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BUBBLE GROWTH FROM FIRST PRINCIPLES

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BUBBLE GROWTH FROM FIRST PRINCIPLES

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We consider the simplest relevant problem in the foaming of molten plastics, the growth of a single bubble in a sea of highly viscous Newtonian fluid, and without interference from other bubbles. This simplest problem has defied accurate solution from first principles. Despite plenty of research on foaming, classical approaches from first principles have neglected the temperature rise in the surrounding fluid, and we find that this oversimplification greatly accelerates bubble growth prediction. We use a transport phenomena approach to analyze the growth of a solitary bubble, expanding under its own pressure. We consider a bubble of ideal gas growing without the accelerating contribution from mass transfer into the bubble. We explore the roles of viscous forces, fluid inertia, and viscous dissipation. We find that bubble growth depends upon the nucleus radius and nucleus pressure. We begin with a detailed examination of the classical approaches (thermodynamics without viscous heating). Our failure to fit experimental data with these classical approaches, sets up the second part of our paper, a novel exploration of the essential decelerating role of viscous heating. We explore both isothermal and adiabatic bubble expansion, and also the decelerating role of surface tension. The adiabatic analysis accounts for the slight deceleration due to the cooling of the expanding gas, which depends on gas polyatomicity. We also explore the pressure profile, and the components of the extra stress tensor, in the fluid surrounding the growing bubble. These stresses can eventually be frozen into foamed plastics. We find that our new theory compares well with measured bubble behavior.

Keywords: cellular plastics, plastics foam, bubble growth, bubble expansion, foaming, bubble polyatomicity

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I. INTRODUCTION

The polymer foam physical properties, such as density, elastic modulus, or tensile and impact strengths, are governed by bubble size (see Chapter 2 of [1]). We use the transport phenomena approach to analyze, from *first principles*, the growth of a solitary bubble of an ideal gas in a highly viscous Newtonian liquid under its own internal gas pressure. By *first principles*, we mean the thermodynamics of an expanding ideal gas, the macroscopic energy balance on the surrounding fluid, the constitutive equation for a Newtonian fluid, the equation of motion and the equation of energy. In the latter, we include the term for viscous dissipation in the surrounding fluid. Our analysis proceeds without reversion to empiricism, and we compare our results to carefully measured bubble growth behavior (see Fig. 4. of [7]). This work deepens our understanding of bubble growth in molten plastics, be it wanted, as in the production of plastics foams (also called cellular plastics) [2], or unwanted, as in the formation of voids in injection molded parts (see FIG. 7a of [3]).

Whereas previous work on related problems require the gas pressure in the bubble to be known as a function of time (see, for example, pp. 479-481 of [4]) or its growth rate to be known and constant (see Problem 3-10 of [5]), our analysis predicts the descent of the bubble's internal pressure. We caution that we do not expect the results of this work to apply to systems once they concentrate with bubbles (see, for example, Problem 4D.1. of [6]; see also [7,8,9]), where the fluid displacements caused by growing bubbles interfere with one another (see Figure in [10] for how to calculate when this interference might begin [10]). Nor do we expect this work to apply wherever there is significant mass flux across the bubble interface [11,12,13,14,15,16,17,18,19,20,21]. However, we do expect our work to be a suitable baseline for analysis of cases with bubble interference, or with mass flux across the bubble surface.

Furthermore, the nucleation details are beyond the scope of this work since our work focuses on what happens after the nucleus forms. To apply our work, we must either know or fit two initial conditions: the nucleus radius R_0 , and its nucleus pressure, p_0 .

II. FLUID MECHANICS

We begin by applying the equation of continuity in spherical coordinates to the liquid surroundings and thus displaced by the growing bubble (Eq. (B.4-3) of [[22]]):

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (\rho r^2 v_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\rho v_\theta \sin \theta) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} (\rho v_\phi) = 0 \quad (1)$$

which, subject to our physical intuition for velocity without swirl ([23], see also Problem 3-6 of [5]):

$$v_r(r); v_\theta = v_\phi = 0 \quad (2)$$

and subject to the assumption of constant liquid density. Eq. (1) simplifies to:

$$\frac{d}{dr}(r^2 v_r) = 0 \quad (3)$$

At the bubble boundary:

$$v_r(R) = \dot{R} \equiv \frac{dR}{dt}; R(t) \quad (4)$$

so that Eq. (3) gives:

$$v_r = \frac{R^2 \dot{R}}{r^2} \quad (5)$$

which matches Eq. (1) of [24], the first equation of Article 158 of [25] and Eq. (1) of [32]. Hence:

$$\frac{dv_r}{dr} = \frac{-2R^2 \dot{R}}{r^3} \quad (6)$$

Figure 1 defines our spherical coordinates, as well as the dimensional variables for our analysis. The results of this section thus apply to all of the cases treated below.

III. GAS-FLUID THERMODYNAMICS WITHOUT VISCOUS HEATING

In the foaming of plastics, tiny bubbles nucleate at high internal pressure, and the forces exerted by this pressure on the bubble wall then do work on the surrounding liquid. Bubble growth then begins. In this section, we give a detailed examination of classical approaches to bubbles, growth [4,5] or collapse [24,31,32], which ignore the complication of viscous dissipation in the liquid surrounding the growing bubble, and thus neglect the temperature rise in this liquid. For all variants of the classical approach, whether we include surface tension or not, or whether we model the gas expansion as adiabatic or as isothermal, we find overprediction of the bubble growth rate by orders of magnitude. In this section, we will discover a characteristic time for bubble growth, λ_b , which we will then use throughout this paper to nondimensionalize the interval since nucleation, t .

i. ISOTHERMAL EXPANSION WITHOUT SURFACE TENSION

If we neglect surface tension, the work done by the isothermal expansion of the bubble on the surrounding fluid is:

$$W = -\int_{V_0}^V (p_R - p_\infty) dV = -\int_{V_0}^V \left(\frac{p_0 V_0}{V} - p_\infty \right) dV \quad (7)$$

since, for the isothermal expansion of an ideal gas:

$$p_R V = p_0 V_0 \quad (8)$$

Hence, when the far field pressure is nonzero, the bubble does less work on its surroundings. By our sign convention, *the bubble's work on its surroundings is negative, for a growing bubble.*

If the bubble behaves as an ideal gas, and if its expansion is isothermal, then:

$$W = -p_0 V_0 \int_{V_0}^V \frac{1}{V} dV + p_\infty (V - V_0) = -3p_0 V_0 \log \frac{R}{R_0} + \frac{4\pi p_\infty}{3} (R^3 - R_0^3) \quad (9)$$

where R_0 is the nucleus radius, p_0 is the pressure of the nucleated bubble, and $\log x$ is the natural logarithm of the quantity x (see Subsection III.iii and III.iv for analysis of an adiabatic bubble expansion). We are thus here supposing that the bubble nucleation is isothermal. For a spherical bubble, Eq. (9) yields:

$$W = -4\pi p_0 R_0^3 \log \frac{R}{R_0} + \frac{4\pi p_\infty}{3} (R^3 - R_0^3) \quad (10)$$

The instantaneous kinetic energy in all of the fluid surrounding the bubble is then given by (see Eq. (2) of [24]):

$$E_k = \int_0^{2\pi} \int_0^\pi \int_R^\infty \frac{1}{2} \rho v_r^2 r^2 dr \sin\theta d\theta d\phi = 2\pi\rho \int_R^\infty v_r^2 r^2 dr \quad (11)$$

which matches Eq. (2) of [24]. Substituting Eq. (5) into Eq. (11) gives:

$$E_k = 2\pi\rho \int_R^\infty \left(\frac{R^2 \dot{R}}{r^2} \right)^2 r^2 dr = 2\pi\rho R^4 \dot{R}^2 \int_R^\infty \frac{dr}{r^2} = 2\pi\rho R^4 \dot{R}^2 \left(\frac{-1}{r} \right) \Big|_R^\infty = 2\pi\rho R^3 \dot{R}^2 \quad (12)$$

Following the classical approach, we *neglect the viscous heating* in the fluid surrounding the growing bubble (see Section V below for a detailed treatment of this viscous heating). We can thus assume that all of the work done by the bubble on the fluid is converted to kinetic energy, and thus:

$$E_k = -W \quad (13)$$

so [from Eqs. (12) and (10)]:

$$\rho R^3 \dot{R}^2 = 2p_0 R_0^3 \log \frac{R}{R_0} - \frac{2p_\infty}{3} (R^3 - R_0^3) \quad (14)$$

For the special case of a collapsing cavity, for which $p_0 = 0$, we find that Eq. (14) matches Eq. (4) of [24], as it should. Introducing the dimensionless bubble radius:

$$\bar{r} \equiv R/R_0 \quad (15)$$

yields:

$$\frac{\rho R_0^2}{p_\infty} \bar{r}^3 \left(\frac{d\bar{r}}{dt} \right)^2 = 2\Pi \log \bar{r} - \frac{2}{3} (\bar{r}^3 - 1) \quad (16)$$

where:

$$\Pi \equiv p_0/p_\infty \quad (17)$$

from which we uncover a *characteristic time* for the initial bubble growth:

$$\lambda_b \equiv R_0 \sqrt{\rho/p_\infty} \quad (18)$$

and thus:

$$\lambda_b^2 \bar{r}^3 \left(\frac{d\bar{r}}{dt} \right)^2 = 2\Pi \log \bar{r} - \frac{2}{3} (\bar{r}^3 - 1) \quad (19)$$

Adimensionalizing the time elapsed since nucleation with:

$$\Theta \equiv t/\lambda_b \quad (20)$$

yields:

$$\bar{r}^3 \left(\frac{d\bar{r}}{d\Theta} \right)^2 = 2\Pi \log \bar{r} - \frac{2}{3}(\bar{r}^3 - 1) \quad (21)$$

Differentiating Eq. (21) with respect to Θ and rearranging gives:

$$\frac{d^2\bar{r}}{d\Theta^2} + \frac{3}{2\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{1}{\bar{r}} \left[\frac{\Pi}{\bar{r}^3} - 1 \right] = 0 \quad (22)$$

which is a *homogeneous nonlinear* second order ordinary differential equation, whose nonlinearity comes from the kinetic energy alone. Eq. (22) predicts ringing in $\bar{r}(\Theta)$ when:

$$\frac{3\Pi \log \bar{r}}{(\bar{r}^3 - 1)} < 1 \quad (23)$$

This ringing is not to be confused with the small resonant oscillations of a bubble about its spherical form at a constant mean radius (associated with oscillation of the bubble density). These resonant oscillations, of course, require surface tension (see Eq. 12 of Art. 275. of [31]).

Eq. (22) is the governing equation for isothermal bubble expansion without surface tension and without viscous dissipation, for which we know of no general analytical solution. Eq. (21) is subject to the initial condition:

$$\bar{r}(0) = 1 \quad (24)$$

and is the main result of this section. We obtained Eq. (21) by combining the continuity equation, Eq. (1), with the bubble thermodynamics, Eqs. (7) and (11), and without the use of the equation of motion, Eq. (170). Eq. (21) is thus a universal result for the isothermal expansion of a nucleated bubble of an ideal gas in any fluid. In the absence of viscous dissipation, bubble growth is thus independent of the fluid rheology. Only later do we make use of Eq. (170), and this in combination with Eq. (21), to get the pressure profile in the liquid surrounding the growing bubble (see Subsections IV.i and IV.ii). One consequence of Eq. (21) is that it predicts zero for the initial growth rate:

$$\left. \frac{d\bar{r}}{d\Theta} \right|_{\bar{r}=1} = 0 \quad (25)$$

Hence, the nucleus always begins to grow from rest. Otherwise put, the bubble nucleates at rest. Street supposes Eq. (25) in his analysis of viscoelastic bubble growth (see after Eq. (21) of [26]).

Eq. (22) yields no analytical solution. We solve Eq. (22) subject to Eqs. (24) and (25) using the Fehlberg fourth-fifth order Runge-Kutta method with degree four interpolant (see [27]). We use this method throughout [to solve Eqs. (22), (31), (37), (41), (123), (129), (137) and (143)]. We coded each of these equations into MATLAB (Version R2012b), and employed specifically the *ode23s* subroutine. On a MacBook Air (1.3 GHz Intel Core i5 processor with 4GB 1600MHz DDR3 memory) employing the OS X Yosemite (Version 10.10.2) operating system, we find each such bubble growth computation to consume less than 5 seconds of CPU time.

In this subsection, we explored the result of the classical approach to bubble growth, given by Eq. (21), and its implications, because it represents the main motivation for the work below. Since Eq. (21) overpredicts the bubble growth

rate, in Subsection III.ii we will examine the decelerating effect of surface tension, and in Subsections III.iii and III.iv, the decelerating effect of the cooling of the expanding gas (adiabatic bubble growth).

ii. ISOTHERMAL EXPANSION WITH SURFACE TENSION

The interfacial tension between the bubble gas and the surrounding liquid decelerates bubble growth because with surface tension, the bubble does less work on the surrounding fluid. Thus far, we have neglected this interfacial tension, but we incorporate this here by improving Eq. (7) to:

$$\begin{aligned} W &= -\int_{V_0}^V (p_R - p_\infty) dV + \sigma (S - S_0) \\ &= -\int_{V_0}^V \left(\frac{n\mathcal{R}T}{V} - p_\infty \right) dV + 4\pi\sigma (R^2 - R_0^2) \end{aligned} \quad (26)$$

Eq. (10) thus improves to:

$$W = -4\pi p_0 R_0^3 \log \frac{R}{R_0} + \frac{4\pi p_\infty}{3} (R^3 - R_0^3) + 4\pi\sigma (R^2 - R_0^2) \quad (27)$$

and Eq. (14) to:

$$\rho R^3 \dot{R}^2 = 2p_0 R_0^3 \log \frac{R}{R_0} - \frac{2p_\infty}{3} (R^3 - R_0^3) - 2\sigma (R^2 - R_0^2) \quad (28)$$

Using Eq. (15) we get:

$$\bar{r}^3 \left(\frac{d\bar{r}}{d\Theta} \right)^2 = 2\Pi \log \bar{r} - \frac{2}{3} (\bar{r}^3 - 1) - \Sigma (\bar{r}^2 - 1) \quad (29)$$

where:

$$\Sigma \equiv 2\sigma / p_\infty R_0 \quad (30)$$

Differentiating Eq. (29) with respect to Θ and rearranging gives:

$$\frac{d^2 \bar{r}}{d\Theta^2} + \frac{3}{2\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{1}{\bar{r}} \left[\frac{\Pi}{\bar{r}^3} - 1 - \frac{\Sigma}{\bar{r}} \right] = 0 \quad (31)$$

which we solve numerically [see after Eq. (25)]. Eq. (30) reduces to Eq. (22) in the absence of surface tension, $\Sigma = 0$, as it should.

In this section, we discovered that surface tension decelerates bubble growth and that *ringing* remains. For molten plastics, we will find this deceleration to be less than one order of magnitude. Thus, Eqs. (22) and (31) predict the same qualitative behavior discussed in Subsection III.i.

iii. ADIABATIC EXPANSION WITHOUT SURFACE TENSION

In Subsections III.i and III.ii above, we arrived at predictions for the bubble growth by considering only the isothermal expansion of the gas in the bubble. If we now assume that the bubble expansion is adiabatic, the bubble cools as it expands, and this will decelerate its growth. Whereas isothermal expansion occurs identically for all ideal gasses, the adiabatic expansion will differ from

monatomic, to diatomic, to polyatomic gases, and so the deceleration of the growth rate, we will see, will depend upon the molecular structure (polyatomicity) of the expanding gas. As the molecular structure of the foaming gas goes from monatomic, to diatomic, to polyatomic, the bubble growth will slightly accelerate. This is one reason that carbon dioxide ($\gamma_{\text{CO}_2} \approx 1.28$) is often chosen over steam ($\gamma_{\text{H}_2\text{O}} \approx 1.34$), air ($\gamma_{\text{Air}} \approx 1.40$) and nitrogen ($\gamma_{\text{N}_2} \approx 1.40$) for foam manufacture (γ values given for 15.6°C and 1atm, taken from Pages 34-6 – 34-7 [28]).

The adiabatic and isothermal analyses thus yield lower and upper bounds for the final bubble size. To decide by how much the bubble will cool, we use (see Eq. (3.30a) of [29] or Eq. (1-33a) of [30]):

$$\frac{T}{T_0} = \frac{V_0^{\gamma-1}}{V^{\gamma-1}} = \left(\frac{V_0}{V}\right)^{\gamma-1} = \left(\frac{R_0}{R}\right)^{3(\gamma-1)} \quad (32)$$

so that if $\gamma > 1$, $dT/dR < 0$, and the bubble cools when it expands adiabatically.

For adiabatic bubble expansion:

$$pV^\gamma = p_0V_0^\gamma \quad (33)$$

(see for example Eq. (4) of [32]; Eq. (7) of Article 91 a. in [31]; see Eq. (3.30c) of [29]; Eq. (1-33b) of [30]; compare Eq. (33) with Eq. (8)). Thus, if we neglect surface tension, the work done on the surrounding fluid by adiabatic bubble expansion is:

$$\begin{aligned} W &= -\int_{V_0}^V \frac{p_0V_0^\gamma}{V^\gamma} dV + p_\infty(V - V_0) \\ &= \frac{-p_0}{1-\gamma} \frac{4\pi R_0^3}{3} \left(\left[\frac{R}{R_0} \right]^{3(1-\gamma)} - 1 \right) + \frac{4\pi R_0^3 p_\infty}{3} \left(\left[\frac{R}{R_0} \right]^3 - 1 \right) \end{aligned} \quad (34)$$

where $\gamma \equiv C_p/C_v$. For a treatment of adiabatic bubble collapse without surface tension in a fluid under perfect vacuum (zero far field pressure [$p_\infty = 0$]), see Article 91 a. of [31] or see also Eq. (14) et seq. of [32].

If we neglect the viscous heating in the fluid surrounding the growing bubble (see Section V below for a detailed treatment of this viscous heating), we can assume that all of the work done by the bubble on the fluid is converted to kinetic energy, and thus, $E_k = -W$, so [from Eqs. (12) and (34)]:

$$\rho R^3 \dot{R}^2 = \frac{p_0}{1-\gamma} \frac{2R_0^3}{3} \left(\left[\frac{R}{R_0} \right]^{3(1-\gamma)} - 1 \right) - \frac{2R_0^3 p_\infty}{3} \left(\left[\frac{R}{R_0} \right]^3 - 1 \right) \quad (35)$$

If we set $p_0 = 0$ in Eq.(35), we get a correction to Eq. (15) of [32] or to Eq. (8) of [31]. Adimensionalizing yields:

$$\bar{r}^3 \left(\frac{d\bar{r}}{d\Theta} \right)^2 = \frac{\Pi}{1-\gamma} \frac{2}{3} \left(\bar{r}^{3(1-\gamma)} - 1 \right) - \frac{2}{3} (\bar{r}^3 - 1) \quad (36)$$

and then differentiating with respect to Θ gives:

$$\frac{d^2\bar{r}}{d\Theta^2} + \frac{3}{2\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\Pi\bar{r}^{-3\gamma} - 1}{\bar{r}} = 0 \quad (37)$$

which we solve numerically [see after Eq. (25)]. When $\gamma = 1$, Eq. (37) reduces to Eq.(22), our result for the isothermal bubble expansion, as it should.

In this section we discovered that with adiabatic expansion of the gas, we obtain deceleration of bubble growth and that *ringing* remains. For molten plastics, we will find this deceleration to be less than one order of magnitude. Thus, Eqs. (22) and (37) predict the same qualitative behavior discussed in Subsection III.i.

iv. ADIABATIC EXPANSION WITH SURFACE TENSION

We here add the decelerating effect of surface tension to the adiabatic analysis of the previous Subsection III.iii. If we include surface tension, we can follow the method of Subsection III.ii to improve Eq. (34) to:

$$\begin{aligned} W &= - \int_{V_0}^V \frac{p_0 V_0^\gamma}{V^\gamma} dV + p_\infty (V - V_0) + \sigma (S - S_0) \\ &= \frac{-p_0}{1-\gamma} \frac{4\pi R_0^3}{3} \left(\left[\frac{R}{R_0} \right]^{3(1-\gamma)} - 1 \right) + \frac{4\pi R_0^3 p_\infty}{3} \left(\left[\frac{R}{R_0} \right]^3 - 1 \right) + 4\pi\sigma (R^2 - R_0^2) \end{aligned} \quad (38)$$

and Eq. (35) to:

$$\rho R^3 \dot{R}^2 = \frac{p_0}{1-\gamma} \frac{2R_0^3}{3} \left(\left[\frac{R}{R_0} \right]^{3(1-\gamma)} - 1 \right) - \frac{2R_0^3 p_\infty}{3} \left(\left[\frac{R}{R_0} \right]^3 - 1 \right) - 2\sigma (R^2 - R_0^2) \quad (39)$$

which adimensionalized to:

$$\bar{r}^3 \left(\frac{d\bar{r}}{d\Theta} \right)^2 = \frac{\Pi}{1-\gamma} \frac{2}{3} \left(\bar{r}^{3(1-\gamma)} - 1 \right) - \frac{2}{3} (\bar{r}^3 - 1) - \Sigma (\bar{r}^2 - 1) \quad (40)$$

Differentiating Eq. (40) with respect to Θ gives:

$$\frac{d^2\bar{r}}{d\Theta^2} + \frac{3}{2\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\Pi\bar{r}^{-3\gamma} - 1}{\bar{r}} + \frac{\Sigma}{\bar{r}^2} = 0 \quad (41)$$

which we solve numerically [see after Eq. (25)]. When $\gamma = 1$, Eq. (41) reduces to Eq. (31), the result for the isothermal bubble expansion, as it should.

In this section, we discovered that, although the combination of surface tension with adiabatic expansion, we will find the deceleration from this combination to be less than one order of magnitude. Thus, Eqs. (31) and (41) predict the same qualitative behavior discussed in Subsection III.i.

IV. FLUID PRESSURE: **WITHOUT VISCOUS HEATING**

If we neglect both gravity and fluid inertia, Eq. (177) reduces to:

$$\frac{\partial p}{\partial r} = 0 \quad (42)$$

which is unphysical. From this we learn that fluid inertia [the left sides of Eqs. (170) or (172)] is never negligible. Some assume otherwise (see, for example, just above Eq. (22) of [33]).

If we neglect gravity, but not fluid inertia, Eq. (177) reduces to:

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = \frac{-\partial p}{\partial r} \quad (43)$$

which matches Eq. (9) of [24]. We can rewrite this in terms of the bubble radius by substituting Eqs. (5) and (6) into Eq. (43), which then yields:

$$\frac{\partial(R^2 \dot{R})}{\partial t} - \frac{2R^4 \dot{R}^2}{r^3} = -\frac{r^2}{\rho} \frac{\partial p}{\partial r} \quad (44)$$

where $p(r, t)$ and $R(t)$.

From the chain rule:

$$\frac{\partial(R^2 \dot{R})}{\partial t} = 2R\ddot{R} + R^2 \frac{d^2 R}{dt^2} \quad (45)$$

which corrects the second unnumbered equation after Eq. (9) in [24].

Substituting Eq. (45) into Eq. (44) gives:

$$2\frac{\dot{R}^2}{R} \left(1 - \frac{R^3}{r^3} \right) + \frac{d^2 R}{dt^2} = -\frac{r^2}{\rho R^2} \frac{\partial p}{\partial r} \quad (46)$$

Integrating and rearranging Eq. (46) thus gives:

$$\frac{p}{\rho} = \frac{R^2 \ddot{R} - 2R\dot{R}^2}{r} - \frac{R^4 \dot{R}^2}{2r^4} \quad (47)$$

which matches with Eq. (2) of [32]. Eq. (46) applies to the fluid surrounding any growing bubble, and we will use Eq. (46) to arrive at analytical solutions for the fluid pressure for cases without viscous heating (in Subsections IV.i through IV.iv), and also where the decelerating effect of viscous heating in the surrounding fluid is considered (in Subsection VI.iii through VI.iv).

i. ISOTHERMAL GROWTH WITHOUT SURFACE TENSION

We now use our result from the thermodynamics of the isothermal bubble expansion without surface tension (Subsection III.i). Solving Eq. (14) gives:

$$\dot{R}^2 = \frac{2}{\rho} \left[\frac{p_0 R_0^3}{R^3} \log \frac{R}{R_0} - \frac{p_\infty}{3} \left(1 - \frac{R_0^3}{R^3} \right) \right] \quad (48)$$

and then differentiating gives:

$$2\dot{R}\ddot{R} = \frac{2p_0}{\rho} \left\{ -3\frac{R_0^3}{R^4} \dot{R} \log \frac{R}{R_0} + \frac{R_0^3}{R^3} \frac{R_0}{R} \frac{\dot{R}}{R_0} \right\} - \frac{2p_\infty}{3\rho} \left(3\frac{R_0^3}{R^4} \dot{R} \right) \quad (49)$$

and then cancelling coefficients leads to:

$$\ddot{R} = \frac{1}{\rho} \frac{R_0^3}{R^4} \left[p_0 \left\{ -3 \log \frac{R}{R_0} + 1 \right\} - p_\infty \right] \quad (50)$$

Differentiating Eq. (48) and then substituting Eq. (48) into the result, yields:

$$\ddot{R} \equiv \frac{d^2 R}{dt^2} = \frac{-R_0^3}{\rho R^4} \left(3p_0 \log \frac{R}{R_0} + p_\infty - p_0 \right) \quad (51)$$

Substituting Eq. (51) into Eq. (46) yields:

$$\frac{\partial p}{\partial r} = \frac{-\rho}{r^2} \left\{ 2R\dot{R}^2 \left(1 - \frac{R^3}{r^3} \right) - \frac{R_0^3}{\rho R^2} \left(3p_0 \log \frac{R}{R_0} + p_\infty - p_0 \right) \right\} \quad (52)$$

which has solution:

$$p = p_\infty - \frac{1}{4r^4} \left(\rho 2R\dot{R}^2 R^3 + r^3 \left[4 \frac{R_0^3}{R^2} \left(3p_0 \log \frac{R}{R_0} + p_\infty - p_0 \right) - 4\rho 2R\dot{R}^2 \right] \right) \quad (53)$$

which can be adimensionalized to:

$$\mathcal{P} = 1 - \frac{R^4}{2r^4} \left(\frac{\rho \dot{R}^2}{p_\infty} + 2 \frac{r^3}{R^3} \left[\frac{R_0^3}{R^3} \left(3\Pi \log \frac{R}{R_0} + 1 - \Pi \right) - \frac{2\rho \dot{R}^2}{p_\infty} \right] \right) \quad (54)$$

where $\mathcal{P} \equiv p/p_\infty$. Substituting Eq. (48) into Eq. (54) yields:

$$\mathcal{P} = 1 - \frac{1}{2\zeta^4} \left(\frac{2\Pi}{\bar{r}^3} \log \bar{r} - \frac{2}{3} \left(1 - \frac{1}{\bar{r}^3} \right) + 2\zeta^3 \left[\frac{1}{\bar{r}^3} (3\Pi \log \bar{r} + 1 - \Pi) - 4 \left[\frac{\Pi}{\bar{r}^3} \log \bar{r} - \frac{1}{3} \left(1 - \frac{1}{\bar{r}^3} \right) \right] \right] \right) \quad (55)$$

where $\zeta \equiv r/R$. Eq. (55) gives the dimensionless pressure p/p_∞ as a function of dimensionless position in the fluid that surrounds the bubble, ζ , for each stage of bubble growth, $\bar{r}$, for any pressure ratio, Π . From Eq. (22) we learned that, without viscous dissipation, bubble growth is independent of the fluid rheology, and from Eq. (55) we now learn that the developing pressure around the growing bubble is too.

At nucleation, when $\bar{r} = 1$, Eq. (55) gives:

$$\mathcal{P} = 1 + \frac{\Pi - 1}{\zeta} \quad (56)$$

which gives the initial value of $\mathcal{P} = \Pi$ at the bubble surface, as it should. Also, at the final position, when $\bar{r} = \bar{r}_f$, Eq. (55) predicts $\mathcal{P}(\zeta) = 1$, as it should.

Adimensionalizing Eq. (52) gives:

$$\frac{\partial \mathcal{P}}{\partial r} = \frac{-\rho}{r^2} \left\{ \frac{2R\dot{R}^2}{p_\infty} \left(1 - \frac{R^3}{r^3} \right) - \frac{2R_0^3}{2\rho R^2} \left(3\Pi \log \frac{R}{R_0} + 1 - \Pi \right) \right\} \quad (57)$$

Substituting Eq. (48) into Eq. (57), and then introducing $\bar{r} \equiv R/R_0$ gives:

$$\frac{\partial \mathcal{P}}{\partial \zeta} = \frac{-1}{\zeta^2} \left\{ 4 \left[\frac{\Pi}{\bar{r}^3} \log \bar{r} - \frac{1}{3} \left(1 - \frac{1}{\bar{r}^3} \right) \right] \left(1 - \frac{1}{\zeta^3} \right) - \frac{1}{\bar{r}^3} (3\Pi \log \bar{r} + 1 - \Pi) \right\} \quad (58)$$

From which we learn that $\partial\mathcal{P}/\partial\zeta$ will change sign, from negative to positive, for all values of ζ , when:

$$\left[1 + 2\left[\frac{\Pi}{\bar{r}^3} - 1\right]\left(\frac{d\bar{r}}{d\Theta}\right)^{-2}\right]\zeta^3 < 4 \quad (59)$$

that is, when the bubble growth decelerates sufficiently. Evaluating Eq. (58) for the nucleus, when $\bar{r} = 1$ and $d\bar{r}/d\Theta$, gives:

$$\left.\frac{\partial\mathcal{P}}{\partial\zeta}\right|_{\bar{r}=1} = \frac{(1-\Pi)}{\zeta^2} \quad (60)$$

which is negative, and zero when $\Pi = 1$, as it should be.

ii. ISOTHERMAL GROWTH WITH SURFACE TENSION

We now use our thermodynamics of the isothermal bubble expansion with surface tension (Subsection III.ii), by solving Eq. (28):

$$\dot{R}^2 = \frac{2p_0 R_0^3}{\rho R^3} \log \frac{R}{R_0} - \frac{2p_\infty}{3\rho} \left(1 - \frac{R_0^3}{R^3}\right) - \frac{2\sigma}{\rho R} \left(1 - \frac{R_0^2}{R^2}\right) \quad (61)$$

Differentiating Eq. (61) and then substituting Eq. (61) into the result, yields:

$$\frac{d^2 R}{dt^2} = \frac{-R_0^3}{\rho R^4} \left(-\frac{R^2}{R_0^3} \sigma + \frac{3\sigma}{R_0} + 3p_0 \log \frac{R}{R_0} + p_\infty - p_0 \right) \quad (62)$$

which reduces to Eq. (51) for $\sigma = 0$, as it should. Substituting Eq. (62) into Eq. (46) yields:

$$\frac{\partial p}{\partial r} = \frac{-\rho}{r^2} \left[2R\dot{R}^2 \left(1 - \frac{R^3}{r^3}\right) - \frac{R_0^3}{\rho R^2} \left(-\frac{R^2}{R_0^3} \sigma + \frac{3\sigma}{R_0} + 3p_0 \log \frac{R}{R_0} + p_\infty - p_0 \right) \right] \quad (63)$$

which reduces to Eq. (52) for $\sigma = 0$, as it also should. Eq. (63) has solution:

$$p = p_\infty - \frac{1}{4r^4} \left(\rho 2R\dot{R}^2 R^3 + r^3 \left[4 \frac{R_0^3}{R^2} \left(-\frac{R^2}{R_0^3} \sigma + \frac{3\sigma}{R_0} + 3p_0 \log \frac{R}{R_0} + p_\infty - p_0 \right) - 4\rho 2R\dot{R}^2 \right] \right) \quad (64)$$

which reduces to Eq. (53) for $\sigma = 0$, as it must. Adimensionalizing Eq. (64) yields:

$$\mathcal{P} = 1 - \frac{R^4}{2r^4} \left(\frac{\rho \dot{R}^2}{p_\infty} + \frac{2r^3}{R^3} \left[\frac{R_0^3}{R^3} \left(\left[\frac{R^2}{R_0^3} - \frac{3}{R_0} \right] \left(\frac{-\sigma}{p_\infty} \right) + 3\Pi \log \frac{R}{R_0} + 1 - \Pi \right) - \frac{2\rho \dot{R}^2}{p_\infty} \right] \right) \quad (65)$$

Substituting Eq. (61) into Eq. (65) gives:

$$\mathcal{P} = 1 - \frac{1}{2\zeta^4} \left(\left[\frac{2\Pi}{\bar{r}^3} \log \bar{r} - \frac{2}{3} \left(1 - \frac{1}{\bar{r}^3} \right) - \frac{\Sigma}{\bar{r}} \left(1 - \frac{1}{\bar{r}^2} \right) \right] + 2\zeta^3 \left[\left(\frac{-\Sigma}{2\bar{r}} \left[1 - \frac{3}{\bar{r}^2} \right] + \frac{1}{\bar{r}^3} (3\Pi \log \bar{r} + 1 - \Pi) \right) - 4 \left[\frac{\Pi}{\bar{r}^3} \log \bar{r} - \frac{1}{3} \left(1 - \frac{1}{\bar{r}^3} \right) - \frac{\Sigma}{2\bar{r}} \left(1 - \frac{1}{\bar{r}^2} \right) \right] \right] \right) \quad (66)$$

which reduces to Eq. (55) for $\Sigma = 0$, as it should. Also, when $\bar{r} = \bar{r}_f$, Eq. (66)

predicts $\mathcal{P}(\zeta) = 1$, as it must. Differentiating Eq. (66) with respect to ζ gives:

$$\frac{\partial \mathcal{P}}{\partial \zeta} = \left[\frac{2\Pi}{\bar{r}^3} \log \bar{r} - \frac{2}{3} \left(1 - \frac{1}{\bar{r}^3} \right) - \frac{\Sigma}{\bar{r}} \left(1 - \frac{1}{\bar{r}^2} \right) \right] \frac{2}{\zeta^5} + \left[\left(\frac{-\Sigma}{2\bar{r}} \left[1 - \frac{3}{\bar{r}^2} \right] + \frac{1}{\bar{r}^3} (3\Pi \log \bar{r} + 1 - \Pi) \right) - 4 \left[\frac{\Pi}{\bar{r}^3} \log \bar{r} - \frac{1}{3} \left(1 - \frac{1}{\bar{r}^3} \right) - \frac{\Sigma}{2\bar{r}} \left(1 - \frac{1}{\bar{r}^2} \right) \right] \right] \frac{1}{\zeta^2} \quad (67)$$

Evaluating Eq. (67) for the nucleus, when $\bar{r} = 1$, gives:

$$\left. \frac{\partial \mathcal{P}}{\partial \zeta} \right|_{\bar{r}=1} = \frac{1 + \Sigma - \Pi}{\zeta^2} \quad (68)$$

which implies:

$$\Sigma < \Pi - 1 \quad (69)$$

and which is negative, and zero when $\Pi = 1$, as it should be.

iii. ADIABATIC GROWTH WITHOUT SURFACE TENSION

Applying the procedure of Subsection IV.i to Eq. (35) yields:

$$\dot{R}^2 = \frac{2R_0^3}{3\rho} \left[\frac{p_0}{1-\gamma} \frac{1}{R^3} \left(\left[\frac{R}{R_0} \right]^{3(1-\gamma)} - 1 \right) - \frac{p_\infty}{R^3} \left(\left[\frac{R}{R_0} \right]^3 - 1 \right) \right] \quad (70)$$

and:

$$\frac{\partial p}{\partial r} = -\frac{\rho R^2}{r^2} \left(2 \frac{\dot{R}^2}{R} \left(1 - \frac{R^3}{r^3} \right) - \frac{R_0^3 \left(p_\infty - \frac{p_0}{1-\gamma} \right)}{\rho R^4} - \frac{\frac{p_0}{1-\gamma} \gamma}{\rho R \left[\frac{R}{R_0} \right]^{3\gamma}} \right) \quad (71)$$

which has solution:

$$p = p_\infty - \frac{\rho}{2r^4} \left(\frac{\dot{R}^2}{R} R^5 + 2r^3 R^2 \left[\frac{1}{\rho R} \left(\left(p_\infty - \frac{p_0}{1-\gamma} \right) \left[\frac{R_0}{R} \right]^3 + \frac{p_0}{1-\gamma} \gamma \left[\frac{R}{R_0} \right]^{3\gamma} \right) - 2 \frac{\dot{R}^2}{R} \right] \right) \quad (72)$$

which can be adimensionalized to:

$$\mathcal{P} = 1 - \frac{1}{\zeta^4} \left(\frac{\Pi}{3(1-\gamma)} \left(\frac{1}{\bar{r}^{3\gamma}} - \frac{1}{\bar{r}^3} \right) - \frac{1}{3} \left(1 - \frac{1}{\bar{r}^3} \right) + \zeta^3 \left[\left(1 - \frac{\Pi}{1-\gamma} \right) \frac{1}{\bar{r}^3} + \frac{\Pi\gamma}{(1-\gamma)\bar{r}^{3\gamma}} - \frac{4}{3} \left[\frac{\Pi}{1-\gamma} \left(\frac{1}{\bar{r}^{3\gamma}} - \frac{1}{\bar{r}^3} \right) - \left(1 - \frac{1}{\bar{r}^3} \right) \right] \right] \right) \quad (73)$$

which gives the dimensionless pressure $\mathcal{P} \equiv p/p_\infty$ as a function of dimensionless position in the fluid surrounding the bubble, ζ , for each stage of adiabatic bubble growth, $\bar{r}$, for any pressure ratio, Π . At nucleation, when $\bar{r} = 1$, Eq. (73) gives Eq. (56) as it should.

Adimensionalizing Eq. (71) gives:

$$\frac{\partial \mathcal{P}}{\partial r} = -\frac{\rho R^2}{r^2} \left(2 \frac{\dot{R}^2}{p_\infty R} \left(1 - \frac{R^3}{r^3} \right) - \frac{R_0^3 (1 - \frac{\Pi}{1-\gamma})}{\rho R^4} - \frac{\frac{\Pi}{1-\gamma} \gamma}{\rho R \left[\frac{R}{R_0} \right]^{3\gamma}} \right) \quad (74)$$

Substituting Eq. (70) into Eq. (74) yields:

$$\frac{\partial \mathcal{P}}{\partial \zeta} = -\frac{1}{\zeta^2} \left(\frac{4}{3} \left[\frac{1}{r^{-3\gamma}} \frac{\Pi}{1-\gamma} - \frac{1}{r^{-3}} \frac{\Pi}{(1-\gamma)} - 1 + \frac{1}{r^{-3}} \right] \left(1 - \frac{1}{\zeta^3} \right) - \left(\frac{1}{r^{-3\gamma}} \frac{\Pi}{1-\gamma} - \frac{1}{r^{-3}} \frac{\Pi}{1-\gamma} + \frac{1}{r^{-3}} - \frac{\Pi}{r^{-3\gamma}} \right) \right) \quad (75)$$

Evaluating Eq. (75) for the nucleus, when $\bar{r} = 1$, gives:

$$\left. \frac{\partial \mathcal{P}}{\partial \zeta} \right|_{\bar{r}=1} = \frac{(1-\Pi)}{\zeta^2} \quad (76)$$

which is negative, and zero when $\Pi = 1$, as it should be.

iv. ADIABATIC GROWTH WITH SURFACE TENSION

Applying the procedure of Section IV.ii to Eq. (39) yields:

$$\dot{R}^2 = \frac{1}{\rho R^3} \left[\frac{p_0}{1-\gamma} \frac{2R_0^3}{3} \left(\left[\frac{R}{R_0} \right]^{3(1-\gamma)} - 1 \right) - \frac{2R_0^3 p_\infty}{3} \left(\left[\frac{R}{R_0} \right]^3 - 1 \right) - 2\sigma (R^2 - R_0^2) \right] \quad (77)$$

and:

$$\frac{\partial p}{\partial r} = -\frac{\rho R^2}{r^2} \left(2 \frac{\dot{R}^2}{R} \left(1 - \frac{R^3}{r^3} \right) - \frac{R_0^3 \left(p_\infty - \frac{p_0}{1-\gamma} \right)}{\rho R^4} - \frac{\frac{p_0}{1-\gamma} \gamma}{\rho R \left[\frac{R}{R_0} \right]^{3\gamma}} + \frac{\sigma}{\rho R^2} \left(1 - 3 \left[\frac{R_0}{R} \right]^2 \right) \right) \quad (78)$$

which reduces to Eq. (71) for $\sigma = 0$, as it should. Eq. (78) has solution:

$$p = p_\infty - \frac{\rho}{2r^4} \left(R^4 \dot{R}^2 + 2r^3 R^2 \left[\frac{1}{\rho R} \left(\left(p_\infty - \frac{p_0}{1-\gamma} \right) \left[\frac{R_0}{R} \right]^3 + \frac{p_0}{1-\gamma} \gamma \left[\frac{R}{R_0} \right]^{3\gamma} - \frac{\sigma}{R} \left(1 - 3 \left[\frac{R_0}{R} \right]^2 \right) \right) \right] - 2 \frac{\dot{R}^2}{R} \right) \quad (79)$$

which reduces to Eq. (72) for $\sigma = 0$. Adimensionalizing Eq. (79) yields:

$$\mathcal{P} = 1 - \frac{1}{\zeta^4} \left(\frac{\Pi}{3(1-\gamma)} \left(\frac{1}{\bar{r}^{3\gamma}} - \frac{1}{\bar{r}^3} \right) - \frac{1}{3} \left(1 - \frac{1}{\bar{r}^3} \right) + \zeta^3 \left[\left(1 - \frac{\Pi}{1-\gamma} \right) \frac{1}{\bar{r}^3} + \frac{\Pi\gamma}{(1-\gamma)\bar{r}^{3\gamma}} - \frac{4}{3} \left[\frac{\Pi}{1-\gamma} \left(\frac{1}{\bar{r}^{3\gamma}} - \frac{1}{\bar{r}^3} \right) - \left(1 - \frac{1}{\bar{r}^3} \right) \right] + \frac{\Sigma}{2\bar{r}} \left[\zeta^3 \left(3 - \frac{1}{\bar{r}^2} \right) - \left(1 - \frac{1}{\bar{r}^2} \right) \right] \right] \right) \quad (80)$$

which reduces to Eq. (73) for $\Sigma = 0$, as it should. Also, when $\bar{r} = \bar{r}_f$, Eq. (80)

predicts $\mathcal{P}(\zeta) = 1$, as it should. Differentiating Eq. (80) with respect to ζ gives:

$$\frac{d\mathcal{P}}{d\zeta} = \left[\frac{4\Pi}{3(1-\gamma)} \left(\frac{1}{\bar{r}^{3\gamma}} - \frac{1}{\bar{r}^3} \right) - \frac{4}{3} \left(1 - \frac{1}{\bar{r}^3} \right) - \frac{2\Sigma}{\bar{r}} \left(1 - \frac{1}{\bar{r}^2} \right) \right] \frac{1}{\zeta^5} + \left[\left(1 - \frac{\Pi}{1-\gamma} \right) \frac{1}{\bar{r}^3} + \frac{\Pi\gamma}{(1-\gamma)\bar{r}^{3\gamma}} - \frac{4}{3} \left[\frac{\Pi}{1-\gamma} \left(\frac{1}{\bar{r}^{3\gamma}} - \frac{1}{\bar{r}^3} \right) - \left(1 - \frac{1}{\bar{r}^3} \right) \right] + \frac{\Sigma}{2\bar{r}} \left(3 - \frac{1}{\bar{r}^2} \right) \right] \frac{1}{\zeta^2} \quad (81)$$

Evaluating Eq. (81) for the nucleus, when $\bar{r} = 1$, gives:

$$\frac{d\mathcal{P}}{d\zeta} = \frac{1 + \Sigma - \Pi}{\zeta^2} \quad (82)$$

which implies:

$$\Sigma < \Pi - 1 \quad (83)$$

and which is negative, and zero when $\Pi = 1$, as it should be.

V. GAS-FLUID THERMODYNAMICS WITH VISCOUS HEATING

We have seen that, in the foaming of plastics, tiny bubbles nucleate at high internal pressure, and the forces exerted by this pressure on the bubble wall then do work on the surrounding liquid. Bubble growth then begins. In Subsections III.i through III.iv above, we explored bubble growth by neglecting viscous heating. We have also learned that the bubble expansion can either be modeled as isothermal or as adiabatic. However, in our Section VIII below we will learn

that even our best fits for any of these classical approaches (in Subsections III.i through III.iv above) to experimental observations are inaccurate. Specifically, even our best fits overpredict bubble growth rate by a factor of about *one billion*. We thus next explore the deceleration of bubble growth by viscous dissipation. We aim to see if this will relieve the overprediction that we get without viscous heating.

The energy equation, in term of internal energy, including viscous heating in its rightmost term, is given by (Eq. (11.2-2) or Eq. (G) of **Table 11.4-1** of [22]):

$$\rho \frac{D\hat{U}}{Dt} = -(\nabla \cdot \mathbf{q}) - p(\nabla \cdot \mathbf{v}) - (\boldsymbol{\tau} : \nabla \mathbf{v}) \quad (84)$$

where D/Dt is the substantial derivative, and thus, in our spherical coordinates, defined in Figure 1 [Eq. (B.8-3) of [22]):

$$\begin{aligned} \rho \hat{C}_p \left(\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + \frac{v_\theta}{r} \frac{\partial T}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial T}{\partial \phi} \right) \\ = - \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 q_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (q_\theta \sin \theta) + \frac{1}{r \sin \theta} \frac{\partial q_\phi}{\partial \phi} \right] - \left(\frac{\partial \log \rho}{\partial \log T} \right)_p \frac{Dp}{Dt} - (\boldsymbol{\tau} : \nabla \mathbf{v}) \end{aligned} \quad (85)$$

which, for bubble growth in a constant-density liquid, simplifies to:

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} \right) = - \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 q_r) \right] - (\boldsymbol{\tau} : \nabla \mathbf{v}) \quad (86)$$

where:

$$\begin{aligned} (\boldsymbol{\tau} : \nabla \mathbf{v}) = \tau_{rr} \left(\frac{\partial v_r}{\partial r} \right) + \tau_{\theta\theta} \left(\frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right) + \tau_{\phi\phi} \left(\frac{1}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r} + \frac{v_\theta}{r} \cot \theta \right) \\ + \tau_{r\theta} \left(\frac{1}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r} + \frac{\partial v_\theta}{\partial r} \right) + \tau_{r\phi} \left(\frac{1}{r \sin \theta} \frac{\partial v_r}{\partial \phi} - \frac{v_\phi}{r} + \frac{\partial v_\phi}{\partial r} \right) \\ + \tau_{\theta\phi} \left(\frac{1}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} - \frac{v_\phi}{r} \cot \theta + \frac{1}{r} \frac{\partial v_\phi}{\partial \theta} \right) \end{aligned} \quad (87)$$

which, subject to Eq. (2), simplifies to:

$$(\boldsymbol{\tau} : \nabla \mathbf{v}) = \tau_{rr} \left(\frac{\partial v_r}{\partial r} \right) + \tau_{\theta\theta} \left(\frac{v_r}{r} \right) + \tau_{\phi\phi} \left(\frac{v_r}{r} \right) \quad (88)$$

Substituting Eqs. (5) and (6) into Eq. (88), where $\tau_{\theta\theta} = \tau_{\phi\phi}$ [see Eq. (180)], gives:

$$(\boldsymbol{\tau} : \nabla \mathbf{v}) = \left(\frac{2R^2 \dot{R}}{r^3} \right) (-\tau_{rr} + \tau_{\theta\theta}) \quad (89)$$

We now perform a macroscopic balance with this viscous dissipation term, to get the total amount of energy dissipated in the fluid surrounding the growing bubble:

$$\begin{aligned} E_v = \int_0^t \int_0^{2\pi} \int_0^\pi \int_R^\infty -(\boldsymbol{\tau} : \nabla \mathbf{v}) r^2 dr \sin \theta d\theta d\phi dt \\ = 4\pi \int_0^t \int_R^\infty -(\boldsymbol{\tau} : \nabla \mathbf{v}) r^2 dr dt \end{aligned} \quad (90)$$

or substituting Eq. (89) into (90):

$$\begin{aligned}
E_v &= -4\pi \int_0^t \int_R^\infty \left(\frac{2R^2 \dot{R}}{r^3} \right) (-\tau_{rr} + \tau_{\theta\theta}) r^2 dr dt \\
&= 8\pi \int_0^t R^2 \dot{R} \int_R^\infty \frac{\tau_{rr} - \tau_{\theta\theta}}{r} dr dt
\end{aligned} \tag{91}$$

which we will use in Subsections V.ii through V.v below.

When we introduced Eq. (13), we neglected the viscous heating in the fluid surrounding the growing bubble. If we include the viscous heating, we can thus improve Eq. (13) to:

$$E_k + E_v = -W \tag{92}$$

and we can thus see that Eq. (13) is valid whenever:

$$E_v \ll E_k \tag{93}$$

which, for polymeric liquids, is never the case.

i. TEMPERATURE PROFILE

For the Newtonian fluid, we substitute Eqs. (173) and (174) into Eq. (89) to get:

$$(\boldsymbol{\tau} : \nabla \mathbf{v}) = \left(\frac{4\mu R^2 \dot{R}}{r^3} \right) \left(\frac{\partial v_r}{\partial r} - \frac{v_r}{r} \right) \tag{94}$$

Substituting Eqs. (5) and (6) into Eq. (94) yields:

$$(\boldsymbol{\tau} : \nabla \mathbf{v}) = -12\mu \left(\frac{R^2 \dot{R}}{r^3} \right)^2 = -12\mu \left(\frac{R^4 \dot{R}^2}{r^6} \right) \tag{95}$$

Substituting Eq. (95) into Eq. (86) then gives:

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} \right) = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 q_r) + 12\mu \left(\frac{R^4 \dot{R}^2}{r^6} \right) \tag{96}$$

and Eq. (5) into Eq. (96):

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + \frac{R^2 \dot{R}}{r^2} \frac{\partial T}{\partial r} \right) = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 q_r) + 12\mu \left(\frac{R^4 \dot{R}^2}{r^6} \right) \tag{97}$$

Combining this with Fourier's law:

$$q_r = -k \frac{\partial T}{\partial r} \tag{98}$$

then yields:

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + \frac{R^2 \dot{R}}{r^2} \frac{\partial T}{\partial r} \right) = \frac{k}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + 12\mu \left(\frac{R^4 \dot{R}^2}{r^6} \right) \tag{99}$$

Adimensionalizing Eq. (99), we get:

$$\text{Bc} \left(\frac{\partial \mathcal{T}}{\partial \Theta} + \frac{1}{\bar{r} \zeta^2} \left(\frac{d\bar{r}}{d\Theta} \right) \frac{\partial \mathcal{T}}{\partial \zeta} \right) = \frac{1}{\bar{r}^2 \zeta^2} \frac{\partial}{\partial \zeta} \left(\zeta^2 \frac{\partial \mathcal{T}}{\partial \zeta} \right) + 12\text{Bv} \left(\frac{1}{\bar{r}^2 \zeta^6} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 \tag{100}$$

where the dimensionless temperature rise is given by:

$$\mathcal{T} \equiv \frac{T - T_0}{T_0} \quad (101)$$

and where $d\bar{r}/d\Theta$ is calculated, for the case with viscous dissipation [Eqs. (123), (129), (137) and (143)], or for the case without [Eqs. (22), (31), (37) and (41)], as appropriate. From Eq. (100), we learn that for any bubble size, $\bar{r}$, the temperature rise, $\mathcal{T}(\zeta, \Theta)$, due to viscous heating in the fluid surrounding the growing bubble is governed by two dimensionless groups:

$$\text{Bc} \equiv \frac{\rho \hat{C}_p R_0^2}{\lambda_b k} = \frac{\sqrt{\rho p_\infty} \hat{C}_p R_0}{k} \quad (102)$$

and:

$$\text{Bv} \equiv \frac{\mu R_0^2}{T_0 \lambda_b^2 k} = \frac{\mu p_\infty}{\rho T_0 k} \quad (103)$$

where:

$$\lambda_b \equiv R_0 \sqrt{\rho / p_\infty} \quad (18)$$

We call Bc the *bubble thermal convectability*, because it reflects the importance of thermal radial convection (caused by the bubble growth) relative to the thermal conduction away from the bubble. We call Bv the *bubble heatability*, because it reflects the importance of viscous heating around the bubble to the thermal conduction away. For the adiabatic expansion, Eq. (100) is subject to the zero heat flux boundary condition at the bubble wall:

$$\left. \frac{d\mathcal{T}}{d\bar{r}} \right|_{\zeta=1} = 0 \quad (104)$$

and, for isothermal nucleation, to the initial condition:

$$\mathcal{T}(\zeta, 0) = 0 \quad (105)$$

For isothermal expansion, we compute what temperature profile in the fluid would be required to achieve an isothermal bubble surface, by solving Eq. (100) subject to the initial condition, Eq. (105), along with the boundary condition:

$$\mathcal{T}(1, \Theta) = 0 \quad (106)$$

For the special case of no viscous heating, where:

$$\text{Bc} \gg \text{Bv} \quad (107)$$

Eq. (100) reduces to:

$$\text{Bc} \frac{\partial \mathcal{T}}{\partial \Theta} = \frac{1}{\bar{r}^2 \zeta^2} \frac{\partial}{\partial \zeta} \left(\zeta^2 \frac{\partial \mathcal{T}}{\partial \zeta} \right) + \frac{\text{Bc}}{\bar{r} \zeta^2} \left(\frac{d\bar{r}}{d\Theta} \right) \frac{\partial \mathcal{T}}{\partial \zeta} \quad (108)$$

which, subject to the isothermal initial condition given by Eq. (105) gives the isothermal solution, $\mathcal{T}(\zeta, \Theta) = 0$, as it should. In other words, Eq. (107) is a sufficient condition for isothermal bubble growth, and Eq. (107) implies that:

$$\frac{\mu \sqrt{p_\infty}}{\rho^{3/2} T_0 \hat{C}_p R_0} \ll 1 \quad (109)$$

In the alternative special case, where:

$$\text{Bc} \ll \text{Bv} \quad (110)$$

Eq. (100) reduces to:

$$2\frac{d\mathcal{T}}{d\zeta} + \zeta \frac{d^2\mathcal{T}}{d\zeta^2} + 12Bv \left(\frac{1}{\bar{r}^2 \zeta^5} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 = 0 \quad (111)$$

which has general solution:

$$\mathcal{T} = -Bv \left(\frac{1}{\bar{r}^2} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{1}{\zeta^4} - \frac{C_2}{\zeta} + C_1 \quad (112)$$

Since $\mathcal{T}(\infty, \Theta) = 0$:

$$\mathcal{T} = -Bv \left(\frac{1}{\bar{r}^2} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{1}{\zeta^4} - \frac{C_2}{\zeta} \quad (113)$$

and:

$$\frac{d\mathcal{T}}{d\zeta} = 4Bv \left(\frac{1}{\bar{r}^2} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{1}{\zeta^5} + \frac{C_2}{\zeta^2} \quad (114)$$

For isothermal expansion, solving Eq. (113) subject to Eq. (106), yields:

$$\mathcal{T} = Bv \left(\frac{1}{\bar{r}^2} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 \left[\frac{1}{\zeta} - \frac{1}{\zeta^4} \right]; Bc \ll Bv \quad (115)$$

and:

$$\frac{d\mathcal{T}}{d\zeta} = -Bv \left(\frac{1}{\bar{r}^2} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 \left[\frac{1}{\zeta^2} - \frac{4}{\zeta^5} \right]; Bc \ll Bv \quad (116)$$

where $d\bar{r}/d\Theta$ in Eqs. (115) or (116) is then calculated, for the case with viscous dissipation [Eqs. (123) or (129)], or for the case without [Eqs. (22) or (31)], as appropriate.

For adiabatic bubble growth, we subject Eq. (113) to Eq. (104) and get:

$$\mathcal{T} = Bv \left(\frac{1}{\bar{r}^2} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 \left[\frac{4}{\zeta} - \frac{1}{\zeta^4} \right]; Bc \ll Bv \quad (117)$$

and thus:

$$\frac{d\mathcal{T}}{d\zeta} = -4Bv \left(\frac{1}{\bar{r}^2} \right) \left(\frac{d\bar{r}}{d\Theta} \right)^2 \left(\frac{1}{\zeta^2} - \frac{1}{\zeta^5} \right); Bc \ll Bv \quad (118)$$

where $d\bar{r}/d\Theta$ in Eqs. (117) or (118) is then calculated, for the case with viscous dissipation [Eqs. (137) or (143)], or for the case without [Eqs. (37) or (41)], as appropriate.

ii. ISOTHERMAL EXPANSION WITHOUT SURFACE TENSION

For the Newtonian fluid, we substitute Eqs. (173) and (174) into Eq. (91) to get:

$$E_v = 8\pi \int_0^t R^2 \dot{R} \int_R^\infty \frac{-2\mu \frac{\partial v_r}{\partial r} + \frac{2\mu v_r}{r}}{r} dr dt \quad (119)$$

Substituting Eqs. (5) and (6) into Eq. (119) yields:

$$E_v = 8\pi \int_0^t R^2 \dot{R} \int_R^\infty \left[\frac{-2\mu \frac{-2R^2 \dot{R}}{r^3} + \frac{2\mu}{r} \frac{R^2 \dot{R}}{r^2}}{r} \right] dr dt \quad (120)$$

$$= 16\pi\mu \int_{R_0}^R R \dot{R} dR$$

from which we learn that at nucleation, viscous heating is always negligible, but afterward, viscous heating begins to matter, relative to the fluid kinetic energy. We also see that viscous heating always eventually dominates. This is why analyses of bubble growth from first principles must not neglect viscous heating.

Substituting Eqs. (10), (12) and (120) into Eq. (92) gives:

$$2\pi\rho R^3 \dot{R}^2 + 16\pi\mu \int_{R_0}^R R \dot{R} dR = 4\pi p_0 R_0^3 \log \frac{R}{R_0} - \frac{4\pi p_\infty}{3} (R^3 - R_0^3) \quad (121)$$

so that:

$$\bar{r}^3 \left(\frac{d\bar{r}}{d\Theta} \right)^2 + \sqrt{2} \mathbb{V} \int_0^\Theta \bar{r} \left(\frac{d\bar{r}}{d\Theta} \right)^2 d\Theta = 2\Pi \log \bar{r} - \frac{2}{3} (\bar{r}^3 - 1) \quad (122)$$

Differentiating Eq. (122) with respect to Θ , and then rearranging gives:

$$\frac{d^2 \bar{r}}{d\Theta^2} + \frac{3}{2\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^2 + \frac{\mathbb{V}}{\sqrt{2}\bar{r}^2} \frac{d\bar{r}}{d\Theta} - \frac{1}{\bar{r}} \left[\frac{\Pi}{\bar{r}^3} + 1 \right] = 0 \quad (123)$$

which is a **homogeneous nonlinear** second order ordinary differential equation, whose nonlinearity comes from the kinetic energy alone. Comparing Eq. (123) with Eq. (22) we see that the viscous heating term attaches one **variable coefficient**. Since, Eq. (123) yields no analytical solution, we solve it numerically [see after Eq. (25)]. Eq. (123) reduces to Eq. (21) in the absence of viscous dissipation, $\mathbb{V} = 0$, as it should.

To find the bubble final radius, $\bar{r}_f$, we let the speed and acceleration, $d\bar{r}/d\Theta$ and $d^2\bar{r}/d\Theta^2$, equal zero in Eq. (123), then solve for $\bar{r}_f$ to get:

$$\bar{r}_f = \Pi^{1/3} \quad (124)$$

from which we learn that, without surface tension, the final radius depends on the pressure ratio, Π , only.

iii. ISOTHERMAL EXPANSION WITH SURFACE TENSION

In this subsection, we will explore bubble growth deceleration due to surface tension, Σ . Substituting Eq. (61) into Eq. (120) gives the total energy dissipated in the liquid surroundings:

$$E_v = 16\pi\mu \int_{R_0}^R R \sqrt{\frac{2p_0 R_0^3}{\rho R^3} \log \frac{R}{R_0} - \frac{2p_\infty}{3\rho} \left(1 - \frac{R_0^3}{R^3} \right) - \frac{2\sigma}{\rho R} \left(1 - \frac{R_0^2}{R^2} \right)} dR \quad (125)$$

which can be adimensionalized to:

$$E_v = 16\pi\mu R_0^2 \sqrt{\frac{2p_\infty}{\rho}} \int_1^{\bar{r}} \bar{r} \sqrt{\frac{\Pi}{\bar{r}^3} \log \bar{r} - \frac{1}{3} \left(1 - \frac{1}{\bar{r}^3} \right) - \frac{\Sigma}{2\bar{r}} \left(1 - \frac{1}{\bar{r}^2} \right)} d\bar{r} \quad (126)$$

Substituting Eqs. (12), (27), and (120) into Eq. (92), we get:

$$2\pi\rho R^3\dot{R}^2 + 16\pi\mu\int_{R_0}^R R\dot{R}dR = 4\pi p_0 R_0^3 \log \frac{R}{R_0} - \frac{4\pi p_\infty}{3}(R^3 - R_0^3) - 4\pi\sigma(R^2 - R_0^2) \quad (127)$$

so that:

$$\bar{r}^3 \left(\frac{d\bar{r}}{d\Theta} \right)^2 + \sqrt{2}\mathbb{V} \int_1^{\bar{r}} \bar{r} \frac{d\bar{r}}{d\Theta} d\bar{r} = 2\Pi \log \bar{r} - \frac{2}{3}(\bar{r}^3 - 1) - \Sigma[\bar{r}^2 - 1] \quad (128)$$

Differentiating Eq. (128) with respect to Θ gives:

$$\frac{d^2\bar{r}}{d\Theta^2} + \frac{3}{2\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^2 + \frac{\mathbb{V}}{\sqrt{2}\bar{r}^2} \frac{d\bar{r}}{d\Theta} - \frac{\Pi}{\bar{r}^4} + \frac{1}{\bar{r}} + \frac{\Sigma}{\bar{r}^2} = 0 \quad (129)$$

which we solve numerically [see after Eq. (25)]. Eq. (129) reduces to Eq. (31) in the absence of both surface tension and viscous dissipation, $\Sigma = \mathbb{V} = 0$, as it should.

Letting the bubble speed and acceleration, $d\bar{r}/d\Theta$ and $d^2\bar{r}/d\Theta^2$, equal zero in Eq. (129) yields:

$$\bar{r}_f^3 + \Sigma\bar{r}_f^2 - \Pi = 0 \quad (130)$$

whose relevant root is given by:

$$\bar{r}_f = \frac{1}{3} \left[\frac{1}{2}\alpha^{1/3} + 2\Sigma^2\alpha^{-1/3} - \Sigma \right] \quad (131)$$

where:

$$\alpha \equiv 4 \left(27\Pi - 2\Sigma^3 + 3\sqrt{3\Pi(27\Pi - 4\Sigma^3)} \right) \quad (132)$$

which reduces to Eq. (124) in the absence of surface tension, as it should. Eq. (131) with Eq.(132) defines the final radius, and Figure 2 illustrates the corresponding predicted behavior. From Figure 2 we learn that $\bar{r}_f$ increase monotonically with Π but decrease with Σ . Of course, in practice, bubble growth may cease before $\bar{r}_f$ is reached as when (a) bubbles collide, or when foaming polymer solidifies, by (b) cooling, or by (c) crosslinking, for instance.

iv. ADIABATIC EXPANSION WITHOUT SURFACE TENSION

In Subsection V.ii we learnt of the dominating deceleration of bubble growth caused by viscous heating. Here, we will explore the additional deceleration from surface tension. Substituting Eq. (70) into Eq. (120) yields:

$$E_v = 16\pi\mu\int_{R_0}^R R^4 \left[\frac{1}{R^3} \right] \sqrt{\frac{2R_0^3}{3\rho}} \sqrt{\frac{p_0}{1-\gamma} \frac{1}{R^3} \left(\left[\frac{R}{R_0} \right]^{3(1-\gamma)} - 1 \right) - \frac{p_\infty}{R^3} \left(\left[\frac{R}{R_0} \right]^3 - 1 \right)} dR \quad (133)$$

which can be adimensionalized to:

$$E_v = 16\pi\mu R_0^2 \sqrt{\frac{2p_\infty}{3\rho}} \int_1^{\bar{r}} \bar{r} \sqrt{\frac{\Pi}{(1-\gamma)\bar{r}^3} (\bar{r}^{3(1-\gamma)} - 1) - \left(1 - \frac{1}{\bar{r}^3} \right)} d\bar{r} \quad (134)$$

We know of no analytical solution for the integral in Eq. (134).

Substituting Eqs. (12), (34) and (120) into Eq. (92), we get:

$$2\pi\rho R^3\dot{R}^2 + 16\pi\mu\int_{R_0}^R R\dot{R}dR = \frac{p_0}{1-\gamma}\frac{4\pi R_0^3}{3}\left(\left[\frac{R}{R_0}\right]^{3(1-\gamma)} - 1\right) - \frac{4\pi R_0^3 p_\infty}{3}\left(\left[\frac{R}{R_0}\right]^3 - 1\right) \quad (135)$$

so that:

$$\bar{r}^3\left(\frac{d\bar{r}}{d\Theta}\right)^2 + \sqrt{2}\mathbb{V}\int_0^\Theta \bar{r}\left(\frac{d\bar{r}}{d\Theta}\right)^2 d\Theta = \frac{2}{3}\frac{\Pi}{1-\gamma}(\bar{r}^{3(1-\gamma)} - 1) - \frac{2}{3}(\bar{r}^3 - 1) \quad (136)$$

Differentiating Eq. (136) with respect to Θ , and then rearranging gives:

$$\frac{d^2\bar{r}}{d\Theta^2} + \frac{3}{2\bar{r}}\left(\frac{d\bar{r}}{d\Theta}\right)^2 + \frac{\mathbb{V}}{\sqrt{2}\bar{r}^2}\frac{d\bar{r}}{d\Theta} - \frac{\Pi\bar{r}^{-3\gamma}-1}{\bar{r}} = 0 \quad (137)$$

which we solve numerically [see after Eq. (25)]. When $\gamma = 1$, Eq. (137) reduces to Eq. (123), the result for the isothermal bubble expansion with viscous dissipation, as it should.

Letting the bubble speed and acceleration, $d\bar{r}/d\Theta$ and $d^2\bar{r}/d\Theta^2$, equal zero in Eq. (137), we get:

$$\bar{r}_f = \Pi^{\frac{1}{3\gamma}} \quad (138)$$

for the final radius. Eq. (138) matches Eq. (124) when $\gamma = 1$, as it should.

v. ADIABATIC EXPANSION WITH SURFACE TENSION

In the previous subsection about viscous dissipation, we accounted for the molecular structure (polyatomicity) of the expanding gas by incorporating adiabatic expansion. Here we will calculate the deceleration due to surface tension in combination with adiabatic expansion. Substituting Eq. (77) into Eq. (120) yields:

$$E_v = 16\pi\mu\int_{R_0}^R R\sqrt{\frac{2R_0^3}{3\rho}}\sqrt{\frac{\frac{p_0}{1-\gamma}\left(\left[\frac{R}{R_0}\right]^{3(1-\gamma)} - 1\right)\frac{1}{R^3}}{-\frac{p_\infty}{R^3}\left(\left[\frac{R}{R_0}\right]^3 - 1\right) - \frac{3\sigma}{R_0^4}\left(1 - \frac{R_0^2}{R^2}\right)\frac{R_0}{R}}}dR \quad (139)$$

which can be adimensionalized to:

$$E_v = 16\pi\mu R_0^2\sqrt{\frac{2p_\infty}{3\rho}}\int_1^{\bar{r}} \bar{r}\sqrt{\frac{\Pi}{(1-\gamma)\bar{r}^3}(\bar{r}^{3(1-\gamma)} - 1) - \left(1 - \frac{1}{\bar{r}^3}\right) - \frac{3}{2}\Sigma\frac{1}{\bar{r}}\left(1 - \frac{1}{\bar{r}^2}\right)}d\bar{r} \quad (140)$$

We know of no analytical solution for the integral in Eq. (140).

Substituting Eqs. (12), (38) and (120) into Eq. (92), we get:

$$\rho R^3\dot{R}^2 + 8\mu\int_{R_0}^R R\dot{R}dR = \frac{p_0}{1-\gamma}\frac{2R_0^3}{3}\left(\left[\frac{R}{R_0}\right]^{3(1-\gamma)} - 1\right) - \frac{2R_0^3 p_\infty}{3}\left(\left[\frac{R}{R_0}\right]^3 - 1\right) - 2\sigma(R^2 - R_0^2) \quad (141)$$

so that:

$$\bar{r}^3\left(\frac{d\bar{r}}{d\Theta}\right)^2 + \sqrt{2}\mathbb{V}\int_0^\Theta \bar{r}\left(\frac{d\bar{r}}{d\Theta}\right)^2 d\Theta = \frac{2}{3}\frac{\Pi}{1-\gamma}(\bar{r}^{3(1-\gamma)} - 1) - \frac{2}{3}(\bar{r}^3 - 1) - \Sigma(\bar{r}^2 - 1) \quad (142)$$

Differentiating Eq. (142) with respect to Θ , and then rearranging gives:

$$\frac{d^2\bar{r}}{d\Theta^2} + \frac{3}{2\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^2 + \frac{\mathbb{V}}{\sqrt{2}\bar{r}^2} \frac{d\bar{r}}{d\Theta} - \frac{\Pi\bar{r}^{-3\gamma} - 1}{\bar{r}} + \frac{\Sigma}{\bar{r}^2} = 0 \quad (143)$$

which we solve numerically [see after Eq. (25)]. When $\gamma = 1$, Eq. (143) reduces to Eq. (129), the result for the isothermal bubble expansion with viscous dissipation, as it should.

Letting the bubble speed and acceleration, $d\bar{r}/d\Theta$ and $d^2\bar{r}/d\Theta^2$, equal zero in Eq. (143), we get:

$$\Pi\bar{r}_f^{1-3\gamma} - \bar{r}_f - \Sigma = 0 \quad (144)$$

for the final radius, implicitly. When $\gamma = 1$, the relevant root of Eq. (144) matches Eq. (131), our result for the corresponding case without viscous dissipation. This is because, while viscous dissipation profoundly affects the growth rate, it plays no role in determining the final bubble size, $\bar{r}_f$. In practice, bubbles for which

$\gamma > 1$ (such as monatomic gases, for which $\gamma = \frac{5}{3}$, or for diatomic gases such as air and its components, for which $\gamma = \frac{7}{5}$, or for polyatomic gases, for which $\gamma = \frac{13}{10}$) will absorb a little heat from the surrounding fluid as they expand. The final bubble size may thus be a little lower than we predict from our isothermal analysis [see Eq. (131)].

VI. FLUID PRESSURE: **WITH VISCOUS HEATING**

In Section IV, we explored the pressure profile in the liquid surrounding the growing bubble by neglecting the viscous dissipation. In this section, we will learn of the important effect of $\mathbb{V}$ on $\mathcal{P}$.

i. ISOTHERMAL EXPANSION WITHOUT SURFACE TENSION

We begin by solving Eq. (46) for the fluid pressure gradient:

$$\frac{\partial p}{\partial r} = -2\rho R\dot{R}^2 \left(\frac{1}{r^2} - \frac{R^3}{r^5} \right) - \rho R^2 \ddot{R} \frac{1}{r^2} \quad (145)$$

and then integrating yields:

$$p = p_\infty - 2\rho\dot{R}^2 \left(-\frac{R}{r} + \frac{R^4}{4r^4} \right) + \rho R^2 \ddot{R} \frac{1}{r} \quad (146)$$

which can be adimensionalized to:

$$\mathcal{P} = 1 - 2 \left(\frac{d\bar{r}}{d\Theta} \right)^2 \left(-\frac{1}{\zeta} + \frac{1}{4\zeta^4} \right) + \bar{r} \frac{d^2\bar{r}}{d\Theta^2} \frac{1}{\zeta} \quad (147)$$

Solving Eq. (123) for $d^2\bar{r}/d\Theta^2$, and then substituting the result into Eq. (147) gives:

$$\mathcal{P} = 1 - 2 \left(\frac{d\bar{r}}{d\Theta} \right)^2 \left(-\frac{1}{\zeta} + \frac{1}{4\zeta^4} \right) + \left[-\frac{3}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}} \frac{d\bar{r}}{d\Theta} + \frac{\Pi}{\bar{r}^3} - 1 \right] \frac{1}{\zeta} \quad (148)$$

Rearranging Eq. (148) gives:

$$\mathcal{P} = 1 + \left[\frac{1}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}} \frac{d\bar{r}}{d\Theta} + \frac{\Pi}{\bar{r}^3} - 1 \right] \frac{1}{\zeta} - \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{1}{2\zeta^4} \quad (149)$$

where $d\bar{r}/d\Theta$ is calculated from Eq. (123). Evaluating Eq. (149) at nucleation, where $\bar{r} = 1$, gives Eq. (56) as it should. Differentiating Eq. (149) with respect to ζ gives:

$$\frac{\partial \mathcal{P}}{\partial \zeta} = - \left[\frac{1}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}} \frac{d\bar{r}}{d\Theta} + \frac{\Pi}{\bar{r}^3} - 1 \right] \frac{1}{\zeta^2} + 2 \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{1}{\zeta^5} \quad (150)$$

from which we learn that $\partial \mathcal{P} / \partial \zeta$ will change sign, from negative to positive, for all values of ζ when the bubble growth decelerates, such that:

$$\left[1 - \frac{\sqrt{2}\mathbb{V}}{\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^{-1} + 2 \left[\frac{\Pi}{\bar{r}^3} - 1 \right] \left(\frac{d\bar{r}}{d\Theta} \right)^{-2} \right] \zeta^3 < 4 \quad (151)$$

Evaluating Eq. (150) for the nucleus, when $\bar{r} = 1$ and $d\bar{r}/d\Theta = 0$, gives:

$$\left. \frac{\partial \mathcal{P}}{\partial \zeta} \right|_{\bar{r}=1} = \frac{1 - \Pi}{\zeta^2} \quad (152)$$

which is negative, and zero when $\Pi = 1$, as it should be.

ii. ISOTHERMAL EXPANSION WITH SURFACE TENSION

Solving Eq. (129) for $d^2\bar{r}/d\Theta^2$, and then substituting the result into Eq. (147) gives:

$$\mathcal{P} = 1 - 2 \left(\frac{d\bar{r}}{d\Theta} \right)^2 \left(-\frac{1}{\zeta} + \frac{1}{4\zeta^4} \right) + \left[-\frac{3}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}} \frac{d\bar{r}}{d\Theta} + \frac{\Pi}{\bar{r}^3} - 1 - \frac{\Sigma}{\bar{r}} \right] \frac{1}{\zeta} \quad (153)$$

which can be rearranged to give:

$$\mathcal{P} = 1 + \left[\frac{1}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}} \frac{d\bar{r}}{d\Theta} + \frac{\Pi}{\bar{r}^3} - 1 - \frac{\Sigma}{\bar{r}} \right] \frac{1}{\zeta} - \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{1}{2\zeta^4} \quad (154)$$

where $d\bar{r}/d\Theta$ is calculated from Eq. (129). In the absence of surface tension, Eq. (154) reduces to Eq. (149) as it should. Evaluating Eq. (154) at nucleation, where $\bar{r} = 1$, and then letting $\Sigma = 0$ gives Eq. (56) as it also should. Differentiating Eq. (154) with respect to ζ gives:

$$\frac{\partial \mathcal{P}}{\partial \zeta} = - \left[\frac{1}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}} \frac{d\bar{r}}{d\Theta} + \frac{\Pi}{\bar{r}^3} - 1 - \frac{\Sigma}{\bar{r}} \right] \frac{1}{\zeta^2} + \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{2}{\zeta^5} \quad (155)$$

From which we learn that $\partial\mathcal{P}/\partial\zeta$ will change sign, from negative to positive, for all values of ζ when the bubble growth decelerates such that:

$$\left[1 - \frac{\sqrt{2}\mathbb{V}}{\bar{r}}\left(\frac{d\bar{r}}{d\Theta}\right)^{-1} + 2\left[\frac{\Pi}{\bar{r}^3} - 1 - \frac{\Sigma}{\bar{r}}\right]\left(\frac{d\bar{r}}{d\Theta}\right)^{-2}\right]\zeta^3 < 4 \quad (156)$$

which reduces to Eq. (151) when $\Sigma = 0$ as it should. Evaluating Eq. (155) for the nucleus, when $\bar{r} = 1$ and $d\bar{r}/d\Theta = 0$, gives:

$$\left.\frac{\partial\mathcal{P}}{\partial\zeta}\right|_{\bar{r}=1} = \frac{1 + \Sigma - \Pi}{\zeta^2} \quad (157)$$

which is negative when:

$$\Sigma < \Pi - 1 \quad (158)$$

and positive when:

$$\Sigma > \Pi - 1 \quad (159)$$

a condition forbidding bubble growth.

iii. ADIABATIC EXPANSION WITHOUT SURFACE TENSION

We next explore the effect of the cooling of the expanding gas, on the pressure in the fluid surroundings. Solving Eq. (137) for $d^2\bar{r}/d\Theta^2$, and then substituting the result into Eq. (147), gives:

$$\mathcal{P} = 1 - 2\left(\frac{d\bar{r}}{d\Theta}\right)^2\left(-\frac{1}{\zeta} + \frac{1}{4\zeta^4}\right) + \left[-\frac{3}{2}\left(\frac{d\bar{r}}{d\Theta}\right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}}\frac{d\bar{r}}{d\Theta} + \Pi\bar{r}^{-3\gamma} - 1\right]\frac{1}{\zeta} \quad (160)$$

which can be rearranged to give:

$$\mathcal{P} = 1 + \left[\frac{1}{2}\left(\frac{d\bar{r}}{d\Theta}\right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}}\frac{d\bar{r}}{d\Theta} + \Pi\bar{r}^{-3\gamma} - 1\right]\frac{1}{\zeta} - \left(\frac{d\bar{r}}{d\Theta}\right)^2\frac{1}{2\zeta^4} \quad (161)$$

where $d\bar{r}/d\Theta$ is calculated from Eqs. (137). When $\gamma = 1$, Eq. (161) reduces to Eq. (149), as it should. Furthermore, evaluating Eq. (161) at nucleation, where $\bar{r} = 1$, and then letting $\Sigma = 0$ gives Eq. (56) as it also should. Differentiating Eq. (161) with respect to ζ gives:

$$\frac{\partial\mathcal{P}}{\partial\zeta} = -\left[\frac{1}{2}\left(\frac{d\bar{r}}{d\Theta}\right)^2 - \frac{\mathbb{V}}{\sqrt{2}\bar{r}}\frac{d\bar{r}}{d\Theta} + \Pi\bar{r}^{-3\gamma} - 1\right]\frac{1}{\zeta^2} + \left(\frac{d\bar{r}}{d\Theta}\right)^2\frac{2}{\zeta^5} \quad (162)$$

From which we learn that $\partial\mathcal{P}/\partial\zeta$ will change sign, from negative to positive, for all values of ζ when the growth decelerates, such that:

$$\left[1 - \frac{\sqrt{2}\mathbb{V}}{\bar{r}}\left(\frac{d\bar{r}}{d\Theta}\right)^{-1} + 2[\Pi\bar{r}^{-3\gamma} - 1]\left(\frac{d\bar{r}}{d\Theta}\right)^{-2}\right]\zeta^3 < 4 \quad (163)$$

which reduces to Eq. (151) when $\gamma = 1$, as it also should. Evaluating Eq. (163) for the nucleus, when $\bar{r} = 1$ and $d\bar{r}/d\Theta = 0$, gives:

$$\frac{\partial \mathcal{P}}{\partial \zeta} = \frac{1 - \Pi}{\zeta^2} \quad (164)$$

which is negative, and zero when $\Pi = 1$, as it should be.

iv. ADIABATIC EXPANSION WITH SURFACE TENSION

Solving Eq. (143) for $d^2\bar{r}/d\Theta^2$ then substituting it into Eq. (147) gives:

$$\mathcal{P} = 1 - 2 \left(\frac{d\bar{r}}{d\Theta} \right)^2 \left(-\frac{1}{\zeta} + \frac{1}{4\zeta^4} \right) + \left[-\frac{3}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2\bar{r}}} \frac{d\bar{r}}{d\Theta} + \Pi \bar{r}^{-3\gamma} - 1 - \frac{\Sigma}{\bar{r}} \right] \frac{1}{\zeta} \quad (165)$$

Rearranging Eq. gives:

$$\mathcal{P} = 1 + \left[\frac{1}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2\bar{r}}} \frac{d\bar{r}}{d\Theta} + \Pi \bar{r}^{-3\gamma} - 1 - \frac{\Sigma}{\bar{r}} \right] \frac{1}{\zeta} - \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{1}{2\zeta^4} \quad (166)$$

where $d\bar{r}/d\Theta$ is calculated from Eqs. (137) or (143) for the case without or with surface tension. When $\gamma = 1$, Eq. (166) reduces to Eq. (154), the result for the isothermal bubble expansion with surface tension, as it should. Furthermore, evaluating Eq. (161) at nucleation, where $\bar{r} = 1$, and then letting $\Sigma = 0$ gives Eq. (56) as it also should. Differentiating Eq. (166) with respect to ζ gives:

$$\frac{\partial \mathcal{P}}{\partial \zeta} = - \left[\frac{1}{2} \left(\frac{d\bar{r}}{d\Theta} \right)^2 - \frac{\mathbb{V}}{\sqrt{2\bar{r}}} \frac{d\bar{r}}{d\Theta} + \Pi \bar{r}^{-3\gamma} - 1 - \frac{\Sigma}{\bar{r}} \right] \frac{1}{\zeta^2} + \left(\frac{d\bar{r}}{d\Theta} \right)^2 \frac{2}{\zeta^5} \quad (167)$$

From which we learn that $\partial \mathcal{P} / \partial \zeta$ will change sign, from negative to positive, for all value of ζ when the bubble growth decelerates such that:

$$\left[1 - \frac{\sqrt{2}\mathbb{V}}{\bar{r}} \left(\frac{d\bar{r}}{d\Theta} \right)^{-1} + 2 \left[\Pi \bar{r}^{-3\gamma} - 1 - \frac{\Sigma}{\bar{r}} \right] \left(\frac{d\bar{r}}{d\Theta} \right)^2 \right] \zeta^3 < 4 \quad (168)$$

which reduces to Eq. (163) when $\Sigma = 0$ as it also should. Evaluating Eq. (168) for the nucleus, when $\bar{r} = 1$ and $d\bar{r}/d\Theta = 0$, gives Eq. (157) and thus Eqs. (158) and (159) apply.

VII. EXTRA STRESSES IN LIQUID

The extra stresses in the fluid surrounding the growing bubble, τ_{rr} , $\tau_{\theta\theta}$ and $\tau_{\phi\phi}$, matter to plastics engineers because these are frozen into foamed plastics, and these residual stresses can embrittle the foam (see Chapter 2 of [1]). To evaluate these extra stresses, we introduce the r -component of the equation of motion (Eq. (B.5-7) of [22]):

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial v_r}{\partial \phi} - \frac{v_\theta^2 + v_\phi^2}{r} \right) = \frac{-\partial p}{\partial r} - \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{rr}) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\tau_{\theta r} \sin \theta) + \frac{1}{r \sin \theta} \frac{\partial \tau_{\phi r}}{\partial \phi} - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} \right] + \rho g_r \quad (169)$$

which, subject to our physical intuition for the velocity, Eq. (2), simplifies to:

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = \frac{-\partial p}{\partial r} - \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{rr}) - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} \right] + \rho g_r \quad (170)$$

which is the starting point for any analysis of the pressure in the fluid surrounding the growing bubble.

Evaluating the corresponding components of the rate of deformation tensor yields:

$$\begin{aligned} \Delta_{rr} &= 2 \frac{\partial v_r}{\partial r} \\ \Delta_{\theta\theta} &= 2 \left(\frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right) = \frac{2v_r}{r} \\ \Delta_{\phi\phi} &= 2 \left(\frac{1}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r} + \frac{v_\theta \cot \theta}{r} \right) = \frac{2v_r}{r} = \Delta_{\theta\theta} \end{aligned} \quad (171)$$

Since $\Delta_{\theta\theta} = \Delta_{\phi\phi}$, the corresponding components of the extra stress tensor also match, $\tau_{\theta\theta} = \tau_{\phi\phi}$, and so Eq. (170) simplifies to:

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = \frac{-\partial p}{\partial r} - \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{rr}) - \frac{2\tau_{\theta\theta}}{r} \right] + \rho g_r \quad (172)$$

For a Newtonian fluid [see footnote to Table III for our sign convention for the extra stress tensor] (Eq. (B.1-15) and Eq. (B.1-16) of [22]):

$$\tau_{rr} = -\mu \Delta_{rr} = -2\mu \frac{\partial v_r}{\partial r} \quad (173)$$

$$\tau_{\theta\theta} = -\mu \Delta_{\theta\theta} = \frac{-2\mu v_r}{r} \quad (174)$$

Using Eqs. (173) and (174) to eliminate the extra stresses in Eq. (172) yields:

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = \frac{-\partial p}{\partial r} + \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 2\mu \frac{\partial v_r}{\partial r} \right) - \frac{4\mu v_r}{r^2} \right] + \rho g_r \quad (175)$$

If we now substitute Eqs. (5) and (6) into the viscous term [bracketed in Eq. (175)], we get:

$$\begin{aligned} & \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 2\mu \frac{-2R^2 \dot{R}}{r^3} \right) - \frac{4\mu}{r^2} \frac{R^2 \dot{R}}{r^2} \right] \\ &= -4\mu R^2 \dot{R} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(\frac{1}{r} \right) + \frac{1}{r^4} \right] = -4\mu R^2 \dot{R} \left[-\frac{1}{r^4} + \frac{1}{r^4} \right] = 0 \end{aligned} \quad (176)$$

This last pair of substitutions has unfortunately been called “overlooking the viscous term” (see after Eq. (10) of [13]) or “neglecting liquid viscosity” (see after Eq. 1.4 of [34]). For a Newtonian fluid, Eq. (175) thus reduces to:

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = \frac{-\partial p}{\partial r} + \rho g_r \quad (177)$$

which applies to a Newtonian fluid surrounding a growing bubble.

We have proven that, for a Newtonian fluid, the viscous term in the r – component of the equation of motion [Eq. (170)] is zero:

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{rr}) - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} = 0 \quad (178)$$

From Eqs. (176) or (178), we learn that, for a Newtonian fluid, the viscous forces cancel, and thus that bubble growth cannot depend on the fluid viscosity. Some chose to substitute Eq. (174) into Eq. (172), and then not to substitute Eq. (173) into Eq. (172). Integration then leads to a more complicated starting point for the analysis of bubble growth, a starting point that needlessly carries along the Newtonian viscosity (see Eq. (8) of [13]). This complication has been called “viscosity only affecting the boundary” (see after Eq. 1.3 of [34]).

We can now use Eqs. (173) and (174) to evaluate the components of the extra stress tensor in the fluid surrounding the growing bubble. Specifically, substituting Eq. (6) into Eq. (173) yields:

$$\tau_{rr} = 4\mu \frac{R^2 \dot{R}}{r^3} \quad (179)$$

and substituting Eq. (5) into Eq. (174) yields:

$$\tau_{\theta\theta} = \tau_{\phi\phi} = -2\mu \frac{R^2 \dot{R}}{r^3} = -\frac{1}{2} \tau_{rr} \quad (180)$$

so that τ_{rr} is compressive, and both $\tau_{\phi\phi}$ and $\tau_{\theta\theta}$ are tensile. Since these stresses are eventually frozen into the plastics upon solidification, they can govern the toughness of the solid foam. When neglected from the stress field surrounding a bubble void, elastic fracture mechanics will underpredict the stresses surrounding the void, and thus overpredict the toughness of bubble containing solids. We can adimensionalize Eqs. (179) and (180) so that:

$$\frac{\lambda_b \tau_{\theta\theta}}{\mu} = \frac{\lambda_b \tau_{\phi\phi}}{\mu} = -\frac{\tau_{rr} \lambda_b}{2\mu} = -2 \frac{\bar{r}^2}{\zeta^3} \frac{d\bar{r}}{d\Theta} \quad (181)$$

where $d\bar{r}/d\Theta$ is calculated, from Eqs. (129) or (123) for the case of isothermal expansion with or without surface tension, or from Eqs. (143) or (137) for the case of adiabatic expansion with or without surface tension.

We know of no measurements of these components of the extra stress tensor around growing bubbles, or for that matter, measurements of these stresses frozen into the matrix in solid foam. Although the bubble growth and the pressure field surrounding the growing bubbles do not depend on rheology, the components of the extra stress tensor do depend on viscosity.

VIII. RESULTS

In this section, we will fit our theory to bubble growth observations of nitrogen bubble grown in molten polystyrene, and collected before bubble collision. Specifically, we thus use the first 12 observations (all points before 120s) from the top curve ($T = 408\text{ K}$) of Fig. 4. of [7] which we list in columns 1 through 3 of Table IV. We arrive at best fits to the measured values (in columns 2 and 3 of Table IV) for each of the four classical approaches [Eqs. (22), (31), (37) and (41)] and for each version of our theory incorporating viscous dissipation [Eqs. (123), (129), (137) and (143)]. Table V lists the corresponding fitted parameter values, and the corresponding sum of squares of residuals, S_R .

Figure 4 compares the fits from the classical approaches with Eqs. (22), (31), (37) and (41). We find all four of these approaches to overpredict growth by a factor about one billion.

Figure 5 plots the measured values from columns 2 and 3 of Table IV. The microscopy reported in Fig. 2.(c) of [7] confirms bubble collision shortly after 120s. By *bubble collision*, we mean when the nearest neighbors impede each other's motion. From Figure 5, we see that this nitrogen bubble collision at 120s corresponds to $\Theta \approx 3 \times 10^8$.

Figure 5 compares the four best fits for our theory incorporating viscous dissipation [Eqs. (123), (129), (137) and (143)] to the measured values (from columns 2 and 3 of Table IV). Comparing the S_R values for these fits (listed in the last column of Table V), we learn that, although all four theories incorporating viscous heating give reasonable descriptions of the data, isothermal expansion without surface tension, Eq. (123), gives the lowest S_R .

Figure 6 compares the best fit from classical theory [Eq. (22)] with the best fit our theory incorporating viscous dissipation [Eqs. (123)] from which we learn that viscous dissipation sufficiently decelerates bubble growth to explain the observed behavior.

We next calculated the growth rates, $\dot{R}$, from the observation listed in columns 1 through 3 of Table IV, by first spacing the observations evenly in time by cubic spline interpolation (columns 4 and 5 of Table IV), and then by applying the method of Whitaker [35]. Specifically, we employ the equations from row numbers $X = -2, -1$ for the first two rows and $X = 1, 2$ for the last two from Table II. of [35], and from row number $X = 0$ for all points between. We choose the least-squares method of Whitaker [35] to minimize noise from our numerical differentiation (see Section titled "NUMERICAL DIFFERENTIATION" of [36]). We list the results of our numerical differentiation in column 6 of Table IV. Figure 7 compares the measured growth with those predicted from all four theories incorporating viscous heating [Eqs. (123), (129), (137) and (143)]. We find good agreement for the first half of bubble growth but large discrepancy as bubble collision approaches. We attribute these discrepancies to the interferences of velocity profile between approaching bubbles, before collision.

We next explore profiles in the liquid surroundings predicted by all four theories incorporating viscous heating [Eqs. (123), (129), (137) and (143)]. Specifically, we explore profiles of the temperature rise (Figure 8), fluid pressure

(Figure 9) and extra stresses (Figure 10) at collision ($\Theta \approx 3 \times 10^8$). From Figure 8, we calculate a temperature rise of 9°C for the isothermal expansions with viscous dissipation, and 57°C for the corresponding adiabatics. From Figure 9, we see dramatic differences between the pressure profiles for the isothermal expansions with viscous dissipation and the corresponding adiabatics (evaluated at the collision). Specifically, whereas, the isothermal expansions finish with zero pressure gradient ($\mathcal{P} = 1$), the adiabatic expansions finish with $\mathcal{P} > 1$ in the surrounding liquid. From Figure 10, we learn that the adiabatic expansions predict higher stresses in the liquid surroundings than do the isothermal expansions (though the shapes of the stress profiles matches). From Figure 8 through Figure 10 we learn that even though all four theories incorporating viscous heating [Eqs. (123), (129), (137) and (143)] hardly differ on bubble size [Figure 5, Table IV and Table V] (or growth rate [Figure 7 and Table IV]), predictions of temperature rise, liquid pressure or extra stresses can differ markedly for different expansions, adiabatic *versus* isothermal. We know of no measurement of the temperature rise around the growing bubbles, or of the pressure profiles or of the extra stresses in the liquid surroundings. It would appear that one would need such measurements to discriminate between the four theories incorporating viscous heating [Eqs. (123), (129), (137) and (143)].

IX. CONCLUSION

We have defined the simplest relevant problem in bubble growth: the expansion of a bubble, under its own pressure, including the effects of fluid inertia, viscous forces, and viscous heating in the surrounding liquid. We find the inclusion of viscous heating to be essential for obtaining realistic predictions for the bubble growth rate, and thus for its final size. Specifically, we derive the nonlinear ordinary differential equation *for isothermal bubble expansion* (one including surface tension [Eq. (129)], and one not [Eq. (123)]). We find the inclusion of viscous heating to be essential for eliminating most of the inaccuracy arising from predictions without viscous heating. For these predictions without viscous heating, we give detailed consideration for the cases with surface tension [Eq. (31)], and without [Eq. (22)]. Even our best fits from predictions without viscous heating overpredict bubble growth rate by a factor of about *one billion* (see Figure 4).

We find the decelerating effect of viscous heating to be more important than any other decelerating contribution, including from surface tension or from adiabatic expansion. We treat both of these complicating decelerations in detail. The adiabatic expansion allows us to explore the potentially important role of the gas molecular structure (polyatomicity) in bubble growth. We derive the nonlinear ordinary differential equation *for adiabatic bubble expansion* with viscous heating (one including surface tension [Eq. (143)], and one not [Eq. (137)]). We find this inclusion of viscous heating to be essential for eliminating the unphysical predictions that arise without it, for which we give detailed consideration for the cases with surface tension [Eq. (41)], and without [Eq. (37)].

Our theory [Eqs. (123), (129), (137) and (143)] compares well *qualitatively* with the best available data on bubble growth in molten plastics: measured bubble

radius *versus* time (Fig. 4. of [7] or Figs. 17 and 18 of [37]). In Figure 5, we further find that our theory compares well *quantitatively* with measured bubble growth behavior in molten polystyrene (top curve of Fig. 4. of [7]). Unfortunately, the key quantities governing bubble growth, the properties of the nucleus (its radius and its internal pressure), have not been measured. As a result, little is known about the effects of the many process variables on the radius and internal pressure of the nucleus.

For nearly Newtonian polymers, such as many commercial grades of condensation polymers (for example, nylon, polyester and polycarbonate), we would of course expect Eq. (181) to be accurate. However, for non-Newtonian fluids, we would further expect Eq. (181) to be accurate, so long as both the Weissenberg and Deborah numbers in the deforming fluid surroundings fall well below one:

$$Wi \equiv \lambda \dot{\gamma} \ll 1 \quad (182)$$

and:

$$De \equiv \lambda/t \ll 1 \quad (183)$$

where λ is the relaxation time of the viscoelastic fluid surroundings, and where $\dot{\gamma}$ is the magnitude of the rate of deformation tensor at the bubble surface. For detailed discussion of the Weissenberg and Deborah numbers, see Section 1 of [38,39]. In our experience, we find that bubble growth in polymeric liquids is both slow and long, and specifically, both slow enough to satisfy Eqs. (182), and long enough to satisfy Eq. (183). In other words, for non-Newtonian fluids, our results in this paper [Eqs. (123), (129), (137) and (143)] can be used by simply replacing μ with the zero-shear viscosity, η_0 . This, in turn, explains the good agreement we observe between our theory and the observed bubble growth rate in the non-Newtonian polystyrene melt (see Figure 5).

We call theory for a distribution of bubble ages *polychronal*, and otherwise, *isochronal*. In this paper, we have examined a single bubble nucleated at time zero (isochronal). We are, of course, mindful that nucleation persists after time zero, and that it will distribute the bubble ages (polychronal) and sizes, and thus lower the average size. However, bubble sizes measured by single-magnification microscopy (Fig. 4. of [7] or Figs. 17 and 18 of [37]) will miss many bubbles nucleated after time zero. This is why we get such good agreement in Figure 5.

We close with a comment on bubble collapse. In this paper, we have concerned ourselves with bubble growth, for which $p_0 > p_\infty$, but we expect our approach to apply to void shrinkage, for which $p_0 < p_\infty$ [which obtains during the packing stage of the injection molding of unfoamed plastics ([3]; see also [24,40,41,42,43])]. For an isothermal treatment of a collapsing cavity, for which $p_0 = 0$, see Eqs. (5) et seq. of [24], and for $p_0 > 0$ and $p_\infty > p_0$, see up to Eq. (4) of [24] or up to Eq. (13) of [32]. For adiabatic treatments of the collapsing bubble, see Eq. (4) of [32], Eq. (7) of Article 91 a. in [31], Eq. (3.30c) of [29] and Eq. (1-33b) of [30]. Based on the results of this work, we would expect viscous dissipation to be equally important to bubble collapse, and we intend to explore this next.

X. WORKED EXAMPLE: ESTIMATING FINAL BUBBLE SIZE

A manufacturer is processing the nitrogen-polystyrene foam described by Fig. 4. of [7]. To achieve certain physical properties, she requires a bubble size of $R_f = 13.1\mu\text{m}$. She uses $\sigma = 1.50 \times 10^{-2} \text{ N/m}$ for the interfacial tension between molten polystyrene and the diatomic foaming gas. She also uses $\rho = 10^3 \text{ kg/m}^3$ for the polystyrene melt density. From our results above, she gleans the following about the nuclei: $R_0 = 3.50\mu\text{m}$ and $p_0 = 200\text{atm}$ (see caption to Figure 5). Her foam expands freely into an isobaric chamber, held at p_∞ . What value of p_∞ will produce bubbles of the right size?

To calculate the final radius, she begins by calculating $\bar{r}_f = 3.742$ and $\Sigma = 0.1$ by inserting into Eqs. (15) and (30). Solving Eq. (144) yields the pressure ratio:

$$\frac{200 \times 10^5 \text{ Pa}}{p_\infty} \frac{13.1\mu\text{m}}{3.5\mu\text{m}}^{1-3\left(\frac{7}{5}\right)} - \frac{13.1\mu\text{m}}{3.5\mu\text{m}} - \frac{2(1.75 \times 10^{-2})}{p_\infty(3.5\mu\text{m})} = 0 \quad (184)$$

Solving Eq. (184) for p_∞ gives:

$$p_\infty = 7.56 \times 10^4 \text{ Pa} \quad (185)$$

Of course, to learn how long it would take for such a foam to be realized requires the solution of Eq. (143). Lower values of p_∞ can also be used to produce foam of the same average bubble size, $\bar{R} = 13.1\mu\text{m}$ by interrupting the foaming, by cooling or by crosslinking the matrix, for instance. Though this may produce foam of the right average bubble size, bubbles near the skin will be smaller than those in the core. Of course, one can also solve Eq. (143) to estimate when to interrupt foaming (with either cooling or crosslinking or both, for instance).

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Figure 1: Spherical coordinates with origin centered in the growing bubble.

Figure 2: Final radius for the isothermal bubble *versus* pressure ratio, given by Eq. (124) and (131) for the case without or with surface tension effect for $\Sigma = 0, 10^0, 10^1, 10^2$ (black, green, blue and red curves).

Figure 3: Final radius for the adiabatic bubble growth of monatomic ($\gamma = 5/3$), diatomic ($\gamma = 7/5$) and polyatomic gases ($\gamma = 13/10$) [red, blue and black curves] each of which parametrized with surface tension, $\Sigma = 0, 10^0, 10^1, 10^2$ in downward order *versus* pressure, given by Eq. (144).

Figure 4: Best fits for bubble growth observations of Fig. 4. Of [7] to theories without viscous dissipation [Eqs. (22) **Green** and (31) **Black** with $p_0 = 55.0 \text{ atm}$; Eqs. (37) **Red** and (41) **Blue** with $p_0 = 74.1 \text{ atm}$]. For all curves, $R_0 = 3.5 \mu\text{m}$, $p_\infty = 1 \text{ atm}$, $\rho = 10^3 \text{ kg/m}^3$, for the case of adiabatic expansion, $\gamma = 7/5$, and, for those with surface tension, $\sigma = 1.75 \times 10^{-2} \text{ N/m}$.

Figure 5: Best fits for bubble growth observations of Fig. 4. Of [7] to theories with viscous dissipation [Eq. (123) **Blue** and Eq. (129) **Black** with $p_0 = 100 \text{ atm}$; Eq. (137) **Red** and Eq. (143) **Green** with $p_0 = 200 \text{ atm}$]. For all curves, $\mu = 1.957 \times 10^7 \text{ Pa}\cdot\text{s}$, $R_0 = 3.5 \mu\text{m}$, $p_\infty = 1 \text{ atm}$, $\rho = 10^3 \text{ kg/m}^3$, for the case of adiabatic expansion, $\gamma = 7/5$, and, for those with surface tension, $\sigma = 1.75 \times 10^{-2} \text{ N/m}$. Bubbles collide at $\Theta \approx 3 \times 10^8$.

Figure 6: Best fits for bubble growth observations of Fig. 4. of [7] to theories without [Eq. (22) with $p_0 = 74.1 \text{ atm}$] and with [Eq. with $p_0 = 100 \text{ atm}$ and $\mu = 2.26 \times 10^7 \text{ Pa}\cdot\text{s}$] viscous dissipation. For all curves, $R_0 = 3.5 \mu\text{m}$, $p_\infty = 1 \text{ atm}$, $\rho = 10^3 \text{ kg/m}^3$.

Figure 7: Growth rates corresponding to our best fits for bubble growth observations of *Fig. 4*. Of [7] to theories with viscous dissipation [Eq. (123) **Blue**] and Eq. (129) **Black**] with $p_0 = 100 \text{ atm}$; Eq. (137) **Red**] and Eq. (143) **Green**] with $p_0 = 200 \text{ atm}$]. For all curves, $\mu = 1.957 \times 10^7 \text{ Pa}\cdot\text{s}$, $R_0 = 3.5 \mu\text{m}$, $p_\infty = 1 \text{ atm}$, $\rho = 10^3 \text{ kg/m}^3$, for the case of adiabatic expansion, $\gamma = 7/5$, and, for those with surface tension, $\sigma = 1.75 \times 10^{-2} \text{ N/m}$. Bubbles collide at $\Theta \approx 3 \times 10^8$.

Figure 8: Final temperature rise, $\bar{r}_c = 3.76$ and $\dot{\bar{r}}_f = 1.60 \times 10^{-4}$, corresponding to our best fits for bubble growth observations of Fig. 4. of [7] to theories with viscous dissipation [Eq. (117) for adiabatic expansion **[Red]** and Eq. (115) for isothermal expansion **[Blue]** For all curves $\mu = 1.957 \times 10^7 \text{ Pa}\cdot\text{s}$, $R_0 = 3.5 \mu\text{m}$, $p_\infty = 1 \text{ atm}$, $\rho = 10^3 \text{ kg/m}^3$, $\hat{C}_p = 2.087 \times 10^3 \text{ J/kg}^\circ\text{C}$, $k = 0.185 \text{ W/m}\cdot\text{K}$ and $T_0 = 408 \text{ K}$, for the case of adiabatic expansion, $\gamma = 7/5$, and, for those with surface tension, $\sigma = 1.75 \times 10^{-2} \text{ N/m}$.

Figure 9: Final fluid pressure surrounding bubble, $\bar{r}_c = 3.76$ and $\dot{\bar{r}}_c = 1.60 \times 10^{-4}$, corresponding to our best fits for bubble growth observations of Fig. 4. Of [7] to theories with viscous dissipation Eq. (149) with Eq. (123) [Blue] and Eq. (154) with Eq. (129) [Black], $p_0 = 100 \text{ atm}$; Eq. (161) with Eq. (137) [Red] and Eq. (166) with Eq. (143) [Green], $p_0 = 200 \text{ atm}$. For all curves $\mu = 1.957 \times 10^7 \text{ Pa}\cdot\text{s}$, $R_0 = 3.5 \mu\text{m}$, $p_\infty = 1 \text{ atm}$, $\rho = 10^3 \text{ kg/m}^3$, for the case of adiabatic expansion, $\gamma = 7/5$, and, for those with surface tension, $\sigma = 1.75 \times 10^{-2} \text{ N/m}$. Bubbles collide at $\Theta \approx 3 \times 10^8$. These curves provide estimates for the final penetration depth of the pressure wave surrounding the bubbles.

Figure 10: Final stresses, $\bar{r}_c = 3.76$ and $\dot{\bar{r}}_c = 1.60 \times 10^{-4}$, surrounding bubble, $\lambda_b \tau_{\theta\theta} / \mu = \lambda_b \tau_{\phi\phi} / \mu = -\tau_{rr} \lambda_b / 2\mu$, corresponding to our best fits for bubble growth observations of Fig. 4. Of [7] to theories with viscous dissipation Eq. (181) with Eq. (123) [Blue] and Eq. (129) [Black], $p_0 = 100 \text{ atm}$; Eq. (181) with Eq. (137) [Red] and Eq. (143) [Green], $p_0 = 200 \text{ atm}$. For all curves, $\mu = 1.957 \times 10^7 \text{ Pa}\cdot\text{s}$, $R_0 = 3.5 \mu\text{m}$, $p_\infty = 1 \text{ atm}$, $\rho = 10^3 \text{ kg/m}^3$, for the case of adiabatic expansion, $\gamma = 7/5$, and, for those with surface tension, $\sigma = 1.75 \times 10^{-2} \text{ N/m}$. Bubbles collide at $\Theta \approx 3 \times 10^8$.

Table I: Literature on Bubble Growth or Collapse from First Principles

	Assumes known	Expansion/ Collapse	Viscous dissipation	Surface Tension	Results	Form	[Ref.] (Correction to)
Rayleigh (1917)		Collapse $\gamma = 1$			R, p	$\mathcal{H}$	[24]
Lamb (1923)		Collapse $\gamma > 1$			R	$\mathcal{H}$	[32]
Lamp (1932)		Collapse $\gamma > 1$			R, p	$\mathcal{H}$	[31]
Batchelor (1967)	$p(t)$	Expansion $\gamma = 1$			R, p	$\mathcal{H}$	[4]
Street (1968)							[26]
Middleman (1977)	constant $\dot{R}$	Expansion			R	$\mathcal{H}$	[5]
This paper		Expansion $\gamma = 1;$ $\gamma > 1$	X	X	$R, T,$ $p, \boldsymbol{\tau}$	$\mathfrak{N}$	(24,30,32)

R $\equiv$ Bubble size; T $\equiv$ Temperature rise; p $\equiv$ Fluid pressure; $\boldsymbol{\tau}$ $\equiv$ Extra stresses tensor; $\mathcal{H}$ $\equiv$ Analytical; $\mathfrak{N}$ $\equiv$ Finite difference;

Table II: Dimensionless Variables and Groups

Bubble radius	$\bar{r} \equiv R/R_0$
Bubble radius, collision point	$\bar{r}_c \equiv R_c/R_0$
Bubble radius, final position	$\bar{r}_f \equiv R_f/R_0$
Temperature rise	$\mathcal{T} \equiv (T - T_0)/T_0$
Bubble convectability	$Bc \equiv \frac{\rho C_p R_0^2}{\lambda_b k} = \frac{\sqrt{\rho p_\infty} C_p R_0}{k}$
Bubble heatability	$Bv \equiv \frac{\mu R_0^2}{T_0 \lambda_b^2 k} = \frac{\mu p_\infty}{\rho T_0 k}$
Energy ratio, total viscous dissipation to total kinetic energy of fluid	$\mathbb{V} \equiv 4\sqrt{2}\mu/R_0\sqrt{\rho p_\infty}$
Heat capacity ratio	$\gamma \equiv C_p/C_v$
Pressure, nucleus	$\Pi \equiv p_0/p_\infty$
Spherical coordinate, radial	$\zeta \equiv r/R$
Surface tension	$\Sigma \equiv 2\sigma/p_\infty R_0$
Time elapsed since nucleation	$\Theta \equiv t/\lambda_b$
Time elapsed since nucleation to collision point	$\Theta_c \equiv t_c/\lambda_b$
Time elapsed since nucleation to final position	$\Theta_f \equiv t_f/\lambda_b$
Pressure	$\mathcal{P} \equiv p/p_\infty$
Sum of squares of residuals (see Eq. (14.5) of 44])	$S_R \equiv \sum_{i=1}^{12} (\bar{r}_{m,i} - \bar{r}_i)^2$
Bubble radius, i th measurement	$\bar{r}_{m,i}$
Bubble radius predicted from theory [Eqs. (123), (129), (137) and (143)] at time of i th observation	$\bar{r}_i$

Table III: Dimensional Variables

Amount of gas	mole	n
Bubble growth rate	L/t	$\dot{R} \equiv dR/dt$
Bubble acceleration	L/t^2	$\ddot{R} \equiv d^2R/dt^2$
Bubble growth rate, collision point	L/t	$\dot{R}_c \equiv dR/dt _{t_c}$
Bubble radius	L	R
Bubble radius, collision point	L	R_c
Bubble radius, final position	L	R_f
Bubble volume	L^3	V
Bubble volume, nucleus	L^3	V_0
Characteristic time for bubble growth	t	$\lambda_b \equiv R_0 \sqrt{\rho/p_\infty}$
Extra stress tensor ¹	M/Lt^2	$\boldsymbol{\tau}$
Extra stress tensor, ij th component	M/Lt^2	τ_{ij}
Pressure, far field	M/Lt^2	p_∞
Fluid density	M/L^3	ρ
Temperature, fluid	T	T
Temperature, nucleus	T	T_0
Gas constant	$ML^2/t^2T\text{mole}$	$\mathcal{R}$
Heat capacity at constant pressure	ML^2/t^2T	C_p
Heat capacity at constant pressure per unit mass	L^2/t^2T	$\hat{C}_p$
Heat capacity at constant volume	ML^2/t^2T	C_v
Heat flux vector	M/t^3	$\mathbf{q}$

¹ Where τ_{ij} is the force exerted in the j th direction on a unit area of fluid surface of constant x_i by fluid in the region lesser x_i on fluid in the region greater x_i (see Note on p. 19 of [3]).

Heat flux vector, i th component	M/t^3	q_i
Interfacial tension between bubble gas and liquid	M/t^2	σ
Internal Energy	L^2/t^2	$\hat{U}$
Kinetic energy	ML^2/t^2	E_k
Spherical coordinate, angular latitudinal	rad	θ
Spherical coordinate, angular longitudinal	rad	ϕ
Newtonian viscosity	M/Lt	μ
Nucleation absolute temperature	T	T_0
Pressure, nucleus	M/Lt^2	p_0
Radius, nucleus	L	R_0
Pressure outside the bubble	M/Lt^2	p
Pressure inside the bubble	M/Lt^2	p_R
Spherical coordinate, radial	L	r
Rate of deformation tensor	t^{-1}	Δ
Rate of deformation tensor, ij th component	t^{-1}	Δ_{ij}
Surface area	L	S
Surface area at nucleation	L	S_0
Thermal conductivity	ML/t^3T	k
Time elapsed since nucleation	t	t
Time elapsed since nucleation to collision point	t	t_c
Time elapsed since nucleation to final position	t	t_f
Velocity tensor	L/t	$\mathbf{v}$
Velocity tensor, i th component	L/t	v_i
Viscous dissipation term in mechanical energy balance	ML^2/t^2	E_v

Work done on the surrounding fluid	ML^2/t^2	W
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Table IV: Analysis of measured nitrogen bubble growth in molten polystyrene

i	Observed*		Interpolated**		$\dot{R}(\mu\text{m/s})$		Eq. (123); $\aleph$	
	$t(\text{s})$	$R(\mu\text{m})$	$t(\text{s})$	$R(\mu\text{m})$		Eq. from Table II. of [35], Row Number X	$R(\mu\text{m})$	$\dot{R}(\mu\text{m/s})$
1	11.6	3.82	11.6	3.82	0.117	-2	6.10	0.140
2	21.7	4.86	33.8	6.40	0.101	-1	7.25	0.095
3	31.9	6.19	56.0	8.54	0.085	0	8.10	0.073
4	40.7	7.06	78.2	9.76	0.071	0	8.69	0.061
5	50.9	8.05	100.4	11.56	0.054	0	9.26	0.052
6	59.7	8.84	122.5	12.80	0.037	0	9.69	0.046
7	71.1	9.19	144.7	13.00	0.016	0	10.18	0.040
8	80.0	9.91	166.9	13.10	0.027	0	10.52	0.036
9	90.1	10.69	189.1	13.15	0.003	0	10.86	0.033
10	100.3	11.11	211.3	13.18	0.002	0	11.18	0.030
11	110.4	12.66	233.5	13.24	0.002	1	11.46	0.027
12	121.8	13.16	255.7	13.28	0.002	2	11.76	0.025

Legend: *Fig. 4. of [7], $T = 408\text{K}$; **Cubic spline; $\aleph \equiv$ Finite difference

Table V: Best fit for bubble growth observations of *Fig. 4.* of [7] to our theory

Version	$\Pi \equiv p_0/p_\infty$	$\Sigma \equiv 2\sigma/p_\infty R_0$	$\mathbb{V} \times 10^{-9}$	S_R
Eq. (22)	54.9	0	0	1.375
Eq. (31)	54.9	0.1	0	1.386
Eq. (37)	74.1	0	0	1.892
Eq. (41)	74.1	0.1	0	1.903
Eq. (123)	100	0	3.16	4.653
Eq. (129)	100	0.1	3.16	4.654
Eq. (137)	200	0	3.16	5.577
Eq. (143)	200	0.1	3.16	5.599

For all equation: $R_0 = 3.5\mu\text{m}$; $\rho = 1000\text{kg/m}$; $p_\infty = 1\text{atm}$; $\mathbb{V} \equiv 4\sqrt{2}\mu/R_0\sqrt{\rho p_\infty}$

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