. In Ref. 34, we provide error estimates for the calculated free energies and bubble pressures.

A. Parameter choices

The values that were used for the fixed parameters and the conditions were: initial supersaturation ratio $P_{in}/P = 3$, external applied pressure $P = 1$ atm, temperature $T = 298.15$ K, Henry's law constant $K_H = 8.5381 \times 10^4$ atm, initial soft material volume $V_2^0 = 10^6 \mu^3$, λ_2 (Lamé's first parameter) $= 2 \times 10^4$ atm, the surface tension at the soft material/gas bubble interface $\gamma = 70$ dyn/cm
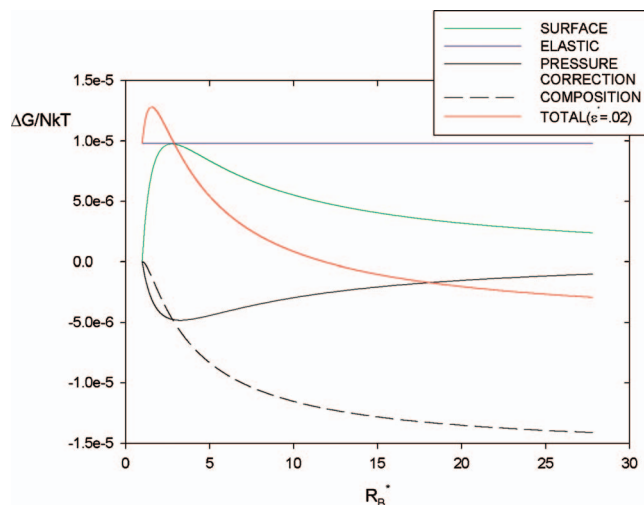

FIG. 2. Components of the reduced relative system Gibbs free energy for $\varepsilon^* = .02$, as determined from the individual terms on the right-hand side of Eq. (18). All the other parameters and conditions are given in Sec. III A.
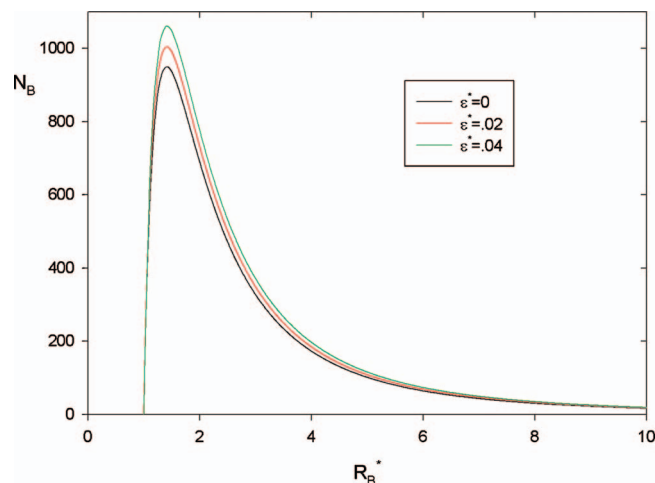
FIG. 3. Number gas of bubbles as determined from Eq. (17), for a range of values of the reduced bubble radius R_B^*, and the reduced shear modulus ε^*. See Sec. III A for the other parameters and conditions, and Ref. 13 for the equations that connect λ_2, K_2, and ε_2.

FIG. 5. Reduced relative Gibbs free energy per bubble as determined from Eq. (19), expressed as a $\beta\Delta g - R_B^* - \varepsilon^*$ surface. Each of the contour lines on the surface represents a fixed value of ε^*. All the other parameters and conditions are given in Sec. III A.

(0.70μ atm). The K_H value is approximately representative of the Henry's law constant for N_2 in water at T =298.15 K[2], the value of γ is close to that for the surface tension of water at this temperature, and the value of λ_2 is roughly representative of Lamé's first parameter for ordinary liquids. The initial mole fraction of N_2 in the one-phase supersaturated medium was $x_2(in) = 3.514 \times 10^{-5}$, and the (constant) total number of moles of both components, $(n_1 + n_2)$ $= 5.5508 \times 10^{-8}$ mol. The molecular weight of water (18.016 g/mol) was used for that of the soft elastic medium.

The calculations were done to elucidate the role of the shear modulus ε_2 on the size and stability of gas bubbles to be expected in elastic media, and so it alone was varied, while all the other independent parameters (λ_2, γ, K_H), and conditions (T, P, P_{in}), were kept fixed at their respective selected values. ε_2 was varied from zero to an upper limit of 0.04 atm. This limit arose from several considerations. Primarily, it was determined from trial calculations, in which it was found that for $\varepsilon_2 = 0.02$ atm (and the above values of the
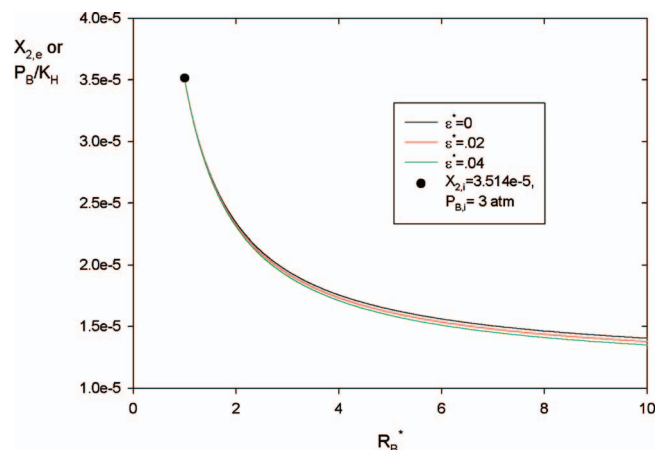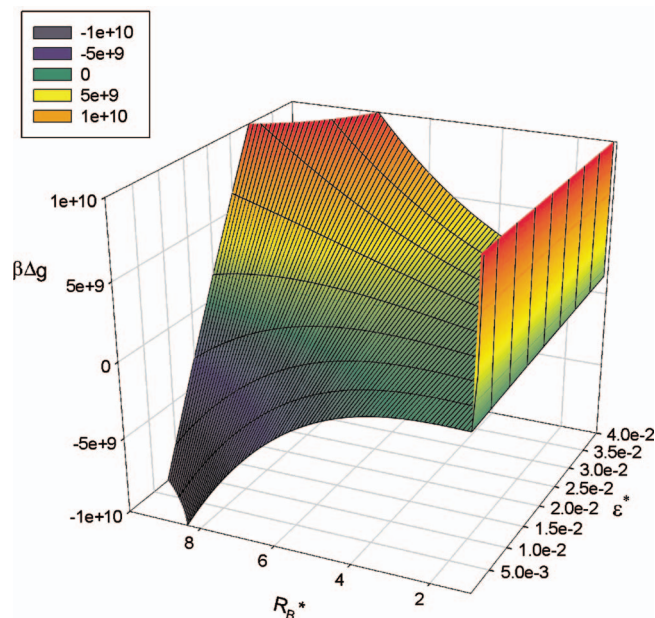
other parameters and conditions), the effect of shear resistance on the free energy functions is comparable to the effect of surface tension, for a waterlike γ of 70 dyn/cm. This was the main factor influencing the range selected for ε_2. Second, though very few measurements of ε_2 exist, its values for some soft elastic materials have been found to be in the range $\approx 1-10$ atm.[35-37] However, as shown in Ref. 34, the uncertainty in the calculated value of $\beta\Delta g$ rises sharply with increasing ε_2. Since the function $\beta\Delta g$ is central to this work, we did not want to risk making a significant error in it. So as a compromise between the desire for generality on the one hand, and caution on the other, our calculations were re-

FIG. 4. Variation of the mole fraction of dissolved N_2 in the medium $(= P_B/K_H)$ for a range of values of the reduced bubble radius and reduced shear resistances. All the other parameters and conditions are given in Sec. III A.
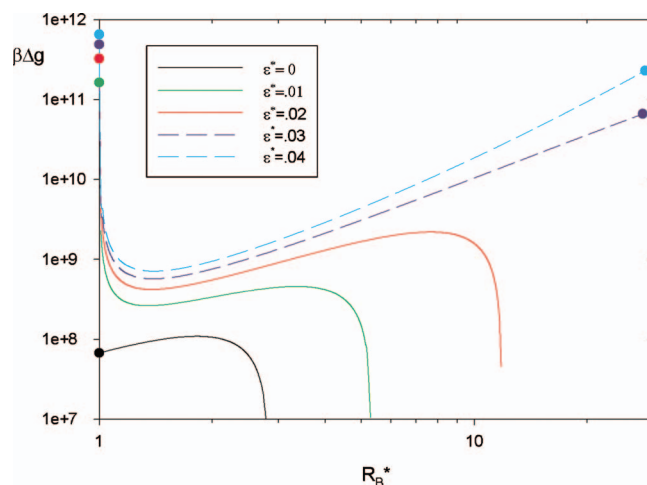

FIG. 6. Selected cuts through the surface in Fig. 5, using a log-log scale. The terminal points shown on the left and right are at the lower and upper critical radii, respectively, for the corresponding plot. The values of these critical radii, and corresponding critical $\beta\Delta g$ values, are entered in Table I. The $R_{crti,u}$ terminal points for $\varepsilon^*=0$, .01, and .02, which here cannot be shown because $\beta\Delta g < 0$, are given in Table I. All the other parameters and conditions are given in Sec. III A.
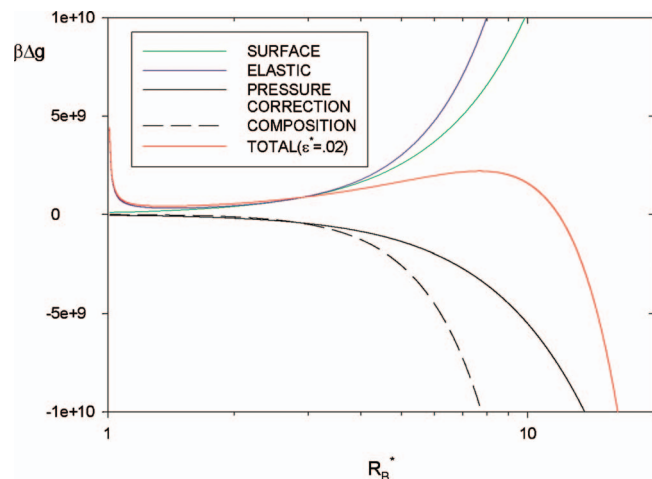
FIG. 7. Components of $\beta\Delta g$ for $\varepsilon^*=.02$, as determined from the individual terms on the right-hand side of Eq. (19). All the other parameters and conditions are given in Sec. III A.

stricted to the range 0 atm $\leqslant \varepsilon_2 \leqslant .04$ atm. As shown in Ref. 34, the uncertainty in the calculated $\beta\Delta g$ values was probably less than 1%, and almost certainly less than 2%, provided $\varepsilon_2 \leqslant .04$ atm.

We assume that Henry's law constant (K_H), Lamé's first parameter (λ_2), and the surface tension (γ) are the same for all the model materials, that the solute concentration in the soft medium is sufficiently low so that Henry's law applies, and that the solute does not influence the characteristic parameters ($\lambda_2, \varepsilon_2, \gamma$) of the soft material. Since the dissolved solute mole fraction $x_{2,l}(R_B)$ will be $\approx 10^{-5}$, last approximation should be essentially exact.

B. Calculations

The calculations are done by using three independent equations to numerically solve for three designated primary unknowns. The values of the other dependent unknowns, here (ν, a_2, R_0, R_S), follow from their relations to the primary unknowns. The latter relations are given by Eqs. (4), (5), (14), and (17). The independent equations are those that ensure mechanical stability of the bubbles [i.e. the expression for P_B given in Eq. (14)], equality of chemical potentials [or equivalently, $P_H \equiv P_{N_2} = K_H x_{2,e}$], which ensures zero net flux of N_2 into or out of the bubbles, and the mass balance con-

TABLE I. The reduced relative Gibbs free energy per bubble at the lower and upper critical bubble radii for the shear modulus values considered in this work. The critical radii were obtained as described in the text (Secs. II E and III B). The values for $\beta\Delta g$ were determined from Eq. (19). The underlying parameters and conditions are given in Sec. III A.

ε_2 (atm)	$R_{crit,l}(\mu)$	$\beta\Delta g \times 10^{-12}$	$R_{crit,u}(\mu)$	$\beta\Delta g \times 10^{-12}$
0	0.7000	0.673×10^{-4}	19.0	−0.425
0.01	0.6955	0.164	19.1	−0.262
0.02	0.6909	0.328	19.2	−0.0976
0.03	0.6864	0.492	19.3	+0.0662
0.04	0.6819	0.657	19.4	+0.230

dition for N_2 [which is contained in, and is equivalent to, the expression for the number of bubbles N_B given by Eq. (17)].

The set of primary unknowns to be determined depends on the calculation being done. When the critical radii are being determined, $N_B=1$ by definition, and the primary unknowns were taken as ($R_B, x_{2,e}, P_B$). When the free energies are being determined, R_B is known, having been set to any desired value greater than $R_{crit,l}$, and the primary unknowns were taken as ($N_B, x_{2,e}, P_B$).

The computational scheme described below was used for all the reported results. It is efficient, and never fails to provide a correct solution to any desired degree of accuracy.

1. Determination of $R_{crit,l}$ (the lower critical radius)

A value for $R_{crit,l}$ is needed initially. One either accepts an approximate value using Eq (20) or (20′), or improves on these values by taking into account the system's finite size. We briefly indicate below how an accurate value of $R_{crit,l}$ is determined, based on the system's finite size.

We seek a value of R_B that satisfies $P_H - P_B = 0$ for $N_B = 1$. Here P_H is the Henry's law-based pressure after formation of the smaller critical bubble $[=K_H x_{2l}(R_{crit,l})]$, P_B is the mechanically stable bubble pressure given by Eq. (14) with $N_B=1$. Any convenient root-finding scheme can be used. "Bisection"[33] was used here, both because it is convenient, and because, while some other root-finding methods are faster, Bisection never fails when properly implemented. Starting lower and upper brackets for the root are needed. For the finite system $R_{crit,l}$, these were taken as $2\gamma/[P_{in}-P+(4\varepsilon_2/3)]$ and $2\gamma/[P_{in}-P]$, respectively, though other brackets are possible. For each trial value of $R_{crit,l}$, which is prescribed by the Bisection routine, the corresponding trial values of both a_2 and ν are needed. There are at least two ways of getting their values. One way is simply to iterate them to convergence, using their respective expressions given in Eq. (14), and setting $N_B=1$. Because it will turn out that a_2 is small $[a_2=O(-10^{-5})]$, a small number of iterations (three to five), starting with $a_2=0$, are sufficient. Another way is to equate the right-hand sides of the expression for a_2 in Eqs. (14) and (21), and to then solve the resulting quadratic equation for ν, taking the physically relevant root (the root between 0 and 1).

$$a_2 = [C - \nu(C + V_2^0)]/3\nu V_2^0,$$

$$C = (4\pi/3)N_B R_B^3; \quad a_1 = -1/3. \quad (21)$$

Equation (21) is obtained by inverting the equation for ν in Eq. (14). Both routes provide the identical trial values of these functions at the trial $R_{crit,l}$. From these functions, the expression for P_B in Eq. (14), $N_B=1$, and the ideal gas law, the number of moles of gas in the critical bubble is obtained. From this and mass balance, one obtains the mole fraction of dissolved gas at this trial $R_{crit,l}$, and subsequently P_H, and $P_H - P_B$. The cycle over the improving $R_{crit,l}$ values is continued until the desired degree of accuracy is obtained. While the $R_{crit,l}$ values we used were obtained in this way, they differ from $R_{crit,l}(\infty)$ by only about 1 part in 10^4.

2. Determination of the free energies, the number of bubbles, and the bubble pressure

Once $R_{crit,l}$ is determined, the evaluation of $P_B(R_B)$, $\Delta G(R_B)$, and $\Delta g(R_B)$, using Eqs. (14), (18), and (19), for $R_B > R_{crit,l}$ can be completed. This calculation is carried out somewhat differently from that for $R_{crit,l}$, because in the latter calculation N_B was known ($=1$) and R_B was unknown, and now R_B is known (it is set equal to any value greater than $R_{crit,l}$), and N_B is unknown. In this calculation, for each selected value of $R_B > R_{crit,l}$, we again use a numerical routine (Bisection) to determine the solute mole fraction in the medium, $x_{2,l}(R_B)$, at the selected R_B. Convenient upper and lower brackets for $x_{2,l}(R_B)$, valid for all radii, are $x_2(in)$ and zero, respectively. Given a value of R_B and a trial value of $x_{2,l}(R_B)$ which is prescribed by the Bisection routine, the corresponding trial value of $P_H(R_B)$ is determined from Henry's law ($P_H(R_B) = K_H x_{2,l}(R_B)$), and the corresponding trial value of $N_B(R_B)$ is determined from its expression in Eq. (17), with $P_H(R_B)$ used for the bubble pressure. As with the calculation for $R_{crit,l}$, the corresponding trial values of a_2 and ν can be determined either by iterating these variables to convergence, or by eliminating a_2 between Eqs. (14) and (21), and solving the resulting quadratic equation for ν. Thus, at each selected value of R_B, and trial value for $x_{2,l}(R_B)$, trial values for $P_H[=K_H x_{2,l}(R_B)]$, P_B [from Eq. (14)], and consequently $P_H - P_B$, are determined. As with the $R_{crit,l}$ calculation, the cycle of calculations over the progressively improving values of $x_{2,l}(R_B)$ is continued until the desired accuracy is reached. The final values of the variables: $x_{1,l}(R_B)$, $x_{2,l}(R_B)$, $N_B(R_B)$, $P_B(R_B)$, $a_2(R_B)$, and $\nu(R_B)$, are used in Eqs. (18) and (19) to determine these free energy functions at the selected value of R_B.

3. Determination of $R_{crit,u}$ (the upper critical radius)

The above calculation is repeated, using progressively larger values of R_B, until the value of $N_B(R_B)$ falls below 1. The upper critical radius $R_{crit,u}$ is then determined by numerically interpolating to that value of R_B in the large R_B regime, for which $N_B(R_B) = 1$.

C. Values of free energies of bubble formation and bubble densities

The variation of ΔG with R_B is illustrated in Fig. 1, from which it is seen that for $\varepsilon_2 \cong .025$ atm or greater, $\Delta G > 0$ for all R_B values. Therefore under these conditions the one-phase homogeneous state is more stable in the long-time thermodynamic limit, than any bubble-containing compound state that can form. Physically, this occurs because for $\varepsilon_2 \cong .025$ atm or greater, the combined positive surface and shear resistance free energy terms outweigh the negative pressure correction and composition terms at all possible radii [see Eq. (18)]. On the other hand, for $\varepsilon_2 \cong .025$ atm or smaller, one can expect thermodynamically stable composite bubble states to form, given sufficient time. For these systems, the right-most terminal point of each of the plots in Fig. 1 is the global minimum of the corresponding plot and is the most stable state that can exist. In this respect, soft elastic materials from which stable bubbles can form behave like simple liquids, i.e., for both, the largest possible single bubble state, which occurs at the upper critical radius $R_{crit,u}$, is the most stable state possible for the system. These terminal points at $R_{crit,u}$ have been studied experimentally for a N_2 bubble in water.[38] For this system our equations, when applied in the $\varepsilon_2 \rightarrow 0$ limit, correctly predicted the observed $R_{crit,u}$ values.[2,38]

The contributions of the components of $\Delta G/NkT$ are shown for the $\varepsilon_2 = .02$ atm plot in Fig. 2 from which it is seen that the shape of the $\Delta G/NkT$ curves is determined by the surface tension, pressure correction, and composition contributions, while the elastic term, which is almost constant, simply shifts the curves upward by an almost constant amount. From Eqs. (16′) and (16″), respectively, the upward shift is given to a good approximation by $(2/3)V_2^0 \varepsilon_2 (1 - \nu^2)/NkT$ or a little less accurately by $(2/3)V_2^0 \varepsilon_2/NkT$. The last expression follows because here $\nu \lesssim .03$. Also, for a given ε_2, ν in all these systems increases monotonically with R_B. For example, for $\varepsilon_2 = .04$ atm, ν increased monotonically from $\cong 1.3 \times 10^{-6}$ at $R_{crit,l}$, to $\cong 3 \times 10^{-2}$ at $R_{crit,u}$.

In Fig. 3, we show plots of the numbers of bubbles N_B for $0 \leq \varepsilon_2 \leq 0.04$, that satisfy the equilibrium requirements and mass balance, as a function of bubble radius R_B, and Fig. 4 is used to physically account for the plots in Fig. 3. Since the total number of molecules (N) is fixed, the number of bubbles is proportional to the bubble number density (N_B/N). The steep rise in N_B shown in Fig. 3, just beyond the lower critical radii, can be understood from a combination of mass balance, equality of chemical potentials, and mechanical effects. Specifically, the initial rapid fall in the bubble pressure P_B with R_B in this region, which is shown in Fig. 4, is mechanically based. It is due to the rapidly falling surface tension term $2\gamma/R_B$ in Eq. (14). Because $x_{2,l}(R_B)$ must remain proportional to P_B for the equality of chemical potentials to be maintained (or equivalently, $x_{2,l}(R_B) = P_B/K_H$), there must also be a correspondingly rapid and proportional fall in the dissolved solute mole fraction $x_{2,l}(R_B)$ in this region. This is also shown in Fig. 4. Because mass balance must be satisfied at all points, a rapid drop in $x_{2,l}(R_B)$ means that the amount of N_2 transferred to the gas phase must rise rapidly in this region. Since the bubbles in this region are small, this can occur only by a rapid increase in the numbers of bubbles.

The relative ordering of the curves in Fig. 3 follows from this as well. Since increasing the shear modulus reduces the bubble pressure at a given radius, (see Fig. 4), the initial rise in the numbers of bubbles must be more pronounced, the greater the shear modulus. The fall in N_B with R_B at large R_B can be understood from the combined effects of the cubic increase in the bubble volume with R_B, and the slowed rate of the fall in P_B and $x_{2,l}(R_B)$ with increasing R_B at large R_B (see Fig. 4). The combination of these small-R_B and large-R_B effects accounts for the asymmetry of the N_B versus R_B plots in Fig. 3.

$\beta \Delta g$ ($\beta \equiv 1/kT$, where k is Boltzmann's constant), which is obtained from Eq. (19), is shown in Figs. 5–7, in the form of a $\beta \Delta g - \varepsilon^* - R_B^*$ surface, constant ε^* cuts through this surface, and the component contributions to one of these cuts, respectively. Before considering the details, it is worth

pointing out in a general way why $\beta\Delta g$ takes the form it does. It is obtained from $\beta\Delta G(R_B)/N_B(R_B)$, where the numerator varies only moderately over the range of R_B (Fig. 1), while the denominator spans some three orders of magnitude, peaking sharply and asymmetrically at small R_B (Fig. 3). Therefore, as $R_B{}^*$ increases beyond unity, and the numbers of bubbles rises to maximum and then falls, the free energy per bubble, must fall to a minimum, and then rise. Consequently $\beta\Delta g$ is expected to go through a nonparabolic minimum at small R_B values that corresponds approximately to the value of R_B at which N_B peaks.

The surface in Fig. 5 shows the wells as a valley that runs along the base of the steep inner wall. The valley floor rises slowly as ε^* increases, and the inner wall remains steep at all $\varepsilon^*>0$. The outer wall gradually gets higher and extends to greater distances with increasing ε^*. When ε^* increases beyond about.025, the outer wall no longer turns down, but terminates at a $R_{\text{crit},u}$ value for which $\beta\Delta g>0$.

It is seen from Fig. 6 that for $\varepsilon^*>0$, the minima in these free energy wells all occur slightly beyond $R_{\text{crit},l}$. The wells shown are of two types: those at the lower ε^* values in which the well leads to a barrier and subsequently a stable bubble, and those at the higher ε^* values that involve a well only. For the latter, the most stable state possible is the initial one-phase homogeneous state. A bubble in either type of well will be both mechanically stable and thermodynamically metastable (because $\Delta G>0$), so that in either case a bubble in the well can be expected to have a degree of longevity.

The free energy plot in Fig. 6 for $\varepsilon_2{}^*=.02$ is deconstructed into its contributing components in Fig. 7. It is seen from this figure that the steep inner wall of the well is due entirely to the elastic contribution to $\beta\Delta g$, while the outer wall has contributions both from the elastic and surface tension terms. The elastic contribution to $\beta\Delta g$, given by the blue curve in Fig. 7, is given by the first term on the right-hand side of Eq. (19). The behavior of this term is governed by the harsh variation of N_B in this region (see Fig. 3). "The physics" is that the maximum in N_B causes a minimum in the undistorted volume of elastic material associated with the bubble ($V_2{}^0/N_B$), which results in a minimum in the local elastic free energy [see Eq. (15)]. For $R_B{}^*\approx10$ the contributions from the pressure correction and composition terms which are negative, begin to outweigh the positive surface and elastic terms, causing $\beta\Delta g$ to turn negative. The full $\beta\Delta g$ curve (shown in red), terminates at the thermodynamically stable bubble radius $R_{\text{crit},u}\cong19.2\mu$, for which $\beta\Delta g\cong-9.8\times10^{10}$ (see Table I).

The meaning and physical significance of these $\beta\Delta g$ plots are central to this work. Depending on whether it is positive or negative, Δg represents the free energy cost or gain per bubble, respectively, to create a composite state of $N_B(R_B)$ bubbles from the initial supersaturated state. Equivalently, Δg also represents the reversible work associated with the creation of one gas bubble of radius R_B from the initial supersaturated state. The bubble is one of the $N_B(R_B)$ bubbles in the composite state.

For definiteness, consider first the $\varepsilon^*=.02$ plot shown in red in Fig. 6. A bubble in the well shown in this plot will

have a half-life that exceeds what it would be in a nonelastic material wherein stabilizing meta-stable wells do not form. A bubble represented by this plot will grow, given sufficient time, because of the combined effects of fluctuations and the tendency of the system to reach its global minimum free energy.[39] The driving force for bubble growth here is reduction of the supersaturation in the medium, and the resultant reduction in the system free energy. This occurs by a reduction the chemical potential of N_2 in both phases of the system as the bubble grows.[39] However, a bubble at or near the bottom of the well (at $R_B\cong1\mu$), will be delayed from leaving the well, because of the free energy (or reversible work) required to leave. Growth to $R_{\text{crit},u}$ cannot occur without the bubble first acquiring the free energy needed to rise from $\beta\Delta g(\min)$ to $\beta\Delta g(\max)$. $\beta\Delta g^*[\beta(\Delta g(\max)-\Delta g(\min))]$ enters as a negative exponential $[\exp(-\beta\Delta g^*)]$ in the TST expression for the rate constant for going over a barrier.[19,22,23] A single large step or a series of concerted smaller steps would be needed for the bubble to get to the barrier top. A "step" here refers to a set of coupled fluctuations. Since these are relatively rare (large fluctuations in systems with large numbers of particles are rare[18,22]), the bubble's growth will be delayed.

Conversely, a bubble represented by the dashed plots in Fig. 6 ($\varepsilon^*=.03$ or $\varepsilon^*=.04$) will, given sufficient time, shrink to its lower critical bubble radius, with an increase both in the bubble pressure and the chemical potentials in the phases, and ultimately dissolve. This is because for these systems the initial dissolved state, for which $\Delta G=0$, is the most stable system state possible. The degree of supersaturation is (in these systems) insufficient to overcome the combined surface and elastic free energy requirements. However, as with a small metastable bubble which ultimately grows to a larger stable bubble, here too there will be a delay in getting to the minimum global free energy state, because of the inner wall to be climbed in shrinking to the lower critical radius. The inner wall is due entirely to the local elastic free energy. As indicated previously, the volume of the medium that a bubble acts upon, and therefore the local elastic free energy, is a minimum in the vicinity of the N_B maximum, or the $\beta\Delta g$ minimum.

In principle, the curvature (second derivative) of $\beta\Delta g$ in the vicinity of the minimum can be used to provide information on the frequency with which the metastable bubble oscillates between smaller and larger radii while residing in the well.[19] It is also noteworthy that, in the region of the well minima, the bubble number density (N_B/N) is some three orders of magnitude greater than in any stable composite state, where it is $(1/N)$ (see Fig. 3). Consequently, fairly large numbers of small bubbles with some degree of longevity would be expected to form in a soft elastic materials with these characteristics.

This behavior differs significantly from what is found for gaseous dissolution from simple liquids, which is illustrated by the solid black curve in Fig. 6. This curve has no well, because it has no inner wall, the existence of which requires the material to have a nonzero shear modulus (see Fig. 7). This curve shows that a critical bubble with radius $R_{\text{crit},l}$, once formed from gas-like embryonic precursors, can do

only one of two things: (1) it may acquire sufficient free energy to get over the barrier and form a stable bubble (by one large step, or by a series of smaller concerted steps) or (2) it may dissolve as a consequence of a negative volume fluctuation. Here, because there is no elastic free energy barrier to slow it down, dissolving would be rapid. Therefore a critical bubble formed in a simple liquid would be expected to have a short half-life, relative to one formed in an elastic medium with a positive shear modulus.

IV. DISCUSSION

Our results may be relevant to the solution of a decades-old puzzle in the field of DCS: the apparent existence of long-lived, small, inert gas bubbles in some tissues of the body. Here, we outline the puzzle, we review an earlier idea for its solution, and we compare our work with the earlier work.

A significant body of evidence suggests that, in many if not all instances, DCS arises from the growth of pre-existing gas bubbles in tissues of the body, following overly rapid decompression.[3,4,40] An alternative possibility—*de nuovo* bubble formation by homogeneous gas bubble nucleation—is not believed to be a significant causal mechanism in DCS because of the very large activation energies involved.[2,41] Put another way, very large supersaturation levels, well beyond what is usually sufficient to cause DCS, would be needed for homogeneous gas bubble nucleation to occur at a significant rate.[2,40,41] If, however, DCS can result from the growth of pre-existing gas bubbles, these pre-existing bubbles must have been sufficiently stable to have had non-negligible half-lives. It is here that the *pièce-de-résistance* arises. Assuming air is the gas being breathed, these bubbles will consist mostly of N_2 since most of the O_2 will have been consumed by metabolism.[3,4] Therefore, for a person equilibrated at 1 atm, the N_2 partial pressure in a bubble will, in the absence of surface tension effects, be approximately 0.75 atm. This value derives from the requirement that the chemical potentials of N_2 in a stable bubble and in the circulatory system be equal. (Because of traces of other gases, the total pressure in the bubble will be slightly higher than this, approximately 0.77 atm.[42–44]) However, on the basis of the YL equation, such a bubble simply could not exist because the mechanical pressure acting on it ($P + 2\gamma/R_B$) would, in the absence of surface tension effects, be 1 atm, i.e., significantly greater than 0.77 atm. How to reconcile the requirements of mechanical stability and equality of chemical potentials in a way that would allow for the existence of small long-lived gas bubbles is the puzzle.

There is a pre-existing body of work, published in the applied literature, wherein it was attempted to resolve this dilemma. The suggestion that received the most attention was put forward by Yount and co-workers.[45–49] These workers suggested that surfactant molecules may exist in the body which, by adsorbing to the bubble/condensed phase interface, form a protective skin around the gas bubble, thereby preventing its collapse. The hydrophyllic polar head-group and the hydrophobic hydrocarbon tail of the putative surfactant were pictured as being, in the aqueous-like condensed

phase and inside the bubble, respectively. The idea was, that because of polar head-group mutual repulsions, the adsorbed surfactant would reduce the effect of surface tension term in the YL equation, thereby reducing the pressure by which the medium acts on the bubble. Yount and co-workers[45–49] and later Weinke[50,51] used this basic idea, and variants of it,[46,50,51] to develop models for predicting ostensibly improved (i.e., safer) decompression protocols relative to those previously available. An underlying assumption in these applications is that the surfactant-stabilized bubbles exist as long-lived gaseous seeds, which can expand during rapid decompressions, possibly leading to the development of DCS.[45–51]

Problems arose with the Yount/Weinke theory. First, Vann pointed out that, in the thirty-odd years since the idea was proposed, not one specific surfactant that exists in any tissue(s) of the body, and that acts in this way, has been identified.[4] Second, Gaskins *et al.*[52] carried out a series of experiments to determine the influence of known surfactants on the extent of bubble formation subsequent to the decompression of water-gelatin solutions containing dissolved N_2. These workers found known surfactants to effect decompression-induced bubble formation in a direction opposite to what is predicted by this surfactant-based theory. Specifically, as the surfactant concentration was increased, the increase in extent of bubble formation subsequent to decompression that surfactant theory would have predicted was not found. Instead, a reduction in bubble formation was found. Notwithstanding these serious concerns, the theory, the models, and decompression protocols based on them continued unabated.

A more basic problem with the surfactant theory and its variants[45–51] is the underlying tacit assumption that mechanical stability somehow ensured the existence of long-lived, small, gaseous bubbles in condensed media. This assumption has no scientific basis whatsoever. Mechanical stability is a necessary but insufficient condition for long-term stability. It is certainly true, that in the absence of mechanical stability, bubbles cannot exist for any appreciable length of time. But in order for a bubble to be sufficiently long-lived for it to act as a nucleation seed for bubble growth in some future decompression, it must be both mechanically stable and thermodynamically stable or metastable. Thermodynamic stability and/or metastability of gaseous bubbles in condensed media were not considered in this pre-existing work.

The work in this paper provides a new and more viable resolution to the puzzle. The difficulty of simultaneously satisfying mechanical stability and equality of chemical potentials can be resolved by using a soft elastic material with a non-zero shear modulus, rather than a simple liquid with a surface tension, as a model for tissues of the body. In so doing, the relevant pressure equation becomes the GYL equation, not the YL equation. The salient difference lies in the second term in Eqs. (2) and (3), which is negative. This term lowers the total pressure acting on the bubble, relative to the YL-predicted pressure. As shown in Ref. 1, and can be readily verified by Eqs. (2) or (3), provided the gas bubble is $\approx 1\mu$ in radius, the surface tension is $\approx 10–70$ dyn/cm, and the shear modulus is ≈ 1 atm, the pressure of the medium acting on the bubble surface can readily be 0.77 atm, when

the external pressure is 1 atm. Consequently, it is possible for such a bubble to simultaneously be mechanically stable and satisfy the requirement of equality of chemical potentials of N_2. Moreover, variations in the values of the parameters that characterize the medium, particularly the shear modulus and the surface tension, will create a range of possible properties and bubble radii, all of which are consistent with maintaining a pressure on the bubble of about 0.77 atm when the external pressure is 1 atm. In other words, our results are consistent with the possibility that bubbles with some degree of longevity exist in a variety of tissues of the body, so that different forms of DCS may potentially arise when these bubbles expand.

The expressions derived here and in Ref. 1 show that small, inert gas bubbles, embedded in soft elastic materials that have a nonzero shear modulus, can be both mechanically stable and thermodynamically metastable. There is no need to invoke elusive and nonspecific stabilizing agents that putatively form protective skins around bubbles, or other nebulous concepts. Rather, it is here suggested that tissue elasticity, which is ubiquitous, may be the physical basis for the existence of small inert gas bubbles with non-negligible half-lives in some tissues of the body. If such bubbles exist, they may act as nucleation seeds for bubble growth following a decompression.

We conclude with a speculative comment on why "some degree of longevity" may be sufficient to ensure an essentially continuous supply of small metastable bubbles in some tissues of the body. Consider two surfaces in adhesive contact with one another that are immersed in a gas-saturated solution. "Tribonucleation" refers to the phenomenon whereby the rapid separation of these surfaces from one another results in the formation of new gas bubbles in the solution.[3,4,53–55] The physical explanation is that rapid separation of mutually attracting surfaces results in momentary negative pressures in the solution where the surfaces separated. This produces some gas dissolution. Physical exercise while super-saturated with N_2 (for example, immediately after surfacing from a scuba dive) is known to increase the likelihood of incurring DCS, and tribonucleation has been suggested as a possible explanation.[3,4] The body is not static, and tissues within it may not be isolated from effects such as tribonucleation. Therefore, while any one meta-stable bubble cannot—by definition—last indefinitely, a very long half-life may not be necessary for the long-term continuing existence of small bubbles in tissues. If those small meta-stable bubbles that are lost because of their finite half-life are replaced periodically by *in vivo* tribonucleation, something akin to a steady-state may exist. According to this picture, tribonucleation would be the source, and finite half-lives the sink, for the generation and loss, respectively, of small bubbles. Based on this paradigm, the long-term presence of small gaseous bubbles in tissues becomes plausible.

ACKNOWLEDGMENTS

[1] S. Goldman, J. Chem. Phys. **131**, 184502 (2009).

[2] S. Goldman, J. Phys. Chem. B **112**, 16701 (2008).

[3] R. D. Vann, in *Bove and Davis' Diving Medicine*, 2nd ed., edited by A. A. Bove and J. C. Davis (Saunders, Philadelphia, PA, 1990), Chap. 4.

[4] R. D. Vann, in *Bove and Davis' Diving Medicine*, 4th ed., edited by A. A. Bove (Saunders, Philadelphia, PA, 2004), Chaps. 4 and 7.

[5] M. B. Strauss, S. S. Miller, A. J. Lewis, J. E. Bozanic, and I. V. Aksenov, Undersea Hyperbaric Med. **35**, 241 (2008).

[6] B. A. Hills, *Decompression Sickness* (Wiley, New York, 1977), Vol. 1, Chaps. 2 and 3.

[7] B. A. Hills and B. P. James, Undersea Biomed. Res. **9**, 185 (1982).

[8] M. P. Spencer, J. Appl. Physiol. **40**, 229 (1976).

[9] R. Y. Nishi, A. O. Brubakk, O. S. Eftedal, in *Bennett and Elliott's Physiology and Medicine of Diving*, 5th ed., edited by A. O. Brubakk and T. S. Neuman (Saunders, Edinburgh, 2003), Chap. 10.3.

[10] E. A. Guggenheim, *Thermodynamics: An Advanced Treatment for Chemists and Physicists* (North-Holland Physics, Amsterdam, The Netherlands, 1967), Chap. 1.

[11] L. D. Landua and E. M. Lifshits, *Theory of Elasticity* (Pergamon, Oxford, 1959), Chap. 1.

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

[13] The modulus of hydrostatic compression (or the modulus of compression) K, the modulus of rigidity (or the shear modulus) ε, Young's modulus E, and Poisson's ratio χ, are related as follows (Refs. 11 and 12):$E = 2\varepsilon(1+\chi) = 3K(1-2\chi)$. Poisson's ratio is defined as the ratio of transverse compression to longitudinal extension and is one of a number of measures of stiffness or rigidity for an isotropic material. E and ε are also measures of stiffness of an isotropic material, and K, ε, and λ are related by $K = \lambda + (2\varepsilon/3)$ which provide the definition of λ. λ and ε, sometimes called Lamé's first and second parameters, 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 $E = \varepsilon = 0$, the elastic characteristics of nonrigid fluids (that resist compression but not shear) are recovered. This limit, in which χ is exactly 0.5, is also known as the "isotropic upper limit of χ." Our interest here is in materials for which $\varepsilon/K \approx 10^{-6}$, or equivalently, $\varepsilon \cong E/3$. For such materials, χ is very slightly less than 0.5.

[14] I. M. Lifshits and V. V. Slyosov, J. Phys. Chem. Solids **19**, 35 (1961).

[15] M. A. Fradkin, J. Phys.: Condens. Matter **9**, 7925 (1997).

[16] Here we provide a slightly different physical basis for deriving Eq. (11). It involves using the approximation that results from setting $u_{rr}^{(2)}(R_0)$ equal to a_2 (rather than to zero). $u_{rr}^{(2)}(r) = a_2 = -P/3K_2$ for an isotropic material under hydrostatic compression, where $N_B = 0$ (Ref. 1). Also, $u_{rr}^{(2)}(\infty) = a_2$ for an isotropic material subjected to a nonhydrostatic compression for $N_B = 1$. In this case, a_2 is obtained from the expression for it given with Eq. (2). Using either of these expressions, it is found for $0 \leq N_B \leq 1$ (and for the materials of interest here), that $a_2 = O(-10^{-5})$. Since a_2 is small relative to 1, both for $N_B = 0$ and $N_B = 1$, we assume that for $N_B > 1$ we will also have $a_2 \approx O(-10^{-5})$, so that $u_{rr}^{(2)}(R_0) \cong a_2 \approx O(-10^{-5})$. We will restrict ε_2 to $\varepsilon_2 \leq .04$ atm, and P will always be 1 atm. Substituting these values for $u_{rr}^{(2)}(R_0)$, ε_2, and P into Eq. (13) gives Eq. (11).

[17] For one bubble in the system R_0 and R_S are identical, and the symbol R_0 was used for the system radius in Ref. 1. In this work, where $N_B \geq 1$, both symbols are needed to distinguish the domain and the system radii, R_0 and R_S, respectively.

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

[19] D. A. McQaurrie and J. Simon, *Physical Chemistry: A Molecular Approach* (University Science Books, Sausalito, California, 1997), Chap. 24.

[20] J. W. Gibbs, Trans. Conn. Acad. Arts Sci. **3**, 343 (1878); *Collected Works*, Vol. 1, (Yale University Press, New Haven, 1948).

[21] I. I. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955), Chap. 7, pp. 164–166.

[22] T. L. Hill, *An Introduction To Statistical Thermodynamics* (Addison-Wesley, Reading, MA, 1960), Chap. 11.

[23] D. G. Truhlar, B. C. Garrett and S. J. Klippenstein, J. Phys. Chem. **100**, 12771 (1996).

[24] F. F. Abraham, *Homogeneous Nucleation Theory. Advances in Theoretical Chemistry. Supplement 1*, edited by H. Eyring and D. Henderson, (Academic, New York, 1974). Chaps. 2 and 5.

[25] Both Debenedetti and Tester and Modell (Refs. 26 and 27 below), whose work is more recent than that in Refs. 21 or 24, use expressions that are equivalent to those used here [and in Refs. 21 and 24], to determine the free energy of a heterogeneous (or compound) system wherein the pressure of the inner phase differs from the external pressure. They also use the same stability criterion as was used here [and in Refs. 21 and 24], for purposes of determining the composition of the system. The external pressure (P) is used to evaluate the underlying chemical potentials in both the external and the inner phases. Also, the same stability criterion was used in this work, as in Refs. 21, 24, 26, and 27. This is needed to determine the composition of the condensed phase, and the actual number of molecules of solute in the bubbles. In our notation [see the equation in the text under Eq. (19)] it is $\mu_{2,l}(x_{2,l}(R_B), P) = \mu_{2,g}(R_B, P_B)$. Therefore, both for the stability criterion, where the actual pressures of the phases are used, and in the chemical potential determination, where the external pressure is used for both phases, the equivalent thermodynamic expressions were applied here, as in Refs. 21, 24, 26, and 27. However, Reiss, whose work on the subject was published both before and after Abraham's work (see Refs. 28 and 30, respectively) believed this stability criterion was inaccurate, and provided a different one for use in these and related problems. Its general form is given by Eq. (11.32) of Ref. 28, and it is written out more explicitly for some specific examples in Ref. 30. However, it was subsequently shown by Wilemsky that Reiss' stability criterion lead to inconsistencies (see Refs. 31 and 32, below), and Debenedetti concluded that Reiss' stability criterion was in fact incorrect (see Ref. 26, Appendix 2). Debenedetti traced the error in Reiss' stability criterion to his use of an approximate equation as the starting point in his derivation (see Ref. 26, pp. 385 and 386).

[26] P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, NJ, 1996), Chap. 3 and Appendix 2, particularly Sec. A.2.3.

[27] J. W. Tester and M. Modell, *Thermodynamics and Its Applications*, 3rd ed. (Prentice Hall, Englewood Cliffs, NJ, 1997), Chap. 19, particularly Eqs. (19-8), (19-19), and associated text.

[28] H. Reiss, *Methods of Thermodynamics* (Blaisdell, New York, 1965).

[29] H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

[30] H. Reiss and M. Shugard, J. Chem. Phys. **65**, 5280 (1976).

[31] G. Wilemsky, J. Chem. Phys. **80**, 1370 (1984).

[32] G. Wilemsky, J. Phys. Chem. **91**, 2492 (1987).

[33] W. H. Press, P. B. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes: The Art of Scientific Computing (FORTRAN Version)* (Cambridge University Press, Cambridge, 1989), p. 246.

[34] See supplementary material at http://dx.doi.org/10.1063/1.3394940 for the uncertainty estimates for the functions P_B, ΔG_{elas}, and Δg_{elas}.

[35] A. N. Gent and D. A. Tompkins, J. Polym. Sci., Part A-2 **7**, 1483 (1969).

[36] A. N. Gent and D. A. Tompkins, J. Appl. Phys. **40**, 2520 (1969).

[37] Soft rubber elastic materials called "elastomers" (as in "elastic polymers") have been measured to have 1 atm $\leq \varepsilon_2 \leq$ 10 atm and, as in this work, a Poisson ratio χ very slightly less than 0.5 [see Refs. 13, 35, and 36]. Therefore the materials modeled here are some one to two orders of magnitude less rigid than these soft rubber polymers. Nevertheless, as shown in the text, the shear resistances used here provided about the same contribution as the surface tension to the free energy functions we evaluate.

[38] C. A. Ward, P. Tikuisis, and R. D. Venter, J. Appl. Phys. **53**, 6076 (1982).

[39] See Ref. 18, Chapter 3 and Ref. 22, Chapter 11, for the Statistical Theory of Fluctuations. In our system, only the external pressure, the temperature, and the total number of molecules of each kind are kept absolutely fixed. This is not very restrictive, and does not preclude fluctuations in other variables in the system, including the number of bubbles and the bubble volume. For definiteness, consider the $\varepsilon^* = .02$ plot in Fig. 6. As

seen from Eq. (19), the values of $\beta \Delta g$ are determined both by R_B and $N_B(R_B)$, which are coupled through the $N_B(R_B)$ equation given in Eq. (17). A positive fluctuation in the volume of the bubble [due, for example, to a positive fluctuation in $\sigma^{(2)}{}_{rr}(R_B)$, see Eq. (9)], would lower both the bubble's pressure and the chemical potential of the N_2 in it. This would result in the influx of a small amount of N_2 from the medium into the bubble. The process would stop when the pressures and chemical potentials rebalance, each at a lower value, relative to their respective values before the fluctuation. Bubble growth is here coupled to an initial rise and a subsequent fall in the total number of bubbles, which can occur by bubble fission and fusion, respectively. As the entire process is repeated, the bubbles grow, their numbers first rise and subsequently fall, but the concentration of N_2 in the elastic medium drops monotonically, as does the pressure of N_2 in the bubbles (as illustrated in Fig. 4). This produces a monotonic drop in the chemical potentials of N_2 in the two phases (which are equal to one another). This drives the process and ultimately produces a reduction of the system free energy. When the system free energy is at the stationary global minimum, the fluctuations act randomly with no net effect on the system. However, away from the global minimum, the fluctuations are not random—they favor the direction that reduces the full system free energy. To understand this, recall that for a system not too far from global equilibrium, the probability of a fluctuation from state 1 to state 2 is given approximately by probabailty $\propto \exp(-\beta \Delta G)$, where $\Delta G \equiv G_2 - G_1$ (see Ref. 21). For systems with large numbers of molecules, this will heavily favor those changes which are in the direction that ultimately lowers G. Here this would most often be a positive volume fluctuation of the bubble, coupled either to an increase or a decrease in the number of bubbles, depending on the bubble radius. Therefore on balance (or given sufficient time) the bubbles will grow, their numbers will initially rise and subsequently fall, and the process will continue until the bubble radius reaches the upper critical radius, and there is one bubble in the system.

[40] E. N. Harvey, D. K. Barnes, W. D. McElroy, A. H. Whitely, D. C. Pease, and K. W. Cooper, J. Cell. Comp. Physiol. **24**, 1 (1944).

[41] P. K. Weathersby, L. D. Homer, and E. T. Flynn, J. Appl. Physiol. **53**, 940 (1982).

[42] For reasons given in Ref. 4, the partial pressure of N_2 in the alveolar, arterial, and venous systems of the human body, after equilibration with air at 1 atm is approximately .75 atm. When the partial pressures of the so-called "fixed venous gases:" water vapor, carbon dioxide, and unmetabolized oxygen, are added to this, (see Refs. 43 and 44), the expected total vapor pressure in the bubble becomes approximately .77 atm.

[43] E. D. Thalmann, E. C. Parker, S. S. Survanshi, and P. K. Weathersby, Undersea Hyperbaric Med. **24**, 255 (1997).

[44] S. Goldman, J. Appl. Physiol. **103**, 484 (2007).

[45] D. E. Yount, in *Mechanics and Physics of Bubbles in Liquids*, edited by L. van Wijngaarden (Martinus Nijhoff, The Hague, 1982).

[46] D. E. Yount, J. Acoust. Soc. Am. **65**, 1429 (1979).

[47] D. E. Yount, Aviat., Space Environ. Med. **50**, 44 (1979).

[48] D. E. Yount and T. K. Kunkle, J. Appl. Physiol. **46**, 4484 (1975).

[49] D. E. Yount, T. D. Kunkle, J. S. D'Arrigo, F. W. Ingle, C. M. Yeung, and E. L. Beckman, Aviat., Space Environ. Med. **48**, 185 (1977).

[50] B. R. Weinke, Comput. Biol. Med. **22**, 389 (1992).

[51] B. R. Wienke, Int. J. Bio-Med. Comput. **26**, 237 (1990).

[52] N. Gaskins, R. D. Vann, E. Hobbs, M. Swingle, S. Lee, and D. Needham, Undersea Hyperbaric Med. **28**, 56 (2001).

[53] K. G. Ikels, J. Appl. Physiol. **28**, 524 (1970).

[54] A. T. J. Hayward, Br. J. Appl. Phys. **18**, 641 (1967).

[55] A. H. Cottrel, *The Mechanical Properties of Matter* (Wiley, New York, 1964).