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Diffusion of Gas from a Liquid into an Expanding Bubble

Abstract: The growth of a bubble within a volume of isothermal viscous liquid containing uniformly distributed dissolved gas is considered. The problem of characterizing this growth-by-mass-transfer is reduced to an integro-differential equation for the bubble radius as a function of time, and a computer solution is obtained. The initial and final stages of growth are treated analytically.

Introduction

A technique now being considered for dry-process photography of documents involves the formation of light-scattering bubbles in a clear plastic medium. The bubbles are formed when a supersaturated solution of gas in the plastic medium is brought to a critical temperature, whereupon nucleation and bubble growth occur. This supersaturated solution of gas in plastic can be brought about in a number of ways. In the dry-photographic process, the gas is formed by photodecomposition of a diazo compound previously dissolved in the plastic. It may also be formed by physically dissolving the gas in the plastic film under high pressures and then bringing the plastic to room pressure.

Although the mechanism of nucleation is not yet fully understood, we know that once nucleation occurs, bubble growth is controlled by the classical laws of motion; the pressure of the gas provides the driving force to expand the bubble while the inertia and viscosity of the plastic, together with the interfacial tension of the bubble wall, provide the resistance. The change in bubble pressure with time is governed by the rate at which dissolved gas can diffuse into the growing bubble; the initial or nucleation pressure is determined experimentally.

Thus, in a complete study of the bubble growth problem the diffusion equation is coupled to the equations of viscous hydrodynamics.

An informal analysis of the problem has been made by W. L. Peticolas;[1] he calculated the limiting cases of extremely rapid and extremely slow gas diffusion. If the diffusion is sufficiently rapid, the bubble pressure remains constant and the growth is determined by the hydrodynamic equations alone. On the other hand, if the diffusion is sufficiently slow, hydrodynamic effects become negligible; an asymptotic solution as developed in Section 6 then applies.

From this analysis, together with his experimental work on bubble growth, Peticolas found that cases of practical interest for his purposes lie between the extremes, being dominated neither by hydrodynamic effects nor by diffusion. Concluding that a more extensive analysis would prove useful, he suggested to us the problem studied in this report.

In Section 1, we specify the physical assumptions behind our mathematical formulation of the bubble growth problem. Section 2 concerns the underlying hydrodynamics and Section 3 deals with the diffusion of gas through the plastic melt.

The general analysis of the bubble growth problem, carried out in Section 4, is based on the assumption that the significant variation of gas concentration is confined to a thin shell surrounding the bubble. The problem is reduced to a single integro-differential equation for the bubble radius as a function of time.

Sections 5 and 6 concern, respectively, the initial and final stages of growth. We find that, initially, the bubble radius grows as a linear function of time; in the final stage, it is proportional to the square root of time.

In Section 7, we carry out the numerical solution for the growth of nitrogen bubbles in vinylidene chloride-acrylonitrile copolymer. The physical constants for this combination of materials were determined experimentally by Peticolas. We find that the thin shell approximation used in Section 4 is justified, since, even in the final stages of growth, the radial variation of concentration is negligible except in a

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region quite close to the bubble. We also find, however, that the initial-stage solution of Section 4 provides a useful approximation only for very small bubbles. In general, the initial stage passes after a few microseconds and, in Peticolas' work, the bubbles are allowed to grow for about 500 milliseconds. Furthermore, the final stage, analyzed in Section 6, is not reached until several seconds have elapsed. Thus, in order to provide a useful correlation between nucleation size and final size of the bubbles in Peticolas' experiments, we must use the general analysis of Section 4, which leads to the numerical results of Section 7.

1. The idealized problem

To permit a mathematically tractable analysis, the actual conditions of bubble growth were somewhat idealized in defining the problem studied here. If we first specify the assumptions involved in this idealization, the consequent limitations of the analysis can be understood *a priori.*

We assume, first of all, that a single bubble of gas is growing in an otherwise unlimited volume of liquid. Thus, we neglect interactions of the bubble with its neighbors and with the boundaries of the liquid volume. Since we find *a posteriori* that the growing bubble is influenced almost exclusively by diffusion from a thin shell surrounding it, this assumption is satisfied almost until the bubbles grow into one another.

We assume that the liquid is a Newtonian fluid. Since it is, in fact, a molten plastic, it exhibits Newtonian behavior only at low rates of deformation; at somewhat higher rates, Newtonian behavior can be assumed as a first approximation. Virtually no data is available on the rheological properties of the plastics being considered for dry-process photography. By analogy with better known polymeric systems, we expect that non-Newtonian effects become important at a rate of deformation somewhere between 10^{-2} reciprocal seconds and 1 reciprocal second.

We also assume that the liquid is incompressible and that its viscosity is constant. If we ignore the effect of the dissolved gas on the much greater density of the melt, the incompressibility assumption is quite well founded; since the viscosity of the plastic is virtually independent of the concentration of dissolved gas, the assumption of constant viscosity is valid if the temperature is effectively uniform and constant throughout most of the bubble's growth. The condition may or may not be met, depending upon the circumstances under which the melting of the plastic is carried out.

Finally, we assume: 1) the gas is ideal, 2) it diffuses through the melt according to Fick's law,[2] 3) the concentration inside the bubble is related to the concentration just outside according to Henry's law,[3] and 4) only a negligible amount of gas is adsorbed on the bubble wall. Henry's law is not precisely satisfied by the gas-polymer system, but it does provide a good approximation. The other assumptions are valid under the conditions which can be expected in dry-process photography.

The mathematical approximations introduced to simplify the analysis will be discussed as they appear.

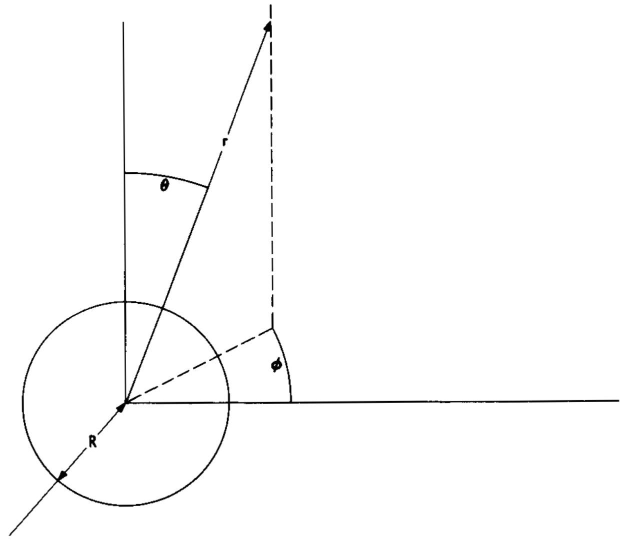


Figure 1 **The coordinate system.**

2. Hydrodynamics of the problem

Consider a spherical bubble of ideal gas with radius R growing in an otherwise unlimited volume of viscous, incompressible liquid. The growing bubble generates a velocity field within the liquid which, in turn, generates a stress field tending to retard the bubble's growth.

The spherical symmetry of the situation makes it convenient to choose a spherical coordinate system with its origin at the center of the bubble, as illustrated in Fig. 1. The velocity field generated in the liquid will have only a radial component $v(r, t)$, where t is time measured from the instant of bubble formation. The pressure p at any point in the liquid is also a function of r and t. The equations of viscous flow[4] then reduce to

$$\rho[(\partial v/\partial t) + (v\partial v/\partial r)] = -(\partial p/\partial r) + \mu[(1/r)(\partial^2 rv/\partial r^2) - (2v/r^2)]\,, \tag{2.1}$$

$$(\partial v/\partial r) + (2v/r) = 0\,. \tag{2.2}$$

In Eq. (2.1), ρ is the density and μ the viscosity of the liquid. Both are assumed uniform and constant.

At the bubble wall, the liquid velocity must equal $\dot{R}(t)$ where a superimposed dot denotes ordinary differentiation with respect to time. Thus, integration of Eq. (2.2) yields

$$v(r, t) = (1/r^2)[R(t)]^2\dot{R}(t)\,. \tag{2.3}$$

Substituting Eq. (2.3) into Eq. (2.1) and integrating, we find

$$(p - p_a)/\rho = (R/r)(2\dot{R}^2 + R\ddot{R}) - (R^4\dot{R}^2/2r^4)\,, \qquad (2.4)$$

in which p_a is the pressure far from the bubble.

The stress components for the velocity field given by Eq. (2.3) are[4]

$$\begin{aligned} \sigma_{rr} &= -p - (4\mu R^2\dot{R}/r^3)\,, \\ \sigma_{\theta\theta} &= \sigma_{\phi\phi} = -p + (2\mu R^2\dot{R}/r^3)\,, \\ \sigma_{\theta\phi} &= \sigma_{\phi r} = \sigma_{r\theta} = 0\,. \end{aligned} \qquad (2.5)$$

Within the bubble,

$$\begin{aligned} \sigma_{rr} &= \sigma_{\theta\theta} = \sigma_{\phi\phi} = -p_g(t)\,, \\ \sigma_{\theta\phi} &= \sigma_{\phi r} = \sigma_{r\theta} = 0\,, \end{aligned} \qquad (2.6)$$

in which p_g is the pressure of the ideal gas forming the bubble.

The stress components $\sigma_{\phi r}$ and $\sigma_{r\theta}$ must be continuous across the bubble surface. A comparison of Eqs. (2.5) and (2.6) reveals that this requirement is automatically satisfied. The stress component σ_{rr} must experience a jump of magnitude $2\sigma/R$, where σ is the coefficient of interfacial tension. The stress inside the bubble is lower (if both media were inviscid, this would reduce to a statement that the pressure inside the bubble is higher). Comparing the first of Eqs. (2.5) with the first of Eqs. (2.6), we find that the pressure just outside the bubble wall is given by

$$p(R+0, t) = p_g(t) - (2\sigma + 4\mu\dot{R})/R\,. \qquad (2.7)$$

By setting $r = (R + 0)$ in Eq. (2.4), we obtain an ordinary differential equation for the bubble radius as a function of the pressure inside the bubble:

$$R\ddot{R} + (3\dot{R}^2/2) + (4\mu\dot{R}/\rho R) + (2\sigma/\rho R) = (p_g - p_a)/\rho\,. \qquad (2.8)$$

A dimensionless form of this equation is obtained by setting

$$t = (2\sigma/p_a)\sqrt{\rho/p_a}\,\tau\,, \qquad (2.9)$$

$$R = (2\sigma/p_a)u\,, \qquad (2.10)$$

so that

$$u\ddot{u} + (3\dot{u}^2/2) + (Q\dot{u}/u) + (1/u) - (p_g/p_a) + 1 = 0\,, \qquad (2.11)$$

in which the superimposed dot now denotes differentiation with respect to τ and where

$$Q = (2\mu/\sigma)\sqrt{p_a/\rho}\,. \qquad (2.12)$$

The dimensionless parameter Q is the reciprocal of a Reynolds number based upon $(2\sigma/p_a)$ as a length scale and $\sqrt{p_a/\rho}$ as a velocity scale. Thus, for large values of Q, viscosity dominates over fluid inertia in retarding the bubble growth.

Heretofore, the pressure inside the bubble has been considered an arbitrary function of time. The size of the bubble is related to this pressure by Eq. (2.8) or its dimensionless equivalent, Eq. (2.11).

The bubble pressure $p_g(t)$ is related to the amount of gas within the bubble at time t according to the ideal gas law. If we assume isothermal conditions,

$$p_g(t) = Ac_g\,, \qquad (2.13)$$

where c_g is the concentration (density) of the gas forming the bubble, and where A is a constant given by

$$A = R_g T/M\,. \qquad (2.14)$$

In Eq. (2.14), R_g is the universal gas constant, T is the absolute temperature, and M is the molecular weight of the gas. Substituting Eq. (2.13) into Eq. (2.8), we obtain

$$\rho R\ddot{R} + (3\rho\dot{R}^2/2) + (4\mu\dot{R}/R) + (2\sigma/R) = Ac_g - p_a\,. \qquad (2.15)$$

3. Diffusion of gas through the liquid

Assume that at time $t = 0$ a homogeneous concentration c_0 of gas is dissolved throughout the liquid. At any subsequent time, the concentration c obeys Fick's law of diffusion,

$$Dc/Dt = D\nabla^2 c\,, \qquad (3.1)$$

where D is the diffusion constant. The material derivative Dc/Dt is used in Eq. (3.1) to account for convection of gas by the moving liquid. In view of the spherical symmetry, Eq. (3.1) becomes

$$(\partial c/\partial t) + v(\partial c/\partial r) = D[(\partial^2 c/\partial r^2) + (2/r)(\partial c/\partial r)]\,, \qquad (3.2)$$

where, according to Eq. (2.3),

$$v = R^2\dot{R}/r^2\,. \qquad (3.3)$$

Equation (3.2) is subject to a boundary condition at the bubble wall. Since buildup of adsorbed gas on the bubble wall is assumed negligible, the rate of increase of gas within the bubble equals the rate of flow inward across the wall. Thus,

$$d(4\pi R^3 c_g/3)/dt = 4\pi R^2 D(\partial c/\partial r)\big|_{r=R}\,. \qquad (3.4)$$

At a sufficiently great distance from the bubble, the effect of the growing bubble should be negligible, so that the concentration at any time is nearly equal to the initial concentration. We therefore take, as our second boundary condition,

$$\lim_{r\to\infty} c(r, t) = c_0 \qquad (t > 0)\,. \qquad (3.5)$$

The assumption of a homogeneous concentration of dissolved gas at time $t = 0$ provides the initial condition

$$c(r, 0) = c_0 \qquad (r > R_0)\,. \qquad (3.6)$$

At any instant of time, the concentration just outside the bubble wall is related to the concentration within the bubble through Henry's law. We have

$$c(R+0, t) = kc_g(t) \qquad (t > 0)\,, \tag{3.7}$$

where k is a constant.

This completes the mathematical formulation of the bubble growth problem. In summary, we find that there are essentially three dependent variables: $R(t)$, $c_g(t)$ and $c(r, t)$. They satisfy the ordinary differential equation

$$R\ddot{R} + (3\dot{R}^2/2) + (4\mu\dot{R}/\rho R) + (2\sigma/\rho R) = (Ac_g - p_a)/\rho\,, \tag{2.15}$$

and the partial differential equation

$$(\partial c/\partial t) + (R^2\dot{R}/r^2)(\partial c/\partial r) = D[(\partial^2 c/\partial r^2) + (2/r)(\partial c/\partial r)] \tag{3.2}$$

subject to the boundary conditions

$$\partial c/\partial r|_{r=R} = [1/3DR^2][d(R^3 c_g)/dt]\,, \tag{3.4}$$

$$\lim_{r\to\infty} c(r, t) = c_0\,, \tag{3.5}$$

to the initial condition

$$c(r, 0) = c_0\,, \tag{3.6}$$

and to the matching condition

$$c(R+0, t) = kc_g(t)\,. \tag{3.7}$$

In the ensuing analysis, we shall find that the bubble's initial radius and growth rate, or their equivalent, must also be specified.

Upon examining this system of equations, we find that both differential equations are nonlinear, as is the boundary condition (3.4). There is the additional complication that Eqs. (3.4) and (3.7) apply on a boundary moving in a manner not specified *a priori.*

One difficulty associated with a moving boundary problem can be avoided by using a Lagrangian description. In this procedure, the independent variables other than time are the initial coordinates of the fluid particles, rather than points in space. Since in a continuum theory, a fluid boundary always consists of the same particles, the Lagrangian coordinates describing the boundary do not change with time.

With the fluid velocity given by Eq. (3.3), any function of $(r^3 - R^3)$ could serve as a Lagrangian radial coordinate. We find it most convenient to choose $(r^3 - R^3)/3$. The equation system can be further simplified by changing the time variable. Thus, we change independent variables from r and t to h and θ according to

$$3h = r^3 - [R(t)]^3\,, \tag{3.8}$$

$$\theta = \int_0^t R^4(t)dt\,. \tag{3.9}$$

In terms of the new variables, the nonlinear convective term disappears from Eq. (3.2), and we have

$$(\partial c/\partial\theta) = D(\partial/\partial h)[(1 + 3h/R^3)^{4/3}(\partial c/\partial h)]\,. \tag{3.10}$$

The boundary conditions (3.4) and (3.5) become

$$\partial c/\partial h|_{h=0} = [d(R^3 c_g)/d\theta]/3D \tag{3.11}$$

$$\lim_{h\to\infty} c(h, \theta) = c_0\,, \tag{3.12}$$

and the initial condition (3.6) becomes

$$c(h, 0) = c_0\,. \tag{3.13}$$

We can now proceed as if the diffusion problem were distinct from the hydrodynamics, solving Eq. (3.10), subject to the boundary conditions (3.11), (3.12) and to the initial condition (3.13), with R and c_g retained as arbitrary functions of θ. We can thus obtain $c(+0, \theta)$ in terms of R and c_g; Henry's law, Eq. (3.7), then yields a relation between R and c_g. The concentration c_g can thereby be eliminated from the hydrodynamic equation (2.15) and the resulting equation for R solved numerically.

The complicated form of the right side of Eq. (3.10) makes it unlikely that an exact solution to the diffusion problem can be obtained. We develop an approximate solution in the next section.

4. The thin shell approximation

Since we assume the bubble nucleates with a finite radius R_0, there will be a time interval during which the bubble radius is much larger than the diffusion length $\sqrt{Dt}$. During this time interval, the concentration of gas in the liquid is significantly disturbed by the growing bubble only in a thin shell surrounding the bubble. Outside this shell, the concentration is virtually equal to c_0.

A similar thin shell approximation was used by Plesset and Zwick[5] in their study of thermal diffusion into a vapor bubble within a volume of superheated water. Their analysis applies directly to our problem.

In the thin shell, where the important variation of concentration is assumed to occur, h is small compared with R^3. Eq. (3.10) can therefore be replaced by

$$\partial c/\partial\theta = D(\partial^2 c/\partial h^2)\,. \tag{4.1}$$

We now let

$$C(h, s) = \mathscr{L}[c(h, \theta)]\,, \tag{4.2}$$

where $\mathscr{L}$ denotes the Laplace transform, i.e.,

$$\mathscr{L}[c(h, \theta)] = \int_0^\infty c(h, \theta)\exp(-s\theta)d\theta\,. \tag{4.3}$$

With the initial condition (3.13), Eq. (4.1) transforms to

$$D(\partial^2 C/\partial h^2) = sC - c_0\,. \tag{4.4}$$

The boundary condition (3.11) transforms to

$$\partial C/\partial h|_{h=0} = f(s)\,, \tag{4.5}$$

where

$$f(s) = (1/3D)\mathscr{L}[d(R^3c_g)/d\theta]. \tag{4.6}$$

The boundary condition (3.12) must be carefully considered. Since it concerns the behavior of $c(h, \theta)$ for large values of h, it cannot, strictly speaking, be applied to Eq. (4.1), which holds only for values of h small compared with R^3. However, in writing Eq. (4.1), we assume that $c(h, \theta)$ is nearly equal to c_0 outside the thin shell. Thus, it is quite proper to apply condition (3.12) to Eq. (4.1), provided we find *a posteriori* that the resulting solution for $c(h, \theta)$ decays rapidly toward c_0 as h increases. Taking the Laplace transform of Eq. (3.12), we obtain

$$\lim_{h\to\infty} C(h, s) = c_0/s\,. \tag{4.7}$$

Integrating Eq. (4.4) subject to conditions (4.5) and (4.7) yields

$$C(h, s) = (c_0/s) - \sqrt{D/s}f(s)\exp(-h\sqrt{s/D})\,. \tag{4.8}$$

The inverse transform of Eq. (4.8) can be obtained by convolution. Using Eq. (4.6), we find that the concentration of gas in the liquid is given by

$$c(h, \theta) = c_0 - \frac{1}{3\sqrt{\pi D}} \times \int_0^\theta \frac{(d/d\lambda)(R^3C_g)\exp[-h^2/4D(\theta-\lambda)]}{\sqrt{\theta-\lambda}}\,d\lambda\,. \tag{4.9}$$

For small values of θ the concentration, as expected, differs appreciably from c_0 only in a thin shell about the bubble, viz., when h is of order $\sqrt{D\theta}$ or smaller.

We can now obtain a relation between R and c_g by setting h equal to zero in Eq. (4.9). Using Henry's law, Eq. (3.7), we have

$$kc_g = c_0 - \frac{1}{3\sqrt{\pi D}}\int_0^\theta \frac{d(R^3c_g)/d\lambda}{\sqrt{\theta-\lambda}}\,d\lambda\,. \tag{4.10}$$

The hydrodynamic equation (2.15) provides an expression for c_g in terms of R:

$$c_g = (1/A)[p_a + \rho R\ddot{R} + (3\rho\dot{R}^2/2) + (4\mu\dot{R}/R) + (2\sigma/R). \tag{4.11}$$

If this expression for c_g is substituted into Eq. (4.10), we obtain an integro-differential equation for $\ddot{R}(t)$. However, we note that $\dddot{R}$ will appear in the integrand. This complication could be avoided by integrating Eq. (4.10) by parts, except that this procedure leads to an indeterminate form of the type $\infty - \infty$:

$$\int_0^\theta \frac{d(R^3c_g)/d\lambda}{\sqrt{\theta-\lambda}}\,d\lambda = -\frac{C_0R_0{}^3}{k\sqrt{\theta}} + \lim_{\varepsilon\to 0}\left[\frac{R^3c_g}{\sqrt{\theta-\lambda}}\Bigg|_{\lambda=\theta-\varepsilon} - \frac{1}{2}\int_0^{\theta-\varepsilon}\frac{R^3c_g}{(\theta-\lambda)^{3/2}}\,d\lambda\right]. \tag{4.12}$$

Observe, however, that

$$\lim_{\varepsilon\to 0}\left[\frac{R^3c_g}{\sqrt{\theta-\lambda}}\Bigg|_{\lambda=\theta-\varepsilon} - \frac{1}{2}\int_0^{\theta-\varepsilon}\frac{R^3c_g}{(\theta-\lambda)^{3/2}}\,d\lambda\right] = \frac{d}{d\theta}\int_0^\theta \frac{R^3c_g}{\sqrt{\theta-\lambda}}\,d\lambda\,. \tag{4.13}$$

Eq. (4.10) therefore becomes

$$kc_g = c_0 - \frac{1}{3\sqrt{\pi D}}\frac{d}{d\theta}\int_0^\theta \frac{R^3c_g d\lambda}{\sqrt{\theta-\lambda}} + \frac{C_0R_0{}^3}{3k\sqrt{\pi D\theta}}\,. \tag{4.14}$$

The problem of simplifying integrals similar to that appearing in Eq. (4.10) arises quite often in the linearized theory of supersonic aerodynamics. In that context, procedures similar to our derivation of Eq. (4.14) have been extensively studied. These studies of divergent integrals have led to an important concept, which Hadamard[6] has termed the finite part of an integral. The derivation of Eq. (4.14) from Eq. (4.10) is, in fact, a special application of Hadamard's technique.

We now integrate Eq. (4.14) over the interval $(0, \theta)$ obtaining

$$(k/c_0)\int_0^\theta \{1 + [R^3/3k\sqrt{\pi D(\theta-\lambda)}]\}c_g d\lambda = (2R_0{}^3/3k)\sqrt{\theta/\pi D} + \theta\,. \tag{4.15}$$

With Eq. (3.9), we can write Eq. (4.15) in terms of the original time variable. Thus,

$$(k/c_0)\int_0^t \left\langle 1 + \left\{[R(t')]^3/3k\left[\pi D\int_{t'}^t R^4 dt\right]^{1/2}\right\}\right\rangle \times [R(t')]^4 c_g(t')dt' = (2R_0{}^3/3k)\left[(1/\pi D)\int_0^t R^4 dt\right]^{1/2} + \int_0^t R^4 dt\,. \tag{4.16}$$

Using the expression for c_g given by Eq. (4.11), we see that $R(t)$ is determined by the integro-differential equation

$$(k/c_0A)\int_0^t \left\{1 + \left[R^3/3k\left(\pi D\int_{t'}^t R^4 dt\right)^{1/2}\right]\right\} \times \{p_a + \rho[R\ddot{R} + (3\dot{R}^2/2)] + (4\mu\dot{R}/R) + (2\sigma/R)\}R^4 dt' = (2R_0{}^3/3k)\left[(1/\pi D)\int_0^t R^4 dt\right]^{1/2} + \int_0^t R^4 dt\,. \tag{4.17}$$

Eq. (4.17) can be rewritten in terms of the dimensionless variables τ and u. According to Eqs. (2.9) and (2.10)

$$\tau = [(p_a/2\sigma)\sqrt{p_a/\rho}]t\,, \tag{4.18}$$

$$u = (p_a/2\sigma)R\,, \tag{4.19}$$

so that

$$\int_0^\tau \left\{M + \left[u^3\Big/\left(\left(\int_{\tau'}^\tau u^4\, d\tau\right)^{1/2}\right]\right\}$$
$$\times \{1 + u\ddot{u} + (3\dot{u}^2/2) + (Q\dot{u}/u) + (1/u)\}u^4 d\tau'$$
$$= Nu_0^3\left(\int_0^\tau u^4 d\tau\right)^{1/2} + (1/2)MN\int_0^\tau u^4 d\tau\,. \tag{4.20}$$

In Eq. (4.20), M and N are dimensionless parameters defined by

$$M = 3k[(\pi D/2\sigma)(p_a\rho)^{1/2}]^{1/2}\,, \tag{4.21}$$

$$N = 2Ac_0/kp_a\,. \tag{4.22}$$

Q is the reciprocal Reynolds number defined earlier (Eq. 2.12) by

$$Q = (2\mu/\sigma)\sqrt{p_a/\rho}\,, \tag{4.23}$$

and u_0 is the initial value of u, i.e.,

$$u_0 = p_a R_0/2\sigma\,. \tag{4.24}$$

Superimposed dots now denote differential with respect to τ.

In principle, the variation of u with τ can be determined by solving the nonlinear integro-differential equation (4.20) subject to the initial condition (4.24), together with an appropriate initial condition on $\dot{u}$. Since it is unlikely that this solution can be found analytically, we turn first to approximate and then to numerical solutions.

In the next section, we make use of the high viscosity of the plastic to determine the bubble size during the early stages of growth. In Section 6 we investigate the asymptotic behavior of the bubble at large times. In Section 7, we compare these approximate solutions with a numerical solution of Eq. (4.20).

5. The initial stage of growth at low Reynolds number

We now consider the bubble growth under conditions such that the reciprocal Reynolds number Q is large compared with unity. Because of the high viscosity of plastic melts, this case is quite important.

The approach used in this section is analogous to that used by Plesset and Zwick[7] to simplify the integro-differential equation governing the early stages of bubble growth by thermal diffusion.

We note first that, for a medium of finite density and infinitely large Q, Eq. (4.20) is satisfied by $\dot{u} = 0$, so that the bubble never grows. If the medium has a high but finite viscosity, the bubble grows quite slowly, so that the bubble radius remains near R_0 for quite some time. We can obtain a perturbation solution to Eq. (4.20) for this initial stage of growth by setting

$$u(\tau) = u_0[1 + \varepsilon g(\tau)]\,, \tag{5.1}$$

where

$$\varepsilon = 1/Q\,, \tag{5.2}$$

i.e., ε is a Reynolds number.

Substitution of Eq. (5.1) into Eq. (4.20) yields a much simpler integro-differential equation. By neglecting terms of the second degree or higher in ε,

$$\int_0^\tau [M + (u_0/\sqrt{\tau - \lambda})]g'(\lambda)d\lambda$$
$$= [(N/2) - 1 - (1/u_0)][2u_0\sqrt{\tau} + M\tau]\,. \tag{5.3}$$

The initial condition (4.24) becomes

$$g(0) = 0\,. \tag{5.4}$$

Note that the second derivative in Eq. (4.20) is absent from Eq. (5.3). This second derivative originated in the inertia term of the hydrodynamic equation (2.1), and use of the Reynolds number as a perturbation parameter suppresses the effect of inertia. We can no longer impose an initial condition on $\dot{u}$. Physically, the effects of intertia are quickly damped out when ε is small. Thus, *except for the first instants of growth, the solution of Eq. (4.20) subject to Eq. (4.24) is virtually independent of the value chosen for $\dot{u}(0)$.*

The solution of Eq. (5.3) subject to Eq. (5.4) is

$$g(\tau) = [(N/2) - 1 - (1/u_0)]\tau\,, \tag{5.5}$$

so that, with Eq. (5.1) and (5.2), the initial stage of bubble growth is governed by

$$u = u_0\{1 + Q^{-1}[(N/2) - 1 - (1/u_0)]\tau\}\,. \tag{5.6}$$

With Eqs. (4.18), (4.19), (4.22), (4.23) and (4.24), we obtain, in terms of the original variables,

$$R/R_0 = 1 + (\sigma/2\mu)[(1/R_{crit}) - (1/R_0)]t\,, \tag{5.7}$$

where

$$R_{crit} = 2\sigma/[(Ac_0/k) - p_a]\,. \tag{5.8}$$

If $R_0 = R_{crit}$, the bubble does not grow. The physical significance of this can be perceived by omitting the inertia terms from Eq. (2.8). We see that $\dot{R}(0)$ vanishes if $2\sigma/R_0$ is equal to $p_g(0) - p_a$, i.e., if the pressure inside the bubble just balances surface tension. Equation (5.8) is obtained as the criterion by using Eq. (2.13) and Eq. (3.7). When R_0 is smaller than R_{crit}, the bubble shrinks.

6. The asymptotic stage

Since the liquid medium is unbounded, and since an unlimited amount of dissolved gas is available, the bubble is free to grow indefinitely large. We now investigate its growth behavior at times long after growth has begun.

In view of the high viscosity of the plastic, we neglect inertia. The hydrodynamic equation (2.8) then reduces to

$$(4\mu\dot{R}/R) + (2\sigma/R) = p_g - p_a . \tag{6.1}$$

Unless the ultimate growth rate is exponential or faster, p_g approaches the ambient pressure. With Eqs. (2.13) and (3.7), therefore, the concentration just outside the bubble wall approaches

$$c_i = kp_a/A . \tag{6.2}$$

At sufficiently large times, $c(R + 0, t)$ will differ from c_i by a negligibly small amount. In order to investigate the bubble growth in this asymptotic stage, we note following Birkhoff et al.,[8] that the diffusion equation (3.2) has a self-similar solution of the form

$$c(r, t) = f(s) , \tag{6.3}$$

where

$$s = r/\sqrt{Dt} , \tag{6.4}$$

provided that the bubble radius is proportional to $\sqrt{Dt}$. Calling the proportionality constant γ,

$$R = \gamma\sqrt{Dt} , \tag{6.5}$$

and we find that $f(s)$ must satisfy the ordinary differential equation

$$f''(s) + [(s/2) + (2/s) - (\gamma^3/2s^2)]f'(s) = 0 . \tag{6.6}$$

Thus,

$$f(s) = A - Bf_\gamma(s) , \tag{6.7}$$

where A and B are constants of integration, and

$$f_\gamma(s) = \int_s^\infty \chi^{-2} \exp[-(\chi^2/4) + (\gamma^3/2\chi)]d\chi . \tag{6.8}$$

If we assume that this self-similar solution obtains during the asymptotic stage, the constants of integration are determined by the boundary conditions

$$f(\gamma) = c_i , \tag{6.9}$$

$$\lim_{s\to\infty} f(s) = c_0 . \tag{6.10}$$

Since $f_\gamma(s)$ approaches zero as s approaches infinity,

$$A = c_0 \tag{6.11}$$

and

$$B = (c_0 - c_i)/f_\gamma(\gamma) , \tag{6.12}$$

so that

$$f(s) = c_0 - [(c_0 - c_i)f_\gamma(s)]/f_\gamma(\gamma) . \tag{6.13}$$

The one boundary condition still to be used is Eq. (3.4). Since in the asymptotic stage

$$c_g = p_a/A , \tag{6.14}$$

substitution of Eqs. (6.5) and (6.13) into Eq. (3.4) yields an implicit equation for γ:

$$(p_a\gamma/2A) + (c_0 - c_i)f'(\gamma)/f(\gamma) = 0 . \tag{6.15}$$

Birkhoff et al.[8] have solved this equation numerically, obtaining the curve shown in Fig. 2.

The asymptotic stage is attained when $p_g - p_a$ is small compared with p_a. In other words, with R given by Eq. (6.5), the left side of Eq. (6.1) should be small compared with p_a. If we wish to determine the influence of inertia on the time when the bubble enters the asymptotic stage, we use Eq. (2.8) instead of Eq. (6.1). Thus, Eqs. (6.3) and (6.5) provide a reliable solution to the bubble growth problem only if

$$(\rho\gamma^2 D/8p_a t) + (2\mu/p_a t) + (2\sigma/p_a\gamma\sqrt{Dt}) \ll 1 . \tag{6.16}$$

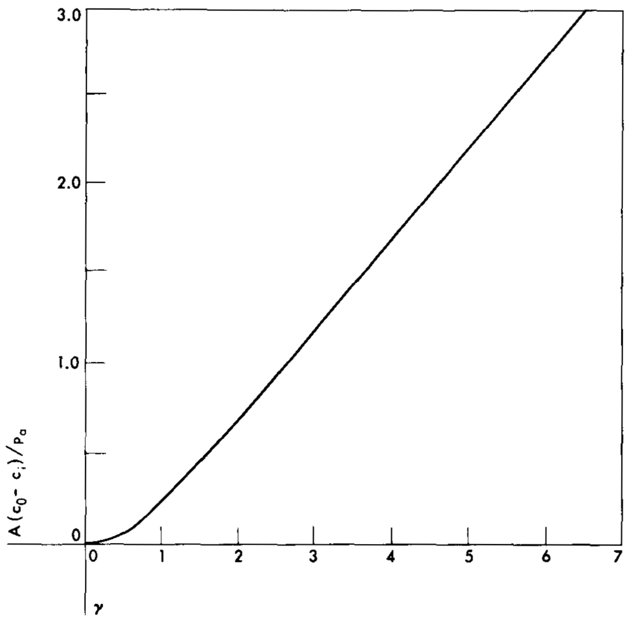
Because of the dominance of viscosity over inertia and surface tension, only the middle term is important. Thus, the criterion (6.16) is satisfied when

$$t \gg 2\mu/p_c . \tag{6.17}$$

If $p_g - p_a$ is small compared with p_a, then $c(R + 0, t) - c_i$ is small compared with c_i. Use of the boundary condition (6.9) introduces only a negligible error.

The criterion (6.17) is not a sufficient condition for the bubble to be in its asymptotic stage. Note that Eqs. (6.3) and (6.13) allow for no dependence on initial radius. If the bubble starts out only slightly larger than the critical radius given by Eq. (5.8), its growth will be extremely slow. Therefore, even if (6.17) is satisfied, the initial condition on R can continue to dominate the growth. Therefore, a bubble enters the asymptotic stage at a time determined both by the criterion (6.17) and, with Eq. (5.7), by the requirement

Figure 2 **Evaluation of proportionality constant γ from Eq. (6.15).**



$$t \gg 2\mu R_{crit}/\sigma[1-(R_{crit}/R_0)] \,. \tag{6.18}$$

7. The numerical solution

In the range where neither the initial solution of Section 5 nor the asymptotic solution of Section 6 apply, we can resort to a numerical solution of Eq. (4.20). In view of the very high viscosity of the plastic, however, it is sufficient to consider instead the equation

$$\int_0^\tau \left\{M + \left[u^3\Big/\left(\left(\int_{\tau'}^\tau u^4 d\tau\right)^{1/2}\right]\right\}\{Q\dot{u} + u + 1\}u^3 d\tau'$$

$$= Nu_0^3\left(\int_0^\tau u^4 d\tau\right)^{1/2} + (1/2)MN\int_0^\tau u^4 d\tau \,, \tag{7.1}$$

which is obtained from Eq. (4.20) by omitting the terms arising from fluid inertia.

We employ a time-sequential approach: The solution at any given time is calculated by numerical integration from the solution at previous times. We choose a mesh Δ fine enough that, in the interval

$$(n-1)\Delta \leqq \tau \leqq n\Delta \,, \tag{7.2}$$

the solution $u(\tau)$ is adequately represented by

$$u(\tau) = U_n + S_n[\tau - (n-1)\Delta] \,. \tag{7.3}$$

Thus, U_n and S_n signify, respectively, the value and the slope of $u(\tau)$ at the mesh-point $\tau = (n-1)\Delta$. A finite difference equation which converges to Eq. (7.1) as Δ approaches zero is provided by

$$MQ(U_n^4 - U_1^4)/4 + MQ\Delta U_n^3 S_n$$

$$+ M\Delta(\sigma_n^{(4)} + \sigma_n^{(3)}) + \sqrt{\Delta}$$

$$\times \sum_{i=1}^{n-1}\left\{U_i^6(QS_i + U_i + 1)\Big/\left[(U_n^4/2) + \sum_{j=i+1}^{n} U_j^4\right]^{1/2}\right\}$$

$$+ 2\sqrt{\Delta}U_n^4(S_n + U_n + 1)$$

$$= Nu_0^3\sqrt{\Delta\sigma_n^{(4)}} + (MN/2)\Delta\sigma_n^{(4)} \,, \tag{7.4}$$

in which

$$\sigma_n^{(k)} = (U_n^k - U_1^k) + \sum_{i=1}^{n} U_i^k \qquad (k = 3, 4) \,. \tag{7.5}$$

Since Eq. (7.3) implies that

$$U_n = U_{n-1} + \Delta S_{n-1} \,, \tag{7.6}$$

Eq. (7.4) can be solved for S_n in terms of $U_1, U_2, \cdots, U_{n-1}, S_1, S_2, \cdots, S_{n-1}$. The mesh point $n = 1$ corresponds to $\tau = 0$, so that

$$U_1 = u_0 \,. \tag{7.7}$$

Equation (5.6), which applies during the initial stage of growth, indicates that

$$S_1 = [(Nu_0/2) - u_0 - 1]/Q \,. \tag{7.8}$$

Thus, the values of U_n and S_n at $\tau = \Delta, 2\Delta, 3\Delta, \cdots$ can be calculated by repeated application of Eqs. (7.4) and (7.6)—a task evidently best done by digital computer. This process was carried out for values of the physical parameters appropriate for the growth of nitrogen bubbles in vinylidene chloride-acrylonitrile copolymer at 100°C. For this combination of materials, Peticolas found these values:

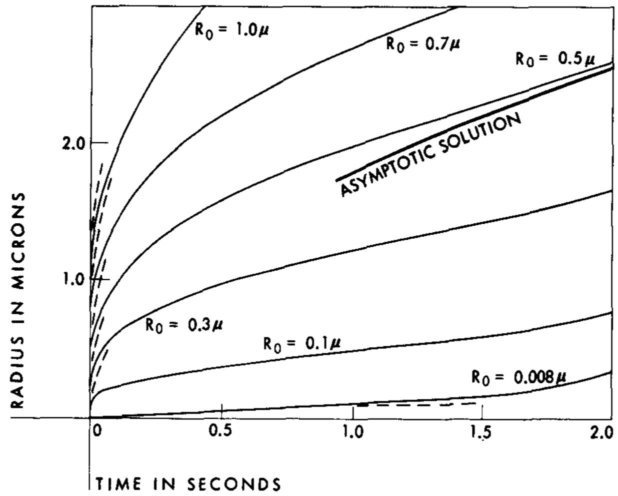


Figure 3 **Bubble ratios vs time, from numerical solution.**
Dotted lines denote small-time solutions.

- Viscosity of the liquid, $\mu = 10^6$ dyne-sec/cm;
- Density of the liquid, 1.45 g/cm^3;
- Coefficient of interfacial tension, $\sigma = 20$ dynes/cm;
- Gas law constant, $A = 1.1 \times 10^9$ dyne-cm/gm;
- Henry's law constant, $k = 3 \times 10^{-2}$;
- Diffusion coefficient, $D = 10^{-9}$ cm^2/sec.

Peticolas' experiments were carried out at an ambient pressure of 10^6 dynes/cm^2 and with an initial nitrogen concentration of 2.7×10^{-3} gm/cm. The critical radius, defined by Eq. (5.8), is therefore 4.07×10^{-7} cm, and the derived parameters M, N, Q, defined, respectively, by Eqs. (4.21), (4.22), (4.23) assume the values:

$$M = 2.78 \times 10^{-5} \,, \quad N = 200 \,, \quad Q = 8.3 \times 10^7 \,. \tag{7.9}$$

The dimensionless initial radius u_0, defined by Eq. (4.24), is related to the actual initial radius according to

$$u_0 = 2.5 \times 10^4\,\mathrm{cm}^{-1} R_0 \,. \tag{7.10}$$

Computer solution of Eqs. (7.4) and (7.6) provided the family of curves in Fig. 3. The dotted tangents to the curves represent the initial stage solution (Section 5), and the bold-face curve represents the asymptotic solution (Section 6) toward which all growing bubbles ultimately tend. Note that, except for very small bubbles, the initial stage solution is practically useless, describing the growth accurately for only a few microseconds. Although the trend toward the asymptotic solution is evident, Fig. 3 confirms the indication from criterion (6.17) that the asymptotic stage is not reached until t greatly exceeds 2 seconds. To carry the numerical solutions this far would require inordinate amounts of computer time, since the number of arithmetic operations increases roughly as the cube of the number of mesh points. Since, in practice, the growth process is stopped (by cooling the plastic) after about half a second, the asymptotic solution is of theoretical interest only.

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