Factors Determining the Stability of a Gas Cell in an Elastic Medium

M. M. Fyrillas, *,[†] W. Kloek,[‡] T. van Vliet,[‡] and J. Mellema[†]

Rheology Group, Faculty of Applied Physics, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands, and Wageningen Centre for Food Sciences, c/o Food Physics Group, Wageningen University, P.O. Box 8129, 6700 EV Wageningen, The Netherlands

Received June 17, 1999. In Final Form: August 26, 1999

In this paper we consider the stability of a gas cell embedded in an infinite elastic medium. The stability criterion obtained extends the classical result by Gibbs, $\gamma < 2E$, to include the shear modulus of the elastic material. Interestingly, besides the shear modulus another parameter appears which is a measure of supersaturation and relates the pressure and the gas concentration at the far field. If it is less than a critical value then any bubble size corresponding to a steady state is stable; above this critical value a condition must be satisfied which is a function of the surface dilatational modulus, the shear modulus, the supersaturation, and the bubble radius, and simplifies to the classical result when the shear modulus is zero. Calculations based on an initial cell size of 10^{-5} m showed that shrinkage of a cell is inhibited by a higher dilatational or bulk modulus. For small values of supersaturation there is a single stable stady states, one stable and one unstable; excessive supersaturation leads to unbounded bubble growth.

I. Introduction

The shrinkage and growth of bubbles is of interest from several points of view. Bubble growth is of importance for phenomena such as cavitation, boiling, foam molding, and extrusion, while bubble shrinkage is of importance for the removal of entrapped bubbles and the dissolution of a gas in a liquid. In the food industry there is a great interest in manufacturing low-density foods such as bread, cakes, or desserts by entrapping large amounts of gas in the product in the form of small gas cells. The gas cell size¹ may range from 10^{-5} to 10^{-3} m. Gas cell size may have a significant influence on consumer sensory characteristics and consequently is of great importance to the food industry. Therefore it is important to understand how bubbles can be stabilized against coalescence and Ostwald ripening. In foam studies it was shown that, for viscous interfaces, an increase in the gas solubility leads to a more rapid coarsening of the foam.² However, if a protein able to form elastic interfaces was used, the accelerating effect of the gas solubility was suppressed.³ Continuation of Ostwald ripening caused the formation of a bimodal bubble size distribution which indicates that the shrinking bubbles are stabilized, suggesting either an important retarding effect of surface elasticity on Ostwald ripening or that the adsorbed protein layers alter the gas permeability of the film. Another parameter that was not considered is the degree of gas supersaturation which, as it is shown in this theoretical study, plays an important role in bubble growth and shrinkage.

The driving force for Ostwald ripening is the pressure difference between bubbles leading to differences in local gas concentration and therefore to gas diffusion. The pressure difference may arise from interfacial and bulk rheological properties. The effect of surface elasticity on bubble growth/shrinkage was first treated by Gibbs^{4–6} for a system of two equally sized bubbles of which one will grow and one will dissolve. This system is stable if the change in bubble pressure due to a change in radius is positive. Combining this criterion with the definition for Gibbs elasticity *E*

$$E = \frac{\mathrm{d}\gamma}{\mathrm{d}A/A} = \frac{\mathrm{d}\gamma}{\mathrm{d}\ln A}$$

where γ is the interfacial tension and A the surface area, yields the Gibbs stability criterion for a completely elastic interface

$$\frac{\mathrm{d}\Delta P}{\mathrm{d}R} = 2 \frac{(\mathrm{d}\gamma(R)/R)}{\mathrm{d}R} = -\frac{2\gamma}{R^2} + \frac{4E}{R^2} > 0 \Longrightarrow E > \frac{\gamma}{2}$$

Experimental data show that indeed high surface elasticities are able to significantly reduce the Ostwald ripening process. Especially the use of small adsorbing particles to increase the elastic modulus is very effective in reducing Ostwald ripening.⁵ Ronteltap⁷ showed that the presence of a finite surface viscosity may retard bubble dissolution but will not stop the process. There are several papers that describe the effect of rheological parameters of the liquid bulk on bubble growth and dissolution but

^{*} Corresponding author. Present address: Department of Mechanical and Aerospace Engineering, University of California at San Diego, La Jolla, CA 92093-0411. Tel.: (858) 534-5451. Fax: (858) 534-7599. E-mail: fyrillas@mae.ucsd.edu.

[†] University of Twente.

[‡] Wageningen University.

⁽¹⁾ van Vliet, T.; Janssen, A. M.; Bloksma, A. H.; Walstra, P. *J. Texture Studies* **1992**, *23*, 439.

⁽²⁾ Bhakta, A.; Ruckenstein, E. Adv. Colloid Interface Sci. 1997, 70, 1.

⁽³⁾ Gandolfo, R. G.; Rosani, H. L. J. Colloid Interface Sci. 1997, 194, 31.

⁽⁴⁾ Gibbs, J. W. *The Scientific Papers*; Academic Press: New York; Vol. 1.

⁽⁵⁾ Lucassen, J. In Anionic Surfactants: Physical Chemistry of Surfactant Action; Lucassen-Reynders, E. H., Ed.; Marcel Dekker: New York, 1981; p 217.
(6) Lucassen-Reynders, E. H. In Anionic Surfactants: Physical

⁽⁶⁾ Lucassen-Reynders, E. H. In *Anionic Surfactants: Physical Chemistry of Surfactant Action*; Lucassen-Reynders, E. H., Ed.; Marcel Dekker: New York, 1981; p 173.

⁽⁷⁾ Ronteltap, A. D.; Damste, B. R.; De Gee, M.; Prins, A. Colloids and Surfaces 1990, 47, 269.

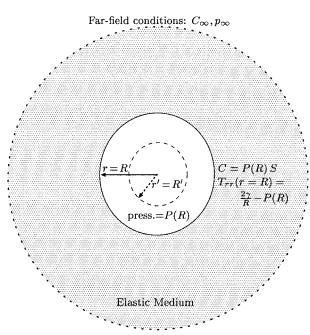


Figure 1. Schematic representation of the conceptual physical model along with boundary conditions. The gas cell deforms spherically from R' to R.

in all studies the surface tension is assumed to be constant, and therefore no surface elasticity is present. Initial theoretical studies mainly focused on the effect of mass transfer and neglected the effects of hydrodynamic interaction between liquid and gas.^{8,9} Barlow and Langlois¹⁰ took into account the presence of a Newtonian liquid. Street¹¹ incorporated fluid elasticity (Oldroyd liquid) and showed that elasticity caused a slow down of bubble shrinkage. Other rheological models for fluids were also considered¹²⁻¹⁶ and one of the last rigorous analyses was carried out by Venerus et al.¹⁷ The presence of increased viscosity retards bubble growth or shrinkage, whereas the introduction of an elastic component in the liquid allows the instantaneous growth or shrinkage of a bubble which overcomes viscous retardation.

In this paper we will focus on the relative importance of the role of bulk and interfacial rheological elastic properties on the stabilization of a gas cell. We will only consider the quasi steady state problem, suppressing any explicit dependence on time.

II. Theory

The theoretical section consists of two parts. They are the mechanical problem, associated with the elasticity problem due to the finite deformation of an elastic shell; and the mass transport problem, associated with gas transport in the elastic medium (Figure 1).

II.A. Mechanical Problem. The analysis of this section closely follows the notation and definitions given in Macosko.18

- (a) Epstein, P. S.; Piesset, M. S. J. Chem. Phys. 1950, 18, 1505.
 (b) Scriven, L. E. Chem. Eng. Sci. 1966, 10, 1.
 (c) Barlow, E. J.; Langlois, W. E. IBM Journal 1962, 6, 329.
 (c) Street, J. R. Trans. Soc. Rheol. 1968, 12, 103.
 (c) Tanasawa, I.; Yang, W. J. J. Applied Phys. 1970, 41, 4526.
 (c) Zana, E.; Leal, L. G. Ind. Eng. Chem. Fundam. 1975, 14, 175.
 (c) Yoo, H. J.; Han, C. D. AIChE 1982, 28, 1002.
 (c) Strements A.: Advantis, C. Bhael, Acta 1001, 20, 274.

- (15) Arefmanesh, A.; Advani, S. G. *Rheol. Acta* **1991**, *30*, 274.
 (16) Vrentas, J. S.; Vrentas, C. M. *J. Appl. Pol. Sci.* **1998**, *67*, 2093.
 (17) Venerus, D. C.; Yala, N.; Bernstein, B. J. *Non Newt. Fluid Mech.* **1998**, 75, 55.
- (18) Macosko, W. C. Rheology: Principles, Measurements and Applications; VCH: New York, 1994.

Consider a spherical thick shell with inner radius r =R' which is deformed symmetrically to r = R. Due to incompressibility the displacement functions become

$$r^{3} = r'^{3} + (R^{3} - R'^{3})$$
 $\theta = \theta'$ and $\phi = \phi'$

where prime (') denotes the undeformed state. Applying these, we can determine the deformation gradient tensor (F) and the Finger strain tensor (B) in spherical coordinates

$$\mathbf{F} = \begin{pmatrix} (r'/r)^2 & 0 & 0\\ 0 & r/r' & 0\\ 0 & 0 & r/r' \end{pmatrix}$$
$$\mathbf{B} = \mathbf{F}\mathbf{F}^{\mathbf{T}} = \begin{pmatrix} (r'/r)^4 & 0 & 0\\ 0 & (r/r')^2 & 0\\ 0 & 0 & (r/r')^2 \end{pmatrix}$$

To obtain the stress distribution inside the elastic material a stress/strain relation is required. A constitutive equation that is valid for large deformations and provides a good fit to rubber samples is the Neo-Hookean solid

$$\mathbf{\Gamma} = -p\mathbf{I} + G\mathbf{B} = -p\mathbf{I} + \mathbf{i}$$

where G is the shear modulus and τ the local stress tensor. Assuming that the body is in static equilibrium the θ -component of the momentum equation leads to $\tau_{\theta\theta} = \tau_{\phi\phi}$, while the *r*-component leads to a differential equation for p

$$\frac{\mathrm{d}p}{\mathrm{d}r} = \frac{\mathrm{d}\tau_{rr}}{\mathrm{d}r} + 2\frac{(\tau_{rr} - \tau_{\theta\theta})}{r} = -\frac{2G(R^3 - R'^3)^2}{r^5(r^3 - (R^3 - R'^3))^{2/3}}$$

The solution is

,

$$p = -\frac{G}{2r^4}(r^3 - (R^3 - R'^3))^{1/3}((R^3 - R'^3) + 3r^3) + c$$

which gives the following expression for the total radial stress

$$T_{rr} = \frac{G}{2r^4} (r^3 - (R^3 - R^3))^{1/3} (5r^3 - (R^3 - R^3)) - \frac{5}{2}G - p_{\infty}$$

The constant $c = 5G/2 + p_{\infty}$ is set by the boundary condition at infinity $T_{rr}(r \rightarrow \infty) = -p_{\infty}$.

The pressure inside the cell (P) is given by the difference between the Laplace pressure and the radial stress evaluated at the interface $T_{rr}(r = R)$:

$$P = \frac{2\gamma}{R} - T_{rr}(r = R) = \frac{2\gamma}{R} - 2G\frac{R}{R} - \frac{G}{2}\left(\frac{R}{R}\right)^4 + \frac{5}{2}G + p_{\infty}$$
(2.1)

II.B. Mass Transfer Problem. The solution of the steady state diffusion problem assuming spherical symmetry is straightforward

$$C = \frac{R(PS - C_{\infty})}{r} + C_{\infty}$$

To obtain this relation we use that $C(r \rightarrow \infty) = C_{\infty}$ (boundary condition at infinity) and C(r = R) = PS (boundary

⁽⁸⁾ Epstein, P. S.; Plesset, M. S. J. Chem. Phys. 1950, 18, 1505.

condition at the cell interface), where S is the solubility of the gas (Henry's law) at a pressure of 1 atm and C is the solubility at pressure P.

Using above expression for the concentration field the rate of mass transport through the interface leads to an expression for the rate of change of moles in the bubble

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 4\pi R^2 D \frac{\partial C}{\partial r} (r = R) = -4\pi D R (PS - C_{\infty}) \qquad (2.2)$$

where *D* is the diffusion coefficient of the gas in the elastic material.

Assuming that the gas inside the cell can be described by the ideal gas law we can obtain another expression for the rate of change of moles by a time differentiation of $n = (4\pi R^3 P(R))/(3R_u T)$:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{4\pi}{3R_{\mathrm{u}}T}R^2 \left(3\dot{R}P + R\frac{\partial C}{\partial R}\dot{R}\right)$$
(2.3)

where R_u is the universal gas constant, *T* the temperature of the gas, and $\dot{R} \equiv dR/dt$.

Combining eqs 2.2 and 2.3 and solving for \dot{R} we obtain a nonlinear ordinary differential equation governing the evolution of R

$$\dot{R} = -3R_{\rm u}TD \frac{(P(R)S - C_{\rm o})}{R(3P(R) + R \partial P(R)/\partial R)} \qquad (2.4)$$

The assumption underlying above equation is the quasi steady state approximation for the stress and concentration fields.

II.C. Stability Analysis. Equation 2.4 has a readily obtained steady state solution,

$$P(\bar{R}) = \frac{2\gamma}{\bar{R}} - 2G\frac{R'}{\bar{R}} - \frac{G(R')}{2} + \frac{5}{2}G + p_{\infty} = \frac{C_{\infty}}{S}$$

where \overline{R} denotes the bubble radius that satisfies this algebraic equation. Requiring that the equilibrium point $R = \overline{R}$ is asymptotically Liapunov-stable¹⁹ we obtain two conditions either of which should be satisfied

$$\frac{\partial P}{\partial R}(R=\bar{R}) < -\frac{3C_{\infty}}{\bar{R}S}$$
$$\frac{\partial P}{\partial R}(R=\bar{R}) > 0$$

Making use of the dilatational modulus E (or Gibbs' elasticity, see Edwards, Brenner & Wasan²⁰) defined as

$$E = \frac{1}{2} \frac{\mathrm{d}\gamma}{\mathrm{d}\ln R} \tag{2.5}$$

we obtain

$$\frac{\partial P}{\partial R} = \frac{4E}{R^2} - \frac{2\gamma}{R^2} + 2G\frac{R}{R^2} + 2G\frac{R'^4}{R^5}$$

(19) Greenberg, M. D. *Foundations of Applied Mathematics*; Prentice-Hall: New York, 1978.
(20) Edwards, D. A.; Brenner, H.; Wasan, D. T. *Interfacial Transport*

Fyrillas et al.

To recapitulate the results obtained in this section

$$z^{4} + 4z - 5 - \frac{2p_{\infty}}{G} - \frac{4\gamma}{G\bar{R}} = -\frac{2C_{\infty}}{GS} \quad \text{steady state}$$
(2.6)

$$z^{4} + z + \frac{2E - \gamma}{\bar{R}G} < -\frac{3C_{\infty}}{2SG} \text{ condition 1} \\ z^{4} + z + \frac{2E - \gamma}{\bar{R}G} > 0 \text{ condition 2} \end{cases} \text{ stable} \text{ steady state}$$

where $z = R' / \overline{R}$.

A necessary and sufficient condition for the existence of a steady state solution is that

$$SS < \frac{2\gamma}{\bar{R}} + \frac{5G}{2}$$
(2.8)

where $SS = C_{\infty}/S - p_{\infty}$ and is a measure of supersaturation.

To obtain conditions regarding the stability of the steady state we need to consider the inequalities 2.7. Solving eq 2.6 for z (keeping z^4) and substituting in condition 1 of inequality 2.7 we get

$$rac{3z^4}{4}+rac{C_{\infty}}{GS}+rac{5}{4}+rac{p_{\infty}}{2G}+rac{2E}{ar{R}G}<0$$

which does not lead to any stability criterion because above expression is always positive (note that z and E are always positive).

Solving eq 2.6 for z (keeping z^4) and substituting in condition 2 of inequality 2.7 we obtain

$$\frac{3z^4}{4} - \frac{SS}{2G} + \frac{5}{4} + \frac{2E}{\bar{R}G} > 0$$

If

$$SS < \frac{4E}{\bar{R}} + \frac{5G}{2} \tag{2.9}$$

then it can be easily deduced that the relevant bubble size (\bar{R}) is stable. Combining inequalities 2.8 and 2.9, we observe that if SS < 5G/2, then all bubble sizes can exist. Alternatively, solving eq 2.6 for z^4 (keeping z) and

substituting in condition 2 of inequality 2.7 we obtain

$$z < \frac{1}{3G\bar{R}} (2E + 3\gamma - 2SS\bar{R} + 5\bar{R}G)$$

Substituting the above inequality back in condition 2, we obtain a sufficient condition for stability

$$3\gamma > 2\bar{R}SS - 5\bar{R}G - 2E + (3\bar{G}\bar{R})^{3/4} (2\bar{R}SS - 8E - 5\bar{R}G)^{1/4} (2.10)$$

valid when $SS > (4E/\overline{R}) + 5G/2$.

For no deformation z=1 the steady state bubble radius is $\overline{R} = 2\gamma/SS$ and the stability criterion (eq 2.10) becomes

$$(SS - 4G)\gamma < 2SSE$$

The above equation simplifies to Gibbs condition, $\gamma < 2E$, for G = 0. A comparison between present results and Gibbs' stability condition can be displayed on a master curve (Figure 2), noticing that eq 2.6 and condition 2 of

⁽²⁰⁾ Edwards, D. A.; Brenner, H.; Wasan, D. T. *Interfacial Transport Processes and Rheology*; Butterworth-Heinemann: Woburn, MA, 1991.

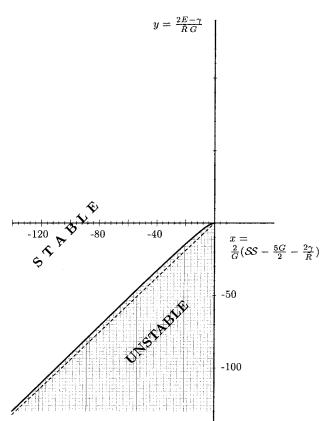


Figure 2. A master curve that shows the region where a gas cell is stable. In the right half-plane no solution exists. When the shear modulus *G* is zero the stability region is restricted to the upper-left quarter and the stability criterion simplifies to $\gamma < 2E$, i.e. Gibbs' stability criterion. The asymptote (dashed line) is the curve $y = x + 3|x|^{1/4}$.

inequality 2.7 represent the parametrization of a curve where the parameter is $z \in (0,\infty)$. For zero *G*, which is a singular limit, the stability region is limited to the upper-left quarter while for nonzero *G* it includes a portion of the lower-left quarter.

III. Model Calculations

A bubble of initial radius R_0 will start to grow or shrink which would result in a change in R, z and also γ in the case of a nonzero surface elasticity E. Consequently, it is more convenient to rewrite eq 2.6 and condition 2 of inequality 2.7 so that surface tension only depends on the bubble radius (R) and the initial surface tension (γ_0). To achieve this we assume the surface elasticity to be independent of surface area and integrate expression 2.5 with respect to time to obtain

$$\gamma(R) = \gamma_0 + 2E \ln \frac{R(t)}{R_0} = \gamma_0 - 2E \ln z$$

In what follows, we also assume that $R_0 = R'$ and that at $R = R_0$ no bulk stresses are present.

A physical explanation of eq 2.6 and condition 2 of inequality 2.7 can be obtained by identifying the three terms

$$P_{\rm i} = \frac{2\gamma_0 \, z - 4Ez \ln z}{R_0} \quad \text{(interfacial pressure)}$$
$$P_{\rm b} = G\left(\frac{5}{2} - 2z - \frac{z^4}{2}\right) \quad \text{(bulk pressure)}$$

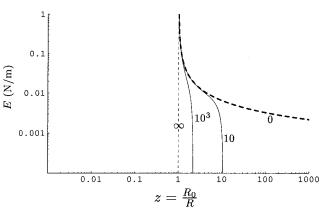


Figure 3. The value of the surface elasticity at which a stable steady state is achieved. The value of the parameters are $R_0 = 10^{-5}$ m, $\gamma_0 = 30$ mN/m, SS = 0 N/m², while *G* is indicated on the figure. The thick dashed line corresponds to zero shear modulus while the thin (vertical) dashed line corresponds to infinite shear modulus.

and SS (supersaturation). Equation 2.6 takes the form P_i + $P_b = SS$ and the stability condition (inequality 3.2) can be expressed as $d(P_i + P_b)/dz < 0$. The sign of dP_i/dz depends on the relative values of E, γ_0 , and z. For $z < \exp[\gamma_0/(2E) - 1]$ the sign of dP_i/dz is positive.

Equation 2.6 and condition 2 of inequality 2.7 may also be rearranged in the form

$$E = \frac{\gamma_0}{2 \ln z} - \frac{R_0}{8z \ln z} (2SS + G(z^4 + 4z - 5)) \quad (3.1)$$

$$\frac{2E(1+\ln z)-\gamma_0}{GR_0}+1+z^3>0$$
 (3.2)

In what follows we use eq 3.1 to calculate *E* for given values of *G*, R_0 , *SS*, and *z* and inequality 3.2 to determine whether the steady state is stable.

III.A. SS = 0. Figure 3 shows the stability plot of a saturated system (SS = 0). When G = 0, a bubble will shrink more before it is stabilized with decreasing E. Additional shrinkage of the bubble will compress the surface which will lead to a decrease in interfacial tension. The bubble will be stabilized at the moment the Laplace pressure has become small enough. For finite \overline{G} the dependence of *E* on *z* initially follows the same curve. At a certain deformation the bulk contribution takes over. If the bubble decreases more in size, the bulk stress becomes sufficient to compensate for the interfacial contribution and bubble stability is independent of the surface elasticity. Equation 3.1 shows that for G = 0 and SS = 0, every bubble will be stabilized as soon as the radius of the bubble is $R_0 \exp(-2E/\gamma_0)$. This shows that stabilization is only achieved on shrinkage. If furthermore E = 0, a bubble would completely dissolve.

Figure 4 shows the effect of the initial radius for SS = 0 with respect to the surrounding (p_{∞}). If the shear modulus is 0 the initial radius has no effect; for a given surface elasticity the bubble is stabilized at the same *z*-value. This can also be seen from eq 3.1 and inequality 3.2, where the stabilizing combination of *E* and *z* is only determined by the value of the initial surface tension. For nonzero (positive) values of *G* one has to distinguish between shrinkage (z > 1) and growth (z < 1). For growth, the second part of the right-hand term in eq 3.1 is always positive and will increase with increasing initial radius. The first part of the right-hand term in eq 3.1 is always negative and will therefore lead to negative values of *E*

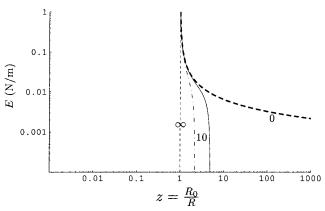


Figure 4. A plot that illustrates the influence of the initial radius. The parameters are the same as in Figure 3 except for the initial radius; the solid line corresponds to $R_0 = 10^{-4}$ m and the dashed-dot curve to $R_0 = 10^{-3}$ m. For further explanation see text.

which is unrealistic. This explains why there is no steady state in the case of bubble growth. In the case of shrinkage both terms of eq 3.1 are positive and would therefore yield realistic *E*-values. Whether the stable steady state criterion (inequality 3.2) is fulfilled, depends on the difference between γ_0 and $GR_0(1 + z^3)$. This difference is smaller for larger values of R_0 which explains that in the case of shrinkage for a constant z-value a larger E is needed to stabilize a smaller bubble. The same rationale can be used to explain that a larger E is needed to stabilize a system with a smaller shear modulus at the same z-value. How does this work out in practice: assume that $\gamma_0 = 40$ mN/m and E = 50 mN/m and that the bubble is allowed to shrink to half its initial size (z = 2). According to inequality 3.2 bubbles of initial radii 10^{-3} , 10^{-4} , and 10^{-5} m are stabilized at shear moduli larger than 3, 30, and 300 Pa, respectively. If the bubbles are allowed to shrink only 10% of their initial size the shear moduli should be larger than 8, 80, and 800 Pa, respectively. This shows that not very large moduli are needed to stabilize small bubbles. These moduli are for instance found in aerated desserts.

III.B. SS < 0. For a sub-saturated system (SS < 0) the same trends are observed as for SS = 0, the only difference being that higher *E*-values are needed to stabilize the bubble at the same *z*-value. This is also clear from eq 3.1; SS only enters the calculation in a linear way and has no effect on the stable steady state criterion. Physically, it can be explained by a larger difference between the system pressure and the bubble pressure which can only be counteracted by either a larger *E* or a larger shear modulus.

III.C. SS > 0. Figures 5 and 6a show the effect of supersaturation (SS > 0). For moderate values of SS (SS < Laplace pressure, Figure 5), there is qualitative agreement with the saturated case in the shrinkage region (z > 1). However, in addition, there is a steady state corresponding to a growing bubble (z < 1), which is unstable; given a small disturbance the cell would either shrink to the stable steady state or grow. For higher values of supersaturation (Figure 6) the stability picture changes drastically since there are two steady states for a shrinking bubble, one of them being unstable, which disappear at large values of the shear modulus. Furthermore, the steady state corresponding to a growing bubble can be stable.

Equation 3.1 clearly indicates that there is a linear dependence between the surface elasticity, the shear modulus (*G*) and surface tension (γ_0). For a shrinking

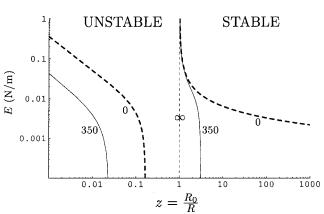


Figure 5. Similar plot as Figure 3 except that SS = 1000 N/m². The value of *G* is indicated. The steady state corresponding to an expanding gas cell (z < 1) is unstable.

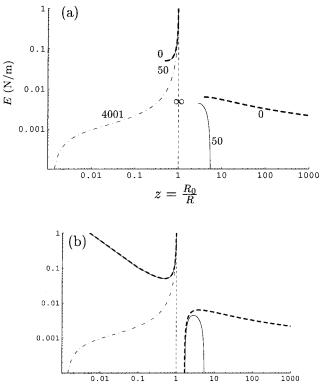


Figure 6. Similar plot as Figure 3 except that $SS = 10\,000$ N/m². Figure 6b shows the steady state curves while Figure 6a the sections corresponding to a stable steady state (see text).

bubble, a higher initial surface tension leads to higher values for the surface elasticity needed to stabilize a bubble; an initial higher surface tension causes a higher Laplace pressure which needs to be compensated by a larger surface elasticity. The opposite holds for an expanding bubble.

III.D. Stability Diagrams. Figures 3–6 suggest that the problem of the stability of a gas cell in an elastic medium is characterized by an intricate coupling between bulk stresses and gas diffusion that results to multiple steady states with a complicated stability. Furthermore, the number of free parameters involved (six in total), does not allow for any concise result that would relate the steady states with their stability. In this section we show diagrams that elucidate the structure of the different stability regions.

Using R_0 and G for nondimensionalization, eq 3.1 and inequality 3.2 take the form

$$SS^* = \frac{5 - 4z + 4\gamma_0^* z - z^4 - 8E^* z \ln z}{2}$$
 (3.3)

$$2E^*(1 + \ln z) - \gamma_0^* + 1 + z^3 > 0 \qquad (3.4)$$

respectively, where $SS^* = SS/G$, $\gamma_0^* = \gamma_0/(R_0G)$ and $E^* = E/(R_0G)$. An analysis of the above equations showed that the structure of the stability regions changes at the values of $\gamma_0^* = 1$ and 2.

In Figures 7–9 we show stability diagrams for three different values of γ_0^* within the regions mentioned above. The straight lines on Figures 7–9 correspond to z = 0 ($SS^* = 2.5$) and z = 1 ($SS^* = 2\gamma_0^*$); the top curve shows the maximum value of SS^* above which no steady state solution exists and the cell will keep growing and actually, $z \rightarrow 0$ in finite time. Below the maximum value and for values of $SS^* > 2.5$ there are two steady states, one stable and one unstable. For values of $SS^* < 1$ there is a single stable steady state corresponding to a shrinking gas cell.

Given two stable steady states corresponding to shrinkage, the one with the higher value of SS^* (everything else being the same) has a higher value of z (smaller shrinkage) while the opposite holds for two stable steady states corresponding to growth, the one with the higher value of SS^* (everything else being the same) has a smaller value of z (bigger growth).

IV. Conclusions

The stability of a gas cell embedded in an infinite elastic medium has been investigated. We have assumed that the cell deforms spherically and finitely and that the elastic medium surrounding the cell corresponds to a Neo-Hookean solid. The expansion/contraction of the cell is controlled by diffusion mass transfer in the medium. The driving force for the mass transfer is the concentration difference between the cell interface, given by Henry's law, and the concentration at infinity. The system is stable if the change in bubble pressure due to a change in radius is positive. The stability criterion obtained extends the classical result by Gibbs, $\gamma < 2E$, to include the shear modulus of the elastic material. Besides the shear modulus another parameter appears which is a measure of supersaturation and relates the pressure and the concentration at the far field. If it is less than 4E/R + 5G/2 then the bubble size is stable; above this critical value a condition must be satisfied which is a function of the surface dilatational modulus, the shear modulus, the surface tension, the supersaturation, and the bubble radius, and simplifies to the classical result when the shear modulus is zero.

Above results are based on the steady state gas cell size (\bar{R}) and surface tension (γ) . Calculations based on an initial cell size of $R_0 = 10^{-5}$ m and an initial surface tension $\gamma_0 = 30$ mN/m showed that shrinkage of a cell is inhibited by higher dilatational or bulk modulus. Stabilization against growth can be achieved by applying either a high surface elasticity in combination with a supersaturation or by using a bulk with high shear modulus.

Stability analysis showed that above a critical value of the dimensionless supersaturation (SS^*) no steady state solution exists and the cell will keep growing and actually

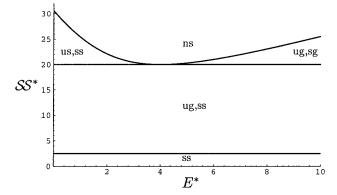


Figure 7. Stability diagram for $\gamma_0^* = 10$ which shows the states of the gas cell; ss: stable shrinkage, us: unstable shrinkage, sg: stable growth, ug: unstable growth, and ns: no steady state. In the ns region the gas cell will burst.

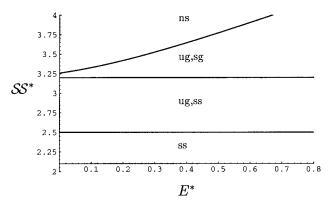


Figure 8. Similar plot as Figure 7 except that $\gamma_0^* = 1.6$.

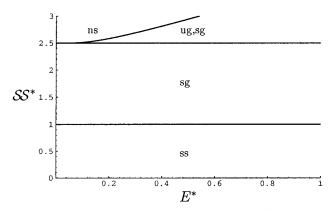


Figure 9. Similar plot as Figure 7 except that $\gamma_0^* = 0.5$.

reach an infinite size in finite time. Below this maximum value and for values of $SS^* > 2.5$ there are two steady states, one stable and one unstable. For values of $SS^* < 1$ there is a single stable steady state corresponding to a shrinking gas cell.

Acknowledgment. The authors thank Dirk van den Ende for his contribution to this study and the reviewer whose suggestion led to the current (improved) form of the stability diagrams.

LA990784Y