

## Snap-through Expansion of a Gas Bubble in an Elastomer

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*When a gas is injected into a bubble in an elastomer, the bubble may first expand gradually, and then snap suddenly to a large size. This snap-through instability is analyzed here using a model that accounts for both the surface tension and the limiting stretch of the elastomer. In a state of equilibrium, the pressure in the bubble counteracts three contributions: the ambient pressure due to the environment outside the elastomer, the Laplace pressure due to the surface tension of the elastomer, and the additional pressure due to the elasticity of the elastomer. The Laplace pressure is large for a small bubble, but falls as the bubble expands. The additional pressure due to elasticity increases as the bubble expands, and rises steeply when the surface of the bubble approaches the limiting stretch of the elastomer. We show that the bubble snaps only if a sufficient amount of gas can rush into the bubble at the onset of instability.*

**Keywords:** Bubble; Elastomer; Limiting stretch; Snap-through instability; Surface tension

### 1. INTRODUCTION

Gas bubbles are ubiquitous in technological and natural processes, ranging from foaming polymers [1] to raising dough. The significance

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of gas bubbles expanding in soft materials may be illustrated by recalling several examples. Gas bubbles in adhesives often act as sites to initiate cavitation and fracture [2–4]. When a polymer is heated, the absorbed water is expelled, forming bubbles and leading to “popcorn failure” [5,6]. Gas bubbles can form in tissues when a diver rapidly ascends from deep water, and cause decompression sickness [7,8]. Water in the xylem of a tree is under large tensile stress, which may suck air bubbles into the xylem, leading to embolism [9].

Recently, a technique called cavitation rheology has been developed to use air bubbles to probe mechanical properties in the interior of soft materials [10,11]. In this technique, a needle is inserted into a soft material, and is connected through a tube to a syringe. One then pushes the plunger of the syringe, injects an air bubble into the material, and monitors the pressure of the air in the tube. The pressure first ramps up and then drops suddenly. The rate at which the pressure ramps up can be made low by slowly pushing the plunger. The sudden drop of the pressure corresponds to a sudden and large expansion of the bubble. The peak of the pressure is used to identify the elastic modulus and the surface tension of the material.

Expansion of bubbles and cavities in soft materials has been studied by many authors. The earliest studies represented an elastomer by the neo-Hookean model, and ignored the surface tension of the elastomer [12,13]. It was found that, as the bubble expands, the pressure in the bubble increases monotonically, approaching a finite asymptotic value. When the surface tension was included in the model, the pressure was found to rise as the bubble expands, reaches a peak, and then falls to the asymptote [14,15]. In an elastomer, each individual polymer chain has a finite contour length, so that the elastomer exhibits a limiting stretch. On approaching the limiting stretch, the elastomer stiffens steeply. This effect is absent in the neo-Hookean model, but is represented by material models such as those of Arruda and Boyce [16] and of Gent [17]. In particular, Lin and Hui [18] adopted the Gent model to analyze the inflation of a crack-like defect. Further literature on the expansion of bubbles and cavities in elastomers and other materials can be found in an online journal club [19]. An expanding bubble sometimes causes the surrounding elastomer to fracture [11]. This phenomenon deserves a careful analysis, but will not be pursued here.

The object of this paper is to analyze conditions under which a gas bubble snaps to a large size, assuming that the elastomer does not fracture. Our analysis parallels that in [15], which considered a cavity in a soft material subject to external load. Our model will include both the surface tension and the limiting stretch. As the bubble expands, the pressure first rises, reaches a peak, falls, and then rises again.

The shape of the curve is reminiscent of the load-displacement curve of a structure undergoing snap-through instability [20]. Our calculation shows that the gas bubble will only snap to a large size if a sufficient amount of gas can rush into the bubble.

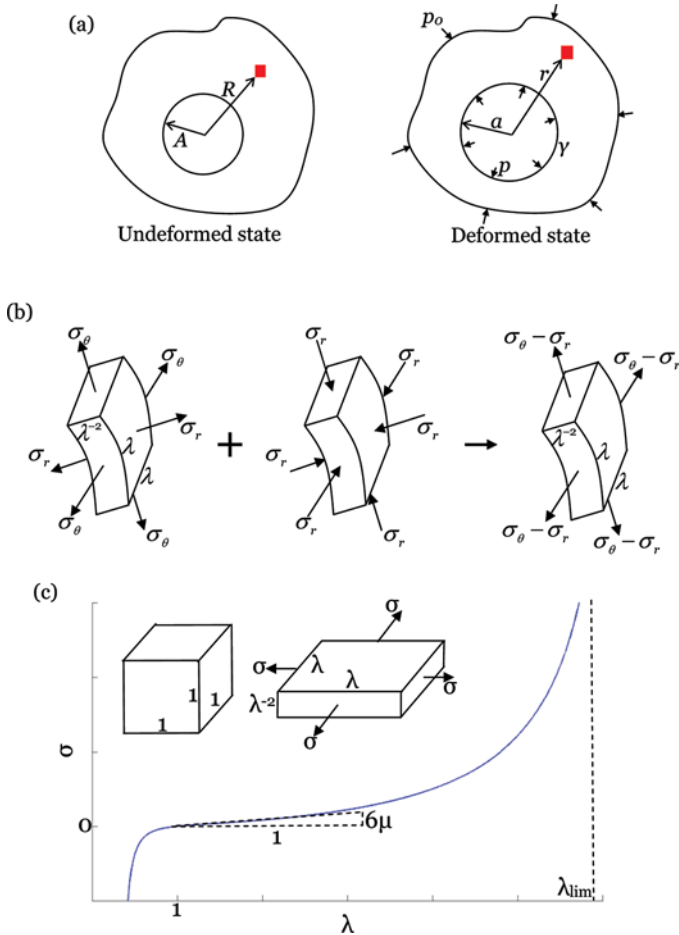
## 2. A GAS BUBBLE IN AN ELASTOMER

Figure 1a illustrates a spherical gas bubble in an elastomer. The environment outside the elastomer is under an ambient pressure  $p_0$ , while the gas in the bubble is under pressure  $p$ . The surface tension of the elastomer is  $\gamma$ , taken to be constant when the elastomer is stretched. Let  $A$  be the radius of the bubble when the elastomer is undeformed, and  $a$  be the radius of the bubble when the elastomer is deformed subject to the pressures and the surface tension. The ratio  $a/A$  is called the stretch of the bubble. This section recalls the basic results that relate the stretch of the bubble to the pressures and the surface tension. The presentation will be brief; see references cited above for additional details.

Figure 1b shows an element of the deformed elastomer, undergoing two equal hoop stretches  $\lambda_\theta = \lambda_\phi$  and a radial stretch  $\lambda_r$ . The elastomer is taken to be incompressible, so that  $\lambda_\theta \lambda_\phi \lambda_r = 1$ . Write the hoop stretches as  $\lambda_\theta = \lambda_\phi = \lambda$  and the radial stretch as  $\lambda_r = \lambda^{-2}$ . The element is under triaxial stresses: two equal hoop stresses  $\sigma_\theta = \sigma_\phi$  and a radial stress  $\sigma_r$ . Due to incompressibility, the state of deformation is unaffected when the element is superimposed with a hydrostatic stress. In particular, superimposing a hydrostatic stress  $(-\sigma_r, -\sigma_r, -\sigma_r)$  to the state of triaxial stresses  $(\sigma_\theta, \sigma_\theta, \sigma_r)$  results in a state of equal-biaxial stresses  $(\sigma_\theta - \sigma_r, \sigma_\theta - \sigma_r, 0)$ . Consequently, the state of deformation of the element subject to the triaxial stresses is the same as the state of deformation of the element subject to equal-biaxial stresses. Denote the biaxial stresses by  $\sigma = \sigma_\theta - \sigma_r$ .

Figure 1c sketches the stress-stretch curve,  $\sigma(\lambda)$ , for the element subject to equal-biaxial stresses. For an isotropic and incompressible elastomer, the small-stress modulus under equal-biaxial stresses is  $6\mu$ , where  $\mu$  is the small-stress shear modulus of the elastomer. Also indicated in the figure is the limiting stretch  $\lambda_{\text{lim}}$ .

As indicated in Fig. 1a, an element of the elastomer is at distance  $R$  from the center of the bubble when the elastomer is undeformed, and moves to a place at distance  $r$  from the center of the bubble when the elastomer is deformed. The stretches and the stresses in the elastomer are functions of the radial position:  $\lambda(r)$ ,  $\sigma_r(r)$  and  $\sigma_\theta(r)$ . At the surface of the bubble, the hoop stretch of the elastomer equals the stretch of the bubble,  $\lambda(a) = a/A$ , while the radial stress in the elastomer is



**FIGURE 1** (a) A spherical gas bubble in an elastomer. The radius of the bubble is  $A$  in the undeformed elastomer, and is  $a$  in the deformed elastomer. (b) Due to incompressibility, the state of deformation of an element subject to triaxial stresses is the same as that of the element subject to equal-biaxial stresses. (c) The stress-stretch curve under equal-biaxial stresses (color figure available online).

balanced by the pressure in the gas and the Laplace pressure due to the surface tension,  $\sigma_r(a) = -p + 2\gamma/a$ . The size of the elastomer is taken to be much larger than the size of the bubble. Far from the bubble, the elastomer is undeformed,  $\lambda(\infty) = 1$ , and is under the ambient pressure,  $\sigma_r(\infty) = -p_0$ .

Recall that  $\lambda = r/R$ , and that the elastomer is taken to be incompressible,  $r^3 - a^3 = R^3 - A^3$ . Consequently,  $r$  is a function of  $\lambda$ , namely,  $r = (a^3 - A^3)^{1/3} \lambda (\lambda^3 - 1)^{-1/3}$ . Differentiating this function, we obtain that  $dr = -(a^3 - A^3)^{1/3} (\lambda^3 - 1)^{-4/3} d\lambda$ . Integration of the equilibrium equation  $d\sigma_r/dr = 2(\sigma_\theta - \sigma_r)/r$  gives that

$$p = p_0 + \frac{2\gamma}{a} + \int_1^{a/A} \frac{2\sigma(\lambda)d\lambda}{\lambda(\lambda^3 - 1)}. \quad (1)$$

In a state of equilibrium, the pressure  $p$  in the bubble counteracts three contributions: the ambient pressure due to the environment outside the elastomer, the Laplace pressure due to the surface tension of the elastomer, and the additional pressure due to the elasticity of the elastomer. When  $p = p_0 + 2\gamma/A$ , the bubble is unstretched,  $a/A = 1$ . When  $p < p_0 + 2\gamma/A$ , the bubble shrinks,  $a/A < 1$ . When  $p > p_0 + 2\gamma/A$ , the bubble expands,  $a/A > 1$ .

Equation (1) is valid for the stress-stretch curve  $\sigma(\lambda)$  of arbitrary form. A specific form of  $\sigma(\lambda)$  can be derived once the elastomer is characterized by a free-energy function. Let  $W$  be the free energy per unit volume of the elastomer. Under equal-biaxial stresses, the free energy is a function of the stretch,  $W(\lambda)$ . The stress-stretch relation is given by

$$\sigma(\lambda) = \frac{\lambda}{2} \frac{dW(\lambda)}{d\lambda}. \quad (2)$$

We adopt the Gent free-energy function [17]

$$W = -\frac{\mu J_{\text{lim}}}{2} \log\left(1 - \frac{J}{J_{\text{lim}}}\right), \quad (3)$$

where  $J = \lambda_\theta^2 + \lambda_\phi^2 + \lambda_r^2 - 3$ ,  $J_{\text{lim}}$  is a constant related to the limiting stretch, and  $\mu$  is the small-stress shear modulus. The value of  $J/J_{\text{lim}}$  is restricted in the interval  $0 \leq J/J_{\text{lim}} < 1$ . When  $J/J_{\text{lim}} \rightarrow 0$ , the Taylor expansion of (3) gives  $W = \mu J/2$ . That is, the Gent model recovers the neo-Hookean model when deformation is small compared with the limiting stretch. When  $J/J_{\text{lim}} \rightarrow 1$ , the elastomer approaches the limiting stretch. Under equal-biaxial stresses,  $J = 2\lambda^2 + \lambda^{-4} - 3$ , and the limiting stretch  $\lambda_{\text{lim}}$  relates to  $J_{\text{lim}}$  through the equation

$$J_{\text{lim}} = 2\lambda_{\text{lim}}^2 + \lambda_{\text{lim}}^{-4} - 3. \quad (4)$$

Inserting (3) into (2), we obtain the stress-stretch curve under the equal-biaxial stresses:

$$\sigma(\lambda) = \frac{\mu(\lambda^2 - \lambda^{-4})}{1 - (2\lambda^2 + \lambda^{-4} - 3)/J_{\text{lim}}}. \quad (5)$$

A combination of (1) and (5) gives that

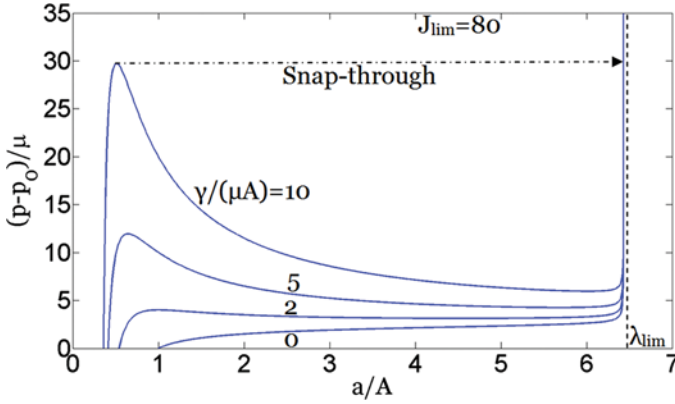
$$p = p_0 + \frac{2\gamma}{a} + 2\mu \int_1^{a/A} \frac{(\lambda^{-2} + \lambda^{-5})d\lambda}{1 - (2\lambda^2 + \lambda^{-4} - 3)/J_{\text{lim}}}. \quad (6)$$

For the neo-Hookean material,  $J_{\text{lim}} \rightarrow \infty$ , the integral in (6) is readily calculated, giving [14]

$$p = p_0 + \frac{2\gamma}{a} + \frac{\mu}{2} \left[ 5 - 4 \left( \frac{a}{A} \right)^{-1} - \left( \frac{a}{A} \right)^{-4} \right]. \quad (7)$$

For the Gent model of a finite value of  $J_{\text{lim}}$ , the integral in (6) is evaluated numerically. The results can be represented in terms of the normalized pressure in the bubble,  $p/\mu$ , as a function of the stretch of the bubble,  $a/A$ . The function is affected by two dimensionless parameters:  $J_{\text{lim}}$  and  $\gamma/(\mu A)$ . For a representative value  $J_{\text{lim}} = 80$ , the limiting stretch is  $\lambda_{\text{lim}} = 6.44$ . The ratio  $\gamma/\mu$  defines a length. Representative values for an elastomer are  $\gamma = 0.025 \text{ J/m}^2$  and  $\mu = 10^6 \text{ J/m}^3$ , giving  $\gamma/\mu = 25 \text{ nm}$ . Representative values for a soft hydrogel are  $\gamma = 0.070 \text{ J/m}^2$  and  $\mu = 10^3 \text{ J/m}^3$ , giving  $\gamma/\mu = 70 \text{ }\mu\text{m}$ . The length  $\gamma/\mu$  need be much larger than the radius of a bubble for the surface tension to play a significant part in resisting the growth of the bubble. In experiments described in Ref. [11], the reported shear modulus ranged from  $0.5 \times 10^3 \text{ J/m}^3$  to  $20 \times 10^3 \text{ J/m}^3$ , and the reported radius of syringe needles used ranged from  $30 \text{ }\mu\text{m}$  to  $200 \text{ }\mu\text{m}$ .

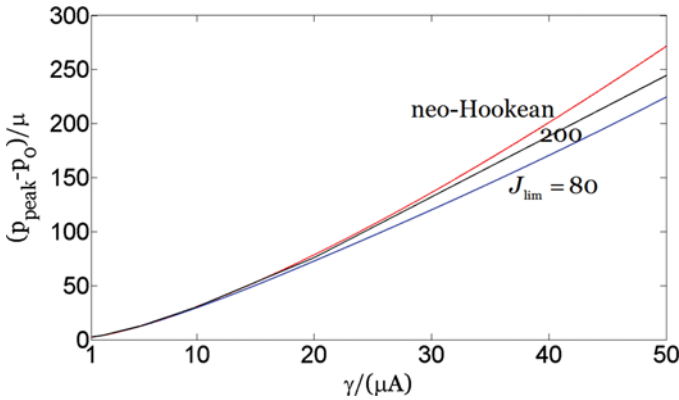
Figure 2 displays (6) by plotting the normalized pressure in the bubble,  $p/\mu$ , as a function of the stretch of the bubble,  $a/A$ . It should be noted that when  $p = p_0$ , the surface energy may make the bubble shrink, and thus  $a < A$ . For a small value of  $\gamma/(\mu A)$ , the expansion of the bubble is mainly resisted by the elasticity of the elastomer, and the pressure monotonically increases with the stretch. For a sufficiently large value of  $\gamma/(\mu A)$ , the pressure-stretch curve exhibits a peak [14]. The surface tension causes the Laplace pressure, which is large for a small bubble, and falls when the bubble expands. The pressure due to the elasticity of the elastomer increases monotonically with the radius of the bubble, and the pressure rises steeply when the stretch of the bubble approaches the limiting stretch,  $a/A \rightarrow \lambda_{\text{lim}}$ .



**FIGURE 2** The normalized pressure in the bubble relative to the ambient pressure as a function of the stretch of the bubble. When the pressure in the bubble is programmed to ramp up with time, upon reaching the peak of the curve, the bubble expands suddenly, without appreciable change in the pressure (color figure available online).

For the neo-Hookean material, the peak pressure can be determined by maximizing the pressure in (7). When the stretch of the bubble is  $a/A = (\gamma/(\mu A) - 1)^{-1/3}$ , the pressure in the gas reaches the peak, given by

$$p_{peak} = p_0 + \frac{5\mu}{2} + \frac{3\mu}{2} \left( \frac{\gamma}{\mu A} - 1 \right)^{4/3}. \tag{8}$$



**FIGURE 3** The normalized peak pressure relative to the ambient pressure as a function of the normalized surface tension (color figure available online).

For the Gent material with a finite value of  $J_{\text{lim}}$ , the peak pressure can be determined numerically from (6). Figure 3 plots the normalized peak pressure as a function of the normalized surface tension. The peak pressure depends weakly on  $J_{\text{lim}}$ , because the pressure peaks when the stretch of the bubble is much smaller than the limiting stretch.

### 3. SNAP-THROUGH INSTABILITY

The shape of the curve in Fig. 2—rising, falling, and then rising again—is reminiscent of the load-displacement curve for a structure undergoing snap-through instability [20]. Consider a hypothetical experiment in which the experimentalist programs the pressure in the gas to ramp up with time. When the pressure reaches the peak of the pressure-stretch curve, the bubble enlarges suddenly without appreciable change in the pressure, and the bubble attains another state of equilibrium near the limiting stretch. This snap-through instability is indicated in Fig. 2 by a horizontal arrow. By “suddenly”, we mean that the rate of the expansion of the bubble, which may be limited by inertia, is much faster than the rate at which the pressure ramps up, which is set by the experimentalist. In such a hypothetical experiment, the pressure is programmed to ramp up at all times, and cannot drop.

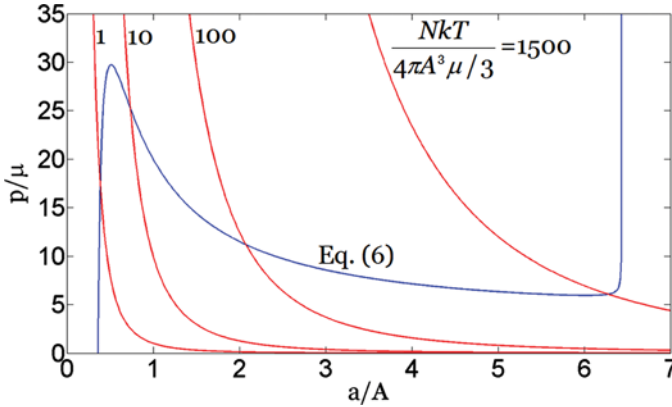
In practice, however, the pressure in the bubble is rarely programmed. Consider the process of decompression. An elastomer is initially placed in an environment with a gas of a high pressure, and the elastomer is saturated with molecules of the gas. When the pressure of the gas in the environment is reduced to a lower level, the gas molecules will diffuse out of the elastomer, release to the environment, and fill the bubbles inside the elastomer. In this case, the number of gas molecules in a bubble ramps up, at a rate limited by the diffusion through the elastomer. We may assume that the number of gas molecules inside the bubble is fixed when the bubble snaps. The gas in the bubble is taken to obey the ideal-gas law:

$$pV_{\text{bubble}} = NkT, \quad (9)$$

where  $V_{\text{bubble}} = 4\pi\alpha^3/3 = 4\pi\alpha^3\lambda^3/3$  is the volume of the bubble,  $N$  is the number of molecules of the gas in the bubble, and  $kT$  is the temperature in the unit of energy. Both the pressure and the temperature are taken to be homogeneous inside the bubble.

The state of equilibrium is determined on the pressure-radius plane by the intersection of the two curves, (6) and (9). Figure 4 plots (6) for  $J_{\text{lim}} = 80$ ,  $\gamma/(\mu A) = 10$ , and  $p_0/\mu = 0$ . Also plotted is (9) for several

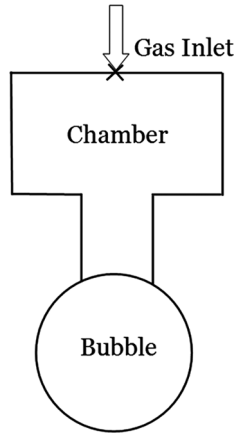




**FIGURE 4** The ideal gas law is plotted on the pressure-stretch plane at several values of the normalized number of gas molecules in the bubble. The parameters used are  $J_{\text{lim}}=80$ ,  $\gamma/(\mu A)=10$ , and  $p_0/\mu=0$  (color figure available online).

values of the normalized number of gas molecules in the bubble,  $NkT/(4\pi A^3\mu/3)$ . For a fixed number of gas molecules, (9) requires the pressure to drop as the bubble expands. When the number of gas molecules ramps up, the pressure in the bubble first rises, reaches a peak, falls, and finally rises again. Meanwhile, the bubble expands gradually, but does not snap.

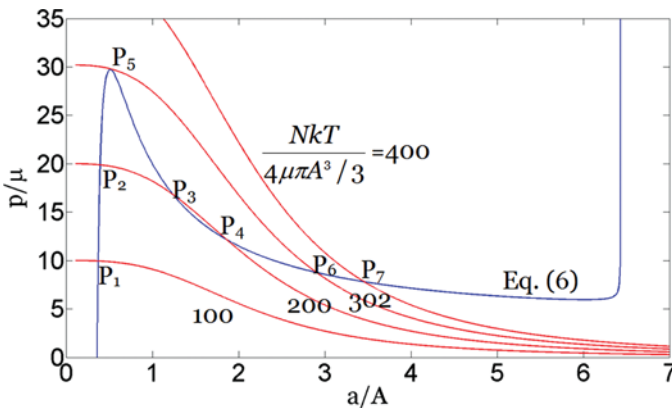
In the experiments described in [10,11], however, the air bubble did undergo a snap-through instability: the pressure dropped, while the bubble enlarged suddenly. These observations are inconsistent with either ramping pressure or ramping number of gas molecules in the bubble. In the experiments, the initial shape of the bubble was not spherical, but was a zone created by inserting a needle into a hydrogel. The response of this zone to the pressure has not been analyzed, and will alter the detailed shape of the pressure-stretch curve. This effect will not be considered here. Instead, we will focus on how air molecules enter the bubble. In the experiment, the needle was connected to a tube, which in turn was connected to a syringe. The plunger of the syringe was pushed at a constant rate, while the total number of air molecules in the combined space of the bubble and the tube was fixed. The volume of the bubble was much smaller than that of the tube. The plunger was pushed at such a slow rate that, prior to the sudden expansion of the bubble, the pressure was homogeneous everywhere in the bubble and the tube, and the pressure ramped up at a rate controlled by the rate at which the plunger was pushed. However,



**FIGURE 5** A schematic of an idealized experiment consisting of a chamber and a bubble. When the bubble snaps to a large size, the total number of gas molecules in the chamber and bubble is fixed, and the pressure in the chamber and bubble is homogeneous.

when the bubble snapped, some additional air molecules may rush into the bubble, but the time was insufficient for the pressure to homogenize throughout the bubble and the tube.

To understand fully this dynamic process will require an analysis of the flow of the air in the needle and tube. This analysis will not be

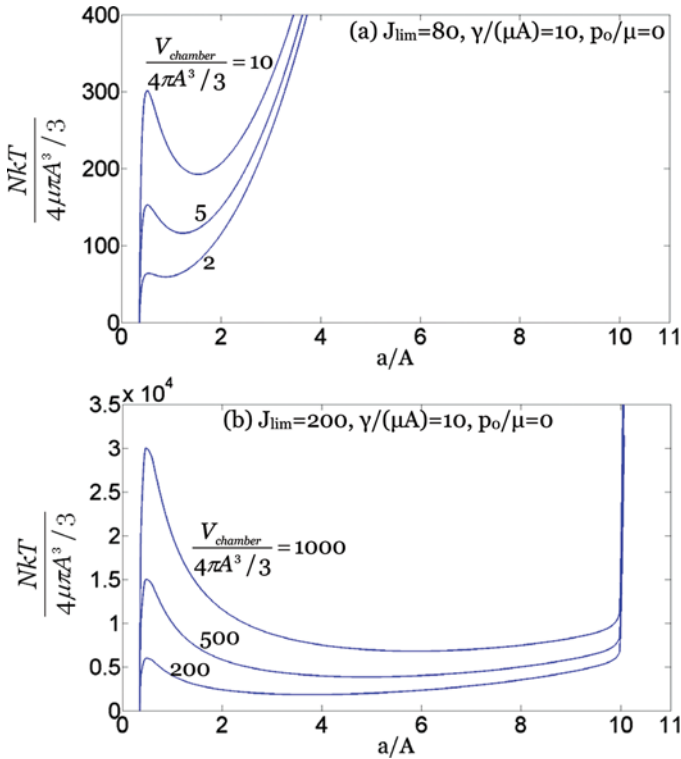


**FIGURE 6** When the number of gas molecules reaches a critical value, the bubble snaps to a large size, and the pressure suddenly drops. The parameters used are  $J_{lim} = 80$ ,  $\gamma/(\mu A) = 10$ ,  $V_{chamber}/(4\pi A^3/3) = 10$ , and  $p_0/\mu = 0$  (color figure available online).

performed here. Instead, we focus on aspects of the process by considering an idealized experiment, in which the bubble is connected to a chamber (Fig. 5). Air molecules come into the chamber from an inlet. When the bubble snaps, the time is taken to be long enough so that the pressure in the bubble and the chamber can homogenize (thus any pressure change due to flow of the gas is negligible), but is short enough so that the inlet is effectively shut. In this idealized experiment, the total number of air molecules,  $N$ , in the bubble and the chamber is constant when the bubble snaps. A similar idealization has been used to analyze the inflation of a balloon [21]. We apply the ideal-gas law to the combined volume of the bubble and the chamber:

$$p(V_{\text{bubble}} + V_{\text{chamber}}) = NkT, \quad (10)$$

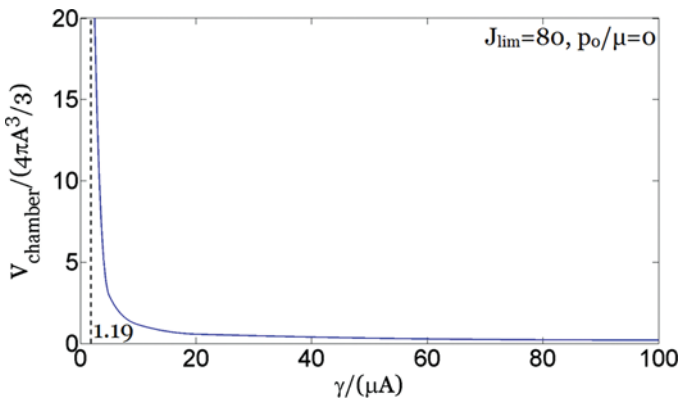
where  $V_{\text{chamber}}$  is the volume of the chamber, and is taken to be fixed.



**FIGURE 7** The number of gas molecules in the chamber and bubble as a function of the stretch of the bubble. (a)  $J_{\text{lim}} = 80$ . (b)  $J_{\text{lim}} = 200$  (color figure available online).

Figure 6 once again plots (6) on the pressure-radius plane. Also plotted is (10) for several values of the normalized number of gas molecules. The volume of the chamber is fixed at  $V_{chamber}/(4\pi A^3/3) = 10$ . As the total number of gas molecules in the chamber and the bubble ramps up, the bubble may equilibrate at different states. When  $NkT/(4\mu\pi A^3/3) = 100$ , there is only one state of equilibrium,  $P_1$ . When  $NkT/(4\mu\pi A^3/3) = 200$ , there are three states of equilibrium,  $P_2$ ,  $P_3$  and  $P_4$ . When  $NkT/(4\mu\pi A^3/3)$  reaches a critical value 302, the bubble snaps from  $P_5$  to  $P_6$ , meanwhile the pressure drops from 30 to 8. As the number of air molecules ramps up further, the bubble expands gradually.

As an alternative visualization of the above discussion, Fig. 7 plots the total number of air molecules as a function of the stretch of the bubble. The total number of air molecules is taken to be fixed when the bubble snaps. As the number of air molecules ramps up, the bubble first expands gradually. On reaching the peak value of  $N$ , the bubble snaps with the fixed number  $N$ , and then reaches another state of equilibrium of a larger size. When the volume of the chamber is small, say,  $V_{chamber}/(4\pi A^3/3) = 2, 5, 10$ , the expansion of the bubble associated with the snap increases with the volume of the chamber (Fig. 7a). When the volume of the chamber is large, say,  $V_{chamber}/(4\pi A^3/3) = 200, 500, 1000$ , the expansion of bubble associated with the snap is insensitive to the size of chamber, but depends on the limiting stretch (Fig. 7b). When  $V_{chamber}/(4\pi A^3/3) \rightarrow \infty$ , ramping up the number of air molecules recovers ramping up the pressure, which can achieve the largest snap-through expansion.



**FIGURE 8** The bubble may snap when the normalized volume of the chamber and the normalized surface tension are above the curve (color figure available online).

A bubble may snap when the volume of the chamber and the surface tension is sufficiently large, as illustrated by the curve in Fig. 8. For example, the bubble cannot snap when  $\gamma/(\mu A) < 1.19$ , even if  $V_{chamber}$  is infinite, corresponding to a ramping pressure in the bubble. As a second example, when  $\gamma/(\mu A) = 10$ , the bubble can snap when  $V_{chamber}$  is larger than 1.15 times the volume of the bubble in the undeformed elastomer.

#### 4. STABILITY OF THE STATES OF EQUILIBRIUM

As mentioned before, in Fig. 6 each intersection of the two curves represents a state of equilibrium. To ascertain the stability of the state of equilibrium, we follow a familiar approach [15] and invoke a free-energy function. We regard all parts—the elastomer, the surface, the gas inside the chamber and the bubble, and the external environment—together as a thermodynamic system. Write the free energy of the system as

$$F = F_{elastomer} + F_{surface} + F_{gas} + F_{environment}. \quad (11)$$

The first contribution to the free energy comes from the elasticity of the elastomer,  $F_{elastomer} = \int W dV$ , where the integral extends over the volume of the elastomer and  $dV = (4\pi/3)d(r^3) = -4\pi(a^3 - A^3)\lambda^2/(\lambda^3 - 1)^2 d\lambda$ . Consequently, the elastic energy stored in the elastomer is

$$F_{elastomer} = 4\pi(a^3 - A^3) \int_1^{a/A} \frac{\lambda^2 W(\lambda)}{(\lambda^3 - 1)^2} d\lambda. \quad (12)$$

The second contribution to the free energy comes from the surface tension:

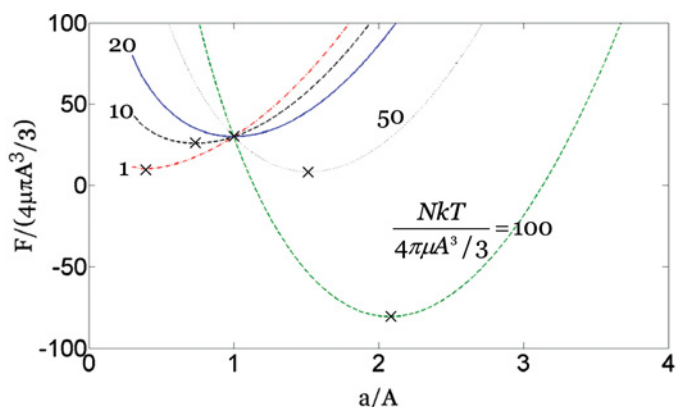
$$F_{surface} = 4\pi a^2 \gamma. \quad (13)$$

The third contribution to the free energy comes from the gas molecules inside the bubble and the chamber. When the volume occupied by  $N$  molecules increases from  $V_0$  to  $V$ , the entropy of the gas increases by  $\Delta S = kN \log(V/V_0)$ , and the free energy of the gas decreases by  $F_{gas} = -T\Delta S = -NkT \log(V/V_0)$ . Thus,

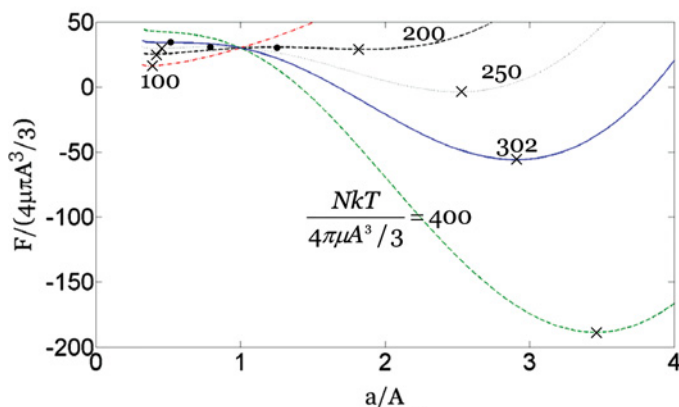
$$F_{gas} = -NkT \log \left( \frac{4\pi a^3/3 + V_{chamber}}{4\pi A^3/3 + V_{chamber}} \right). \quad (14)$$

The fourth contribution to the free energy comes from the environment outside the elastomer. Because the elastomer is taken to be incompressible, an increase in the volume of the bubble causes a decrease by the same amount in the volume of the environment, so that

$$F_{environment} = p_0 4\pi a^3 / 3. \quad (15)$$



(a)  $J_{lim}=80$ ,  $\gamma/(\mu A)=10$ ,  $V_{chamber}=0$ ,  $p_o/\mu=0$



(b)  $J_{lim}=80$ ,  $\gamma/(\mu A)=10$ ,  $\frac{V_{chamber}}{4\pi A^3/3} = 10$ ,  $p_o/\mu=0$

**FIGURE 9** The free energy of the system as a function of the stretch of the bubble. (a)  $V_{chamber}=0$ . (b)  $V_{chamber}/4\pi A^3/3=10$  (color figure available online).

The thermodynamic system has a single degree of freedom: the radius of the bubble,  $a$ . Consequently, the free energy of the system is a function of a single variable,  $F(a)$ . By setting  $dF(a)/da = 0$ , we recover the condition of equilibrium (1).

Figure 9 plots the free energy of the system as a function of the radius of the bubble,  $F(a)$ . In the absence of the chamber,  $V_{chamber} = 0$ , for a given number of air molecules, the bubble can attain only one stable state of equilibrium, corresponding to the minimal free energy (Fig. 9a). In other words, the bubble cannot snap if no additional air molecules rush into it, which is consistent with the results shown in Fig. 4. In this case, the states of equilibrium are stable even when the pressure drops.

When the volume of the chamber is sufficiently large, however, the bubble can snap. As shown in Fig. 9b, when  $NkT/(4\mu\pi A^3/3) = 100$  or 400, the bubble can attain only one stable state corresponding to a global minimum of the free energy. When  $NkT/(4\mu\pi A^3/3) = 200$  or 250, the states of equilibrium with the smallest and largest stretches are stable, while the state of equilibrium with the middle stretch is unstable and corresponds to a local maximum. Note that at  $NkT/(4\mu\pi A^3/3) = 200$ , the two points of minimum free energy are at about the same height. These two states correspond to  $P_2$  and  $P_4$  on Fig. 6. To jump from state  $P_2$  to state  $P_4$ , the bubble needs to overcome an energy barrier. This energy barrier decreases as the number of gas molecules increases, and disappears at  $NkT/(4\mu\pi A^3/3) = 302$ , when the local minimum and the local maximum merge to form a point with vanishing second derivative. The bubble snaps to the stable state of equilibrium corresponding to the global minimum. This result is consistent with that shown in Fig. 6.

## 5. CONCLUDING REMARKS

When air is injected into a bubble in a soft material, the bubble may first expand gradually, and then snap suddenly to a large size. We study the snap-through instability by analyzing a model that accounts for both the surface tension and the limiting stretch of the elastomer. The surface tension causes the Laplace pressure, which is large for a small bubble, and falls when the bubble expands. The pressure due to the elasticity of the elastomer increases monotonically with the radius of the bubble, and rises steeply when the stretch of the bubble approaches the limiting stretch. We show that the bubble snaps to a large size only if a sufficient number of gas molecules can rush into the bubble at the onset of instability.

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