ON THE DYNAMICS OF SMALL VAPOR BUBBLES IN LIQUIDS

S. A. Zwick and M. S. Plesset
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I. Introduction. When a vapor bubble in a liquid changes size, evaporation or condensation of the vapor takes place at the surface of the bubble. Because of the latent heat requirement of evaporation, a change in bubble size must therefore be accompanied by a heat transfer across the bubble wall, such as to cool the surrounding liquid when the bubble grows (or heat it when the bubble becomes smaller). Since the vapor pressure at the bubble wall is determined by the temperature there, the result of a cooling of the liquid is a decrease of the vapor pressure, and this causes a decrease in the rate of bubble growth. A similar effect occurs during the collapse of a bubble which tends to slow down the collapse. In order to obtain a satisfactory theory of the behavior of a vapor bubble in a liquid, these heat transfer effects must be taken into account.

In this paper, the equations of motion for a spherical vapor bubble will be derived and applied to the cases of a bubble expanding in superheated liquid and a bubble collapsing in liquid below its boiling point. Because of the inclusion of the heat transfer effects, the equations are nonlinear, integro-differential equations. In the case of the collapsing bubble, large temperature variations occur; therefore, tabulated vapor pressure data were used, and the equations of motion were integrated numerically. Analytic solutions are obtainable for the case of the expanding bubble if the period of growth is subdivided into several regimes and the simplifications possible in each regime are utilized. The growth is considered here only during the time that the bubble is small. An asymptotic solution of the equations of motion, valid when the bubble becomes large (i.e. observable), has been presented previously, together with experimental verification.1

We shall be specifically concerned in the following discussion with the dynamics of vapor bubbles in water. This restriction was made for convenience only, since the theory is applicable without modification to many other liquids.

II. Formulation of the Problem. The vapor bubble is taken to be spherical. The radial velocity of the bubble wall is considered to be negligible in comparison with sonic velocity in either the liquid or the vapor so that the water will be assumed incompressible, and it will be further assumed that conditions of dynamic and thermal equilibrium exist in the vapor so that the vapor pressure within the bubble will be uniform and equal to the equilibrium vapor pressure of the liquid at temperature of the bubble wall. Viscosity and gravity effects are ignored.† Then in terms of the external pressure $P_0$, the vapor pressure $p_v$ of the fluid at the bubble wall, the density of the water $\rho$ and the surface tension $\sigma$, the radius $R(t)$ of the bubble wall satisfies the differential equation

\[ \frac{dR}{dt} = \frac{1}{\rho} \left( P_0 - p_v - \frac{2\sigma}{R(t)} \right) \]

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† The justification for these physical assumptions will be found in Ref. 1.


with initial conditions
\[ R(0) = R_0, \quad (dR/dt)_{t=0} = 0. \] (2)

Unlike the vapor, the liquid cannot be assumed to be in thermal equilibrium. The heat problem in the liquid has been discussed in a previous paper,\(^3\) where a solution was obtained under the assumption that significant heat exchange takes place only in a thin layer of liquid surrounding the bubble wall. If the liquid contains a uniformly distributed heat source per unit volume of magnitude \( \eta(t) \), with \( \eta(0) = 0 \), the temperature at the bubble wall is given by\(^*\)

\[ T = T_0 + \frac{D}{k} \eta(t) - \left( \frac{D}{\pi} \right)^{\frac{1}{2}} \int_0^t R^2(x) (\partial T/\partial r)_{r=R(x)} dx, \] (3)

corresponding to an initial temperature \( T_0 \) and a temperature

\[ T_\infty = T_0 + (D/k)\eta(t) \] (4)
in the liquid far from the bubble wall. Here \( D \) is the thermal diffusivity and \( k \) the thermal conductivity of the liquid. The temperature gradient in the liquid at the bubble wall, which appears in (3), is obtained from the boundary condition

\[ 4\pi k R^2 (\partial T/\partial r)_{r=R} = (4\pi/3) L d(\rho'R^3)/dt, \] (5)

relating the heat flow across the bubble wall to the rate of heat transfer into the bubble due to evaporation or condensation, under the assumption of thermal equilibrium within the bubble. \( L \) is the latent heat of evaporation of the water and \( \rho' \) the density of vapor within the bubble.

The parameters \( \rho, \sigma, D, k, \) and \( L \) appearing above will be taken as constant, and equal to their values at the initial temperature \( T_0 \). The vapor density \( \rho' \) will be allowed to vary if significant temperature variations occur. The equilibrium vapor pressure \( p_v \) is assumed to be a known function of \( T \).

In terms of the constants

\[ \alpha^2 = \frac{2\sigma}{\rho R_0^3}, \quad c = \frac{L\rho' R_0}{3k} \left( \frac{\alpha D}{\pi} \right)^{\frac{1}{2}}, \] (6)

where \( \rho_0' = \rho'(T_0) \), we may define a set of dimensionless parameters

\[ p = \frac{R^2}{R_0^3}, \quad u = (\alpha/R_0) \int_0^t R^4(y) dy, \]

\[ \phi = R_0(P_0 - p)/2\sigma, \quad r = \rho'(T)/\rho_0', \] (7)

\(^*\)See Ref. 3, Eq. (20).
in terms of which the system of equations to be solved becomes

\[
\frac{1}{6} \frac{d}{dp} \left[ p^{7/3} \left( \frac{dp}{du} \right)^2 \right] + \frac{1}{p^{1/3}} + \phi = 0,
\]

\[
\phi = \phi(T),
\]

\[
T = T_0 + \frac{D}{k} \eta - c \int_0^u \frac{d(rp)/dv}{(u - v)^3} dv,
\]

\[
r = r(T).
\]

The initial conditions for (8) are

\[
p = 1, \quad \frac{dp}{du} = 0 \quad \text{for} \quad u = 0.
\]

The physical quantities we eventually wish to find are then given by

\[
t = \frac{1}{\alpha} \int_0^u \frac{dv}{p^{1/3}}, \quad R(t) = R_0 p^{1/3}, \quad \frac{dR}{dt} = \frac{\alpha R_0}{3} p^{2/3} \frac{dp}{du},
\]

\[
T = T_0 + \frac{D}{k} \eta - c \int_0^u \frac{d(rp)/dv}{(u - v)^3} dv.
\]

III. The Expanding Bubble. The vapor bubble which is to grow in superheated water must at some stage of the superheat be in unstable dynamic equilibrium under the effects of surface tension, vapor pressure and external pressure. Further superheating of the liquid increases the vapor pressure in the bubble and upsets the equilibrium. We shall idealize the actual physical situation by assuming the bubble to be initially in equilibrium in the shape of a sphere; then the condition for equilibrium at the time of release of the bubble \( t = 0 \) is that

\[
\frac{dR}{dt}_0 = \frac{d^2R}{dt^2}_0 = 0,
\]

and hence by Eq. (1) that

\[
p_s(T_0) - p_0 = \frac{2\sigma}{R_0}.
\]

For a given initial temperature \( T_0 \) and external pressure \( p_0 \), Eq. (14) fixes the equilibrium radius of the bubble. By Eq. (7), this is equivalent to the condition

\[
\phi(T_0) = -1.
\]

As the bubble grows, the temperature at the bubble wall decreases toward the boiling point. Inasmuch as water will support only a few degrees of superheat under ordinary conditions, the temperature variation involved in the growth is small and an approximate expression for the dependence of vapor pressure on temperature will suffice. For \( p_0 = 1 \) atm, a close fit to equilibrium vapor pressure data for water can be obtained between 100°C and 110°C by taking

\[
[p_s(T) - p_0]/\rho = A(T - 100),
\]

with \( A = 40,800 \) c.g.s. units. By combining (16) with (6), (7), (10), and (14) or (15), we obtain for \( \phi \) the relation

\[
-\phi(T) = 1 + \frac{AD}{R_0^2 \alpha^2 k} \eta - \frac{Ac}{R_0^2 \alpha^2} \int_0^u \frac{d(rp)/dv}{(u - v)^3} dv.
\]
The choice of $\eta(t)$ depends on the physical situation being described, but in any case the $\eta$ term in (17) is extremely small, and affects the bubble directly only for a minute portion of its growth: the $\eta$ term serves to upset the initial equilibrium. For a temperature rise of $1^\circ C/min$ in the liquid, this term is of order $10^{-8}$, and it may be neglected once the bubble growth has begun. To fix the model, assume that

$$(D/k)\eta(t) = at,$$  

(18)

corresponding (cf. Eq. (4)) to a temperature rise of $1^\circ C$ in $(1/a)$ sec in the liquid far from the bubble. Then from (18), (13),

$$(AD/R_0^2\alpha^2 k)\eta(t) = \gamma \int_0^u p^{-4/3} \, dv,$$  

(19)

where the constant

$$\gamma = aA/R_0^2 \alpha^3.$$  

(20)

In keeping with the above discussion, (19) may be approximated by

$$(AD/R_0^2\alpha^2 k)\eta(t) = \gamma u.$$  

(21)

Because of the small temperature range occurring for the expanding bubble, we shall further approximate $r$ in Eq. (17) by unity, and write Eq. (17) as*

$$\phi(T) = 1 + \gamma u - \mu \int_0^u p'(v) \, dv,$$  

(22)

where $p'(v) = dp/dv$ and

$$\mu = Ac/R_0^2 \alpha^2.$$  

(23)

The system of equations thus simplifies to

$$\frac{1}{6} \frac{d}{dp} \left[ p^{7/3} p' r^2 \right] = 1 - \frac{1}{p^{1/3}} + \gamma u - \mu \int_0^u p' \, dv,$$  

(24)

$$p' = 0, \quad p = 1 \quad \text{for} \quad u = 0.$$

A solution to Eq. (24) will be found in three parts, corresponding to three overlapping phases of bubble growth, which may be labeled the "delay period", "early phase", and "intermediate phase".

**Delay Period.** Since the bubble growth starts from equilibrium, put

$$p = 1 + w(u),$$  

(25)

and assume that initially $w(u)$ and its derivatives are small. On neglecting the

* It is possible, by using the formulas for the temperature given below and a table of equilibrium vapor pressure values, to estimate what the variation in the dimensionless vapor density $r$ would have been, had it been allowed to vary, and to compare this variation with that of $p$. It was found that the ratio $(r'/r)/(p'/p)$ remains less than 5% at any time for the situation considered here.
second or higher powers of $w, w', \ldots$, or products of such terms, we may re-write Eq. (24) in an approximate (linearized) form as

$$w''(u) - w(u) = 3\gamma u - 3\mu \int_0^u \frac{w'(v) \, dv}{(u - v)^{\frac{3}{2}}}$$

$$w(0) = w'(0) = 0.$$  \hspace{1cm} (26)

If we now put

$$y(s) = \int_0^\infty e^{-su} w(u) \, du$$

and take the Laplace transform of (26), we obtain for $y(s)$ the equation

$$s^3 y(s) - y(s) = (3\gamma/s^2) - 3\mu s y(s)(\pi/s)^{\frac{3}{2}},$$

whence

$$y(s) = \frac{3\gamma}{s^2} \frac{1}{s^2 - 1 + 3\mu(\pi s)^{\frac{3}{2}}}.$$  \hspace{1cm} (28)

In order to match a later solution, we shall be mainly interested in the asymptotic form of the solution of (26) as $u \to \infty$, obtainable from the expansion of (28) about the singularities of $y(s)$. It is possible to obtain a solution to (26) in closed form by the means described below, and also to find a series expansion of $w(u)$ in powers of $u$ from a Laurent expansion of (28) about $s = \infty$, although these will not be used here.

The roots $s^\frac{3}{2} = \beta^\frac{3}{2}$, say, of

$$s^2 + 3\mu(\pi s)^{\frac{3}{2}} - 1 = 0$$  \hspace{1cm} (29)

correspond to simple poles of $y(s)$. Eq. (28) may therefore be expanded in partial fractions, using the factors indicated in (29); for a given root $s^\frac{3}{2} = \beta^\frac{3}{2}$, we obtain terms of the form

$$\frac{1}{s^2(s^\frac{3}{2} - \beta^\frac{3}{2})} = \frac{1}{\beta^2} \left[ \frac{1}{(s^\frac{3}{2} - \beta^\frac{3}{2})} - \frac{\beta^{3/2} + s\beta^{\frac{3}{2}} + s^\frac{3}{2}}{s^2} \right]$$  \hspace{1cm} (30)

multiplied by constant complex coefficients. By the use of the Laplace inversion integral it may be shown that

$$L^{-1} \left[ \frac{1}{s^\frac{3}{2} - \beta^\frac{3}{2}} \right] = \frac{1}{\pi \beta^\frac{3}{2}} e^{\beta u} \left[ 1 + \text{erf} (\beta u)^i \right]$$  \hspace{1cm} (31)

for all complex $\beta^\frac{3}{2}$, and hence that for

$$\pi/4 < | \arg \beta^\frac{3}{2} | < \pi,$$

(31) vanishes as $u \to \infty$. It follows that the behavior of $w(u)$ as $u \to \infty$ is determined by the singularities of $y(s)$ for which

$$| \arg s^\frac{3}{2} | < \pi/4.$$  \hspace{1cm} (32)
Actually, there is but one root \( s^1 = \beta^1 \) of (29) satisfying condition (32) for \( 0 < \mu < \infty \), and this root is real.

The residue of \( y(s) \) at \( s = \beta \) is given by

\[
\frac{3 \gamma}{\beta^2} \cdot \frac{1}{2 \beta + (3 \mu \pi^1 / 2 \beta^1)}
\]
or, since \( \beta \) satisfies (29), by

\[
(3 \gamma / \beta^2) (2 \beta / (3 \beta^2 + 1)).
\]

Hence as \( s \to \beta \),

\[
y(s) \sim \frac{6 \gamma}{\beta (3 \beta^2 + 1)} \cdot \frac{1}{s - \beta^1}
\]

so that as \( u \to \infty \),

\[
w(u) \sim \frac{6 \gamma}{\beta (3 \beta^2 + 1)} \cdot e^{\beta u}, \quad (33)
\]

where, again, \( \beta \) is that root of (29) satisfying (32). Alternatively, Eq. (33) may be written in the form

\[
u \sim \frac{1}{\beta} \ln \left[ \frac{\beta (3 \beta^2 + 1)}{6 \gamma} \cdot w \right] \quad \text{as } w \to \infty. \quad (34)
\]

Since the Laplace transform

\[
L[T - T_\infty] = -cL \left[ \int_0^u \frac{p' \, dv}{(u - v)^1} \right] = -c(\pi s^1) y(s)
\]
is asymptotic to \(-c(\pi \beta)^1 y(s)\) as \( s \to \beta \), we have that

\[
T - T_\infty \sim -c(\pi \beta)^1 w(u) \quad \text{as } u \to \infty. \quad (35)
\]

Moreover, to the degree of approximation used in the linearization,

\[
u = a t, \quad w = 3 \left( \frac{R}{R_0} - 1 \right). \quad (36)
\]

From (33), (35), (36), we thus obtain the relations

\[
R \sim R_0 \left[ 1 + \frac{2 \gamma}{\beta (3 \beta^2 + 1)} \cdot e^{\alpha s t} \right], \quad T \sim T_0 + a t - 3c(\pi \beta)^1 [(R/R_0) - 1]. \quad (37)
\]

By defining a time \( t_0 \) by

\[
2 \gamma / \beta (3 \beta^2 + 1) = e^{-a s t_0}, \quad (38)
\]

we may write the first of Eqs. (37) as

\[
R \sim R_0 \left[ 1 + e^{\alpha s (t - t_0)} \right], \quad (39)
\]

from which we see that the bubble radius remains practically equal to \( R_0 \) until the time \( t \approx t_0 - 1/\alpha \beta \) when it begins to increase, reaching \( 2R_0 \) at time \( t \approx t_0 \).
A tabulation of the significant parameters in Eqs. (37), (39) as functions of the initial temperature \(T_0\) will be found in Table I, with the choice \(a = 0.01^\circ\text{C/sec.}\) Because \(1/\alpha\beta \ll t_0\), the bubble growth appears to start abruptly near \(t = t_0\), rather than at the time of its release \(t = 0\). It is for this reason that the interval of time \(0 < t \leq t_0\) has been called a "delay period".* For given initial conditions \(T_0, P_0\), the duration of the delay period is completely determined by the choice of the constant \(\gamma\), i.e. by the choice of the heat source term \(\eta(t)\).

In terms of \(t_0\), the last of Eqs. (37) may be written

\[
T \sim T_0 + \alpha t_0 (t/t_0) - 3c(\pi\beta)^{\frac{1}{2}} [(R/R_0) - 1].
\]

It is evident from Table I that the heat source term \(\alpha t_0 (t/t_0)\) in (40) becomes negligible in comparison with the other terms near the end of the delay period. It will be omitted from the subsequent development. From a physical standpoint, this means that the observable bubble behavior is independent of the particular conditions initiating its growth.

The asymptotic formulas for the linearized Eq. (26) presented above are accurate over a range roughly defined by

\[
u > 1/\alpha, \quad \omega \ll 1;
\]

or

\[
1/\alpha\beta < t < t_0 - (1/\alpha\beta).
\]

Because of the smallness of \(\gamma\), \(w(u)\) increases over the range by a factor of several powers of \(10(\approx 10^5)\).

**The Early Phase.** Neglecting the heat source term and using \(w = \rho - 1\) as independent variable, we may write Eq. (24) as

\[
\frac{1}{6} \frac{d}{dw} \left( \frac{(1 + w)^{7/3}}{(du/dw)^{1/3}} \right) = 1 - \frac{1}{(1 + w)^{1/3}} - \mu \int_0^w [u(w) - u(v)]^1
\]

For small \(w\) this reduces to

\[
\frac{1}{6} \frac{d}{dw} \left( \frac{du}{dw} \right)^{-2} \approx \frac{1}{3} w - \mu \int_0^w [u(w) - u(v)]^1
\]

which is satisfied by

\[
u = (1/\tau) \ln(Cw)
\]

* The existence of such a delay period is important for the macroscopic (asymptotic) bubble growth, cf. Ref. (1).

**Table I**

<table>
<thead>
<tr>
<th>(T_0) ((^\circ\text{C}))</th>
<th>(R_0) ((10^{-3}) cm)</th>
<th>(t_0) (sec)</th>
<th>(1/\alpha\beta) ((10^{-3}) sec)</th>
<th>(3c(\pi\beta)^{1/2}) ((10^{-1}))</th>
<th>(0.01 t_0) ((10^{-3}))</th>
</tr>
</thead>
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<tr>
<td>102</td>
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<td>7.34</td>
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<td>1.97</td>
<td>7.34</td>
</tr>
<tr>
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<td>0.75</td>
<td>8.08</td>
<td>4.48</td>
<td>3.30</td>
<td>8.08</td>
</tr>
<tr>
<td>106</td>
<td>0.48</td>
<td>3.09</td>
<td>1.56</td>
<td>3.71</td>
<td>3.09</td>
</tr>
</tbody>
</table>

*For given initial conditions \(T_0, P_0\), the duration of the delay period is completely determined by the choice of the constant \(\gamma\), i.e. by the choice of the heat source term \(\eta(t)\).*
for arbitrary $C$, provided that

$$
\tau^2 = 1 - 3\mu r^3 \int_0^1 \frac{dv}{(\ln 1/v)^3}.
$$

(43)

Since the integral has the value $\pi^3$, Eq. (43) is identical with Eq. (29). From the discussion of the delay period it is clear that of the various roots of (43) we must choose that one which satisfies condition (32), $\tau = \beta$. In order to match the previous solution we must further set

$$
C = \beta(3\beta^2 + 1)/6\gamma
$$

in (42) (cf. Eq. 34). It is apparent from (42) that the derivative $du/dw$ of the solution $u(w)$ of (41) has a simple pole at $w = 0$, and we are therefore led to try a solution of the form

$$
du/dw = (1/\beta w) [1 + a_1 w + a_2 w^2 + \cdots],
$$
or

$$
u = \frac{1}{\beta} \ln \left[ \frac{\beta(3\beta^2 + 1)}{6\gamma} w \right] + \frac{a_1}{\beta} w + \frac{a_2}{2\beta} w^2 + \cdots.
$$

(44)

By substituting (44) into the integral of (41), we obtain

$$
\int_0^w \frac{dv}{[u(w) - u(v)]^3} = w \int_0^1 \frac{dv}{[u(w) - u(vw)]^3}
$$

$$
= \beta^4 w \left\{ \int_0^1 \frac{dv}{(\ln 1/v)^3} - \frac{a_1}{2} w \int_0^1 (1 - v) \frac{dv}{(\ln 1/v)^{3/2}}
$$

$$
+ \left[ \frac{3a_1^2}{8} \int_0^1 \frac{(1 - v)^2 dv}{(\ln 1/v)^{8/2}} - \frac{a_2}{4} \int_0^1 (1 - v) \frac{dv}{(\ln 1/v)^{3/2}} \right] w^2 + \cdots \right\}.
$$

(45)

Now, for $Re(\nu), Re(\lambda) > 0$

$$
\int_0^1 2^{\lambda-1}(\ln 1/z)^{\nu-1} dz = \Gamma(\nu)/\lambda^\nu.
$$

(46)

Consider a typical integral in (45), for example that appearing in the coefficient of $w$ within the braces,

$$
I = \int_0^1 (1 - z) \frac{dz}{(\ln 1/z)^{3/2}}.
$$

If the exponent of the ln $1/z$ factor were instead $1 - \nu$, then for $Re(\nu) > 0$ Eq. (46) would give for $I$

$$
\int_0^1 (1 - z) \frac{dz}{(\ln 1/z)^{1-\nu}} = [1 - \frac{1}{2}]\Gamma(\nu).
$$

(47)

But it is readily verified that both sides of (47) are regular functions of the complex variable $\nu$ for $Re(\nu) > -1$, the singularity at $\nu = 0$ being only apparent.
Therefore, by the theory of analytic continuation, the equality (47) remains valid for \( Re(v) > -1 \). In particular, for \( v = -\frac{1}{2} \) (47) gives

\[
I = [1 - 2^{\frac{1}{2}}]\Gamma(-\frac{1}{2}).
\]

The other integrals appearing in (49) may be similarly evaluated.

From (45), (46), we thus obtain

\[
3\mu \int_0^w \frac{dv}{[u(v) - u(w)]^{1/2}} = 3\mu w^{3/2} \left\{ \Gamma(1) - \frac{1}{2}a_1(1 - 2^{1/2})\Gamma(-\frac{1}{2})w + \left[ \frac{3}{2}a_1^2 + \frac{3}{2}a_1 a_2 \right]w^2 + \cdots \right\}. \tag{48}
\]

By (41), this must equal

\[
3 - 3(1 + w)^{-1/2} - \frac{1}{2} \frac{d}{dw} \left[ \frac{(1 + w)^{7/3}}{(dw/dw)^2} \right] = (1 - \beta^2)w - \left[ \frac{3}{2} + \frac{1}{2}\beta^2(7 - 6a_1) \right]w^2 + \left[ \frac{3}{4} - 2\beta^2(\lambda_6^{A}) - \lambda_6^{A}a_1 + 3a_1^2 - 2a_2 \right]w^3 + \cdots. \tag{49}
\]

The parameters \( a_1, a_2, \cdots \) are then found by equating the coefficients of corresponding powers of \( w \) in (48), (49).

From (13), the time becomes

\[
t = \frac{1}{\alpha} \int_0^w \frac{u'(v) \, dv}{(1 + v)^{4/3}} \sim \frac{1}{\alpha \beta} \left\{ \ln \left[ \frac{\beta(3\beta^2 + 1)}{6\gamma} w \right] + (a_1 - \frac{3}{2})w + \frac{1}{2}(a_2 - \frac{3}{2}a_1 + \lambda_6^{A})w^2 + \cdots \right\}, \tag{50}
\]

the logarithmic term having been chosen to match (34), (36). The temperature at the bubble wall may be found from (48).

Because the above solution depends upon expansions in powers of \( w \) of fractional powers of \( 1 + w \), it is not expected to be valid for \( w \) as large as unity.

**Intermediate Phase.** The early phase solution carries the radius up to about twice its initial value. The asymptotic solution\(^1\) becomes valid at a value of the radius several times larger than this, depending on the superheat, and it becomes necessary to find a solution which will join the other two. This "intermediate phase" solution is conveniently obtained as an expansion about one or two intermediate points on the growth curve and is constructed to fit smoothly onto preceding solutions. The asymptotic solution contains an arbitrary parameter which may be chosen to provide a match between it and the intermediate phase solution.

We have shown that for small \( u \), \( w'(u) = p'(u) \) grows exponentially. For large \( u \), the asymptotic solution gives

\[
p(u) \sim \left( \frac{2}{\pi \mu} \right)^{1/2} u^{1/3} \quad \text{as} \quad u \to \infty,
\]

so that \( p'(u) \) dies away as \( u^{-1} \). Hence the derivative must reach a maximum in
the course of bubble growth, and the function $p(u)$ must pass through a point of inflection. We shall obtain an intermediate solution in the form of an expansion of $p(u)$ about the point $u = u_0$ defined by

$$p''(u_0) = 0. \quad (51)$$

Since the early phase solution is not expected to be accurate at this point, the actual value of $u_0$ or $p(u_0)$ is unknown. In order to determine these quantities, we require that the intermediate solution and its derivative shall coincide with values obtained from the early phase solution at a point $u = u_1$, where that solution is accurate.

The differential equation (24) (with the heat source term omitted) may be written

$$pp'' + \frac{3}{p^{1/3}} p'^2 = \frac{3}{p^{1/3}} \left[ 1 - \frac{1}{p^{1/3}} - \mu \int_0^u \frac{p'(v) \, dv}{(u - v)^{1/3}} \right]. \quad (52)$$

Assume that $p''(u)$ has an expansion about $u_0$

$$p''(u_0 + z) = c_1 z + c_2 z^2 + c_3 z^3 + \cdots,$$

so that

$$p'(u_0 + z) = p'_0 + \frac{1}{2} c_1 z + \frac{1}{6} c_2 z^2 + \frac{1}{24} c_3 z^3 + \cdots,$$

$$p(u_0 + z) = p_0 + p'_0 z + \frac{1}{2} c_1 z^2 + \cdots,$$

where

$$p'_0 = p'(u_0), \quad p_0 = p(u_0).$$

Now, the integral in (52), evaluated at $u + z$, may be written

$$\int_0^{u+z} \frac{p'(v) \, dv}{(u + z - v)^{1/3}} = \int_0^{u+z} p'(u + z - v) \frac{dv}{v^{1/3}}$$

$$= \int_0^u p'(u + z - v) \frac{dv}{v^{1/3}} + \int_u^{u+z} p'(u + z - v) \frac{dv}{v^{1/3}},$$

$$= \sum_{k=1}^{\infty} \frac{z^k}{k!} \int_0^u p^{(k+1)}(u - v) \frac{dv}{v^{1/3}} + \int_0^z p'(v) \frac{dv}{u + z - v^1}, \quad (54)$$

valid for sufficiently small $z$. But for small $z$, $p'(z) \approx 0$, so that when (54) is valid, the last integral in (54) is negligible. Thus for $u = u_0$, (54) gives

$$\int_0^{u_0+z} \frac{p'(v) \, dv}{(u_0 + z - v)^{1/3}} \approx I_0 + I_1 z + \frac{z^2}{2!} + \cdots, \quad (55)$$

say, where

$$I_k = \int_0^{u_0} \frac{p^{(k+1)}(v) \, dv}{(u_0 - v)^{1/3}}. \quad (56)$$

With the aid of (53), (55), we are now able to write an expansion of (52) about
$u = u_0$. By equating the coefficients of powers of $z$ in this expansion, we obtain a set of relations

$$
\frac{7}{6}c_2^2 = \frac{3}{p^{1/3}} \left[ 1 - \frac{1}{p^{1/3}} - \mu I_0 \right], \quad c_1 = \frac{1}{p^{1/3}} \left[ -4x + \frac{5}{p^{1/3}} x - 3\mu \left( I_1 - \frac{4}{3} x I_0 \right) \right],
$$

$$
\frac{13}{6}c_1x + c_2 = \frac{1}{p^{1/3}} \left[ \frac{14}{3} c_2^2 - \frac{20}{3p^{1/3}} x^2 - 3\mu \left( \frac{1}{2} I_2 - \frac{4}{3} x I_1 + \frac{14}{9} x^2 I_0 \right) \right],
$$

$$
\frac{16}{9}c_3x + c_3 = \frac{3}{p^{1/3}} \left\{ - \left( \frac{140}{81} x^2 + \frac{2}{9} c_2 \right) + \frac{1}{p^{1/3}} \left( \frac{220}{81} x^3 + \frac{5}{18} c_1 \right) \right\} - \mu \left[ \frac{1}{6} I_3 - \frac{2}{3} x I_2 + \frac{14}{9} x^2 I_1 - \left( \frac{140}{81} x^3 + \frac{2}{9} c_1 \right) I_0 \right], \quad \cdots,
$$

where we have written $p$ for $p_0$, and $x$ for $p \prime/p_0$.

The differential equation is satisfied (in principle) by Eqs. (57); there remains the problem of matching with the earlier solution. Therefore, suppose the solution to (52) to be known for $u \leq u_1$, where $u_1 < u_0$. Put

$$
J_k = \int_{u_1}^{u_0} \frac{p^{(k+1)}(v)}{(u_0 - v)^3} \, dv, \quad L_k = \int_{u_1}^{u_0} \frac{p^{(k+1)}(v)}{(u_0 - v)^4} \, dv,
$$

so that

$$
I_k = J_k + L_k
$$

in (56), and set

$$
\delta = u_0 - u_1, \quad \xi = u_0 - v.
$$

Then in $L_0$, for instance, by (53),

$$
p'(v) = p'(u_0 - \xi) = px + \frac{1}{3}c_1\xi^2 - \frac{2}{3}c_2\xi^3 + \frac{1}{3}c_3\xi^4 + \cdots,
$$

giving

$$
L_0 = \int_{u_1}^{u_0} \frac{p'(v)}{(u_0 - v)^3} \, dv = 25^{3/4} \left( px + \frac{1}{10} c_1 \delta^2 - \frac{1}{21} c_2 \delta^3 + \frac{1}{36} c_3 \delta^4 + \cdots \right).
$$

Thus, $I_0 = J_0(\delta) + I_0(\delta)$ may be found from $p$, $x$, $c_1$, $c_2$, $c_3$, $\cdots$ if $\delta$ is given, since then

$$
J_0(\delta) = \int_{0}^{u_1} \frac{p'(v)}{(u_1 + \delta - v)^3} \, dv
$$

is known. In a similar manner, we obtain

$$
I_0 = J_0(\delta) + 25^{3/4} \left( px + \frac{1}{10} c_1 \delta^2 - \frac{2}{3} c_2 \delta^3 + \frac{1}{3} c_3 \delta^4 + \cdots \right),
$$

$$
I_1 = J_1(\delta) + 25^{3/4} \left( -\frac{1}{3} c_1 \delta^2 - \frac{4}{3} c_2 \delta^3 - \frac{1}{3} c_3 \delta^4 + \cdots \right),
$$

$$
I_2 = J_2(\delta) + 25^{3/4} \left( c_1 - \frac{5}{3} c_2 \delta - \frac{5}{3} c_3 \delta^2 + \cdots \right),
$$

$$
I_3 = J_3(\delta) + 25^{3/4} \left( 2c_2 - 2c_3 \delta + \cdots \right),
$$

\cdots \cdots.
It can be shown that the functions $J_k(\delta)$ satisfy an approximate relation

$$J_k(z_1) \approx J_k(z_0) - (z_1 - z_0) \left[ \frac{p^{(k+1)}(u_1)}{z_0^3} - J_{k+1}(z_0) \right]. \quad (63)$$

Since in the delay period or early phase $p^{(k+1)} \ll p^{(k)}$, we conclude that $J_k(\delta)$ is a slowly varying function of $\delta$.

Assuming that the contributions to $I_0, I_1, I_2, I_3$ from higher powers of $\delta$ than those written in (62) may be neglected, we terminate the expansions as written and substitute them into (57). Together with the conditions

$$p'(u_1) = px + \frac{1}{3} c_1 \delta^2 - \frac{1}{6} c_2 \delta^3 + \frac{1}{4} c_3 \delta^4,$$

$$p(u_1) = p - px \delta - \frac{1}{4} c_1 \delta^2 + \frac{1}{3} c_2 \delta^3 - \frac{1}{2} c_3 \delta^4,$$  

from (53), the equations (57) constitute a system of six simultaneous (nonlinear) equations for the six unknowns $p, x, c_1, c_2, c_3, \delta$. Inasmuch as one and only one point of inflection of $p(u)$ is known to exist (from physical considerations), these equations have a unique solution.

![Fig. 1. Theoretical radius vs. time curve for the growth of a spherical vapor bubble in water at 1 atm external pressure, superheated to 103°C. The bubble is originally (at time $t = 0$) in unstable equilibrium. The growth is initiated by the introduction of a uniform heat source in the liquid (e.g. by irradiation), such as to produce a temperature rise in the liquid of 1°C in 100 sec.](image)
The solution of Eqs. (57), (53') was accomplished by a combination iteration and weighted mean procedure. The method is discussed in Appendix I. Use was made of relation (63) in the evaluation of the $J_k$ integrals. Having obtained the solution to (57), (53'), we are able to write down the desired intermediate phase expansions.

It should be noted that because of the definitions of $u$ and $p$, the maximum radial velocity $dR/dt$ of the bubble wall does not occur at the same value of $u$ (or $t$) as the maximum value of $p'(u)$. The discrepancy is not great for small superheats, but for larger superheats the point defined by $d^2R/dt^2 = 0$ moves onto the asymptotic end of the $p(u)$ curve.

Solution for the Expanding Bubble. The results of the above theory for initial temperature $T_0 = 103{\circ}C$ and external pressure $P_0 = 1$ atm have been plotted in Figs. 1, 2, 3. The bubble was taken to be in equilibrium at time $t = 0$, when the distributed heat source $\eta(t)$ is introduced; $\eta(t)$ was arbitrarily chosen to produce a temperature rise of 1$^\circ$C in 100 sec in the liquid far from the bubble. The initial radius $R_0$ of the vapor bubble for $T_0 = 103{\circ}C$ is $1.02 \times 10^{-3}$ cm.

The division between the phases of growth is most clearly seen in Fig. 2, which gives the radial velocity $dR/dt$ of the bubble wall as a function of time. The delay period and early phase cover the curve from $t = 0$ to the knee of the curve (at about $t = 0.15$ millisecond). The asymptotic solution (treated in Ref. 1) starts just beyond the maximum (at about $t = 0.25$ millisecond).

IV. The Collapsing Bubble. Because of the large temperature variations which occur within the bubble which collapses in water below the boiling temper-
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Fig. 3. The temperature at the bubble wall for the vapor bubble of Fig. 1 is shown as a function of time. The temperature in the liquid at a large distance from the bubble remains essentially constant at 103°C.

ature, a simple analytic expression for the vapor pressure or vapor density variations cannot be found. If we take our data from equilibrium vapor pressure tables, we commit ourselves from the beginning to a numerical treatment of the problem.

The system of equations to be solved, Eqs. (8) through (12), is unchanged. In this case, however, the vapor pressure at the initial temperature $T_0$ is less than the external pressure, and initial conditions of dynamic equilibrium cannot prevail. There is therefore no need to retain the heat source term, and we shall put $\eta(t) = 0$ in (10). We continue to assume that initially the vapor bubble and surrounding fluid are in thermal equilibrium at temperature $T_0$.

It is convenient to transform the temperature equation. Define

$$\theta = T - T_0,$$  \hspace{1cm} (64)

so that Eq. (10) becomes

$$\theta = -c \int_0^z \frac{(rp)' \, dv}{(u - v)^i}.$$  \hspace{1cm} (65)

If we multiply (65) by $1/(z - u)^i$ and integrate it from $u = 0$ to $z$, we obtain

$$\int_0^z \frac{\theta(u) \, du}{(z - u)^i} = -c \int_0^z \frac{(rp)' \, dv}{(z - u)^i(u - v)^i}.$$  \hspace{1cm} (66)
after a change in the order of integration. Inasmuch as

\[ \int_{v}^{z} \frac{du}{(z - u)^{1}(u - v)^{1}} = \int_{0}^{1} \frac{dx}{x^{1}(1 - x)^{1}} = \pi, \]

(66) then gives

\[ \int_{0}^{z} \frac{\theta \, du}{(z - u)^{1}} = -\pi c(rp - 1), \]

or, after an integration by parts,

\[ r(u)p(u) - 1 = \left(\frac{2}{\pi c}\right) \int_{0}^{u} \theta'(v)(u - v)^{1} \, dv, \]

(67) where we have used \( \theta(0) = 0 \).

The system of equations to be solved becomes

\[
\frac{1}{6} \frac{d}{dp} \left[ p^{7/3} p'^{2} \right] + \frac{1}{p^{1/3}} + \phi = 0, \quad \phi = \phi(\theta), \]

\[ rp - 1 = \frac{2}{\pi c} \int_{0}^{u} \theta'(u - v)^{1} \, dv, \quad r = r(\theta); \]

\[ p(0) = 1, \quad p'(0) = 0, \quad \theta(0) = 0. \]

(68)

The system (68) was solved numerically for initial temperature \( T_0 = 22^\circ C \), external pressure \( P_0 = .544 \text{ atm} \), and initial bubble radius (which is undetermined for the collapsing bubble) \( R_0 = .25 \text{ cm} \). The method of solution is given in Appendix II. The particular initial data chosen here correspond to values which have been obtained experimentally.

Although the temperature effects become significant during the collapse, the dynamics of the bubble collapse differ very little from the Rayleigh solution of the problem over most of the collapse. The Rayleigh solution, which neglects heat transfer effects is readily obtained from (68) under the assumption that \( \phi \) is constant, and equal to \( \phi(T_0) \). We have

\[
\frac{1}{6} \frac{d}{dp} \left[ p^{7/3} p'^{2} \right] + \frac{1}{p^{1/3}} + \phi_{0} = 0, \quad p(0) = 1, \quad p'(0) = 0,
\]

which yields

\[ \frac{1}{6} p^{7/3} p'^{2} = \phi_{0}(1 - p) + \frac{3}{2}(1 - p^{2/3}) \]

(69) on integration. Since \( \phi_{0} \) is much larger than \( \frac{3}{2}(\phi_{0} \approx 10^{5}) \) (69) may be approximated by

\[ \frac{1}{6} p^{7/3} p'^{2} = \phi_{0}(1 - p), \quad \text{or} \quad p' = -\left(\frac{1}{6}\phi_{0}\right)^{3} p^{-7/6}(1 - p)^{1}, \]

(70) where the negative square root of \( p'^{2} \) must be chosen to correspond to the collapsing bubble. From (13)

\[ dp/dt = \alpha p^{3/6} p', \]


5 Rayleigh, Phil. Mag. 34, 94 (1917).
so that by Eq. (70),
\[ \frac{dp}{dt} = -\alpha (6\phi_0)^{1/3} p^{1/6} (1 - p)^{1/3}, \]
which yields
\[ t = \frac{1}{\alpha (6\phi_0)^{1/3}} \int_{(R/R_o)^2}^1 p^{-1/6} \frac{dp}{(1 - p)^{1/3}}. \]  
(71)
The time corresponding to the full system (68) was found by a numerical integration of the relation
\[ t = \frac{1}{\alpha} \int_0^u p^{-4/3} \, dv, \]
using the values of \( p \) obtained from the numerical solution of (68).
A comparison of the two solutions for the collapsing bubble is given in Fig. 4. The magnitude of radial velocity of the bubble wall obtained from the numerical

![Fig. 4. The radius vs. time curve predicted for the collapsing bubble by the theory developed in the text (solid curve in the figure) is compared with that predicted by the Rayleigh theory (dashed curve). The vapor bubble considered has an initial radius of 0.25 cm; it collapses in water at 22°C with an external pressure of 0.544 atm.](image-url)
solution is plotted in Fig. 5, and the corresponding temperature at the bubble wall in Fig. 6.

The numerical solution was not carried out farther than shown in Figs. 5, 6. In the first place, the large temperature variations make the assumption of the constancy of the parameters $\rho$, $\sigma$, $D$, $k$, $\cdots$ relating to the fluid untenable. Secondly, the assumption of thermal and dynamic equilibrium within the bubble and incompressibility in the fluid break down when the bubble wall velocity becomes comparable with sonic velocity in the fluid or vapor. A correction to the equation of motion of a spherical bubble in a liquid which takes compressibility into account has been given by Gilmore, who made use of the Kirkwood-Bethe hypothesis.

Perhaps the most significant error in the above theory lies in the fact that the spherical shape is unstable for rapidly collapsing bubbles near the end of their collapse. It would therefore be meaningless to carry the numerical solution further, even if the problems mentioned above could be handled.

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V. Conclusion. The theory presented here covers bubble behavior not yet accessible to observation. For this reason, a full tabulation of numerical results for various initial conditions has not been given. The validity of the theory can only be inferred from observations made on bubbles which have grown in superheated water to an observable size, where the asymptotic solution to the equations of bubble growth applies (cf. Ref. 1). The agreement for this range is quite good.

Appendix I. Iteration with Weighted Mean. The method presented here was designed to solve a system of nonlinear simultaneous equations for which a fair estimate of the solution is known, and the calculations involved are lengthy. It is based essentially on linear interpolation (or extrapolation). When the calculations are simple, methods based on parabolic interpolation may prove more useful.

Consider a set of simultaneous equations of the form (or which can be thrown into the form)

\[ x_i = \phi_i(x_1, \cdots, x_n), \quad i = 1, \cdots, n, \]
to be solved by an iteration procedure,

$$x_i^{(k+1)} = \phi_i(x^{(k)})$$  \hspace{1cm} (1)

Let $x_i^{(1)}$ be a first estimate of the solutions, and $x_i^{(2)} = \phi_i(x^{(1)})$ the iterated second estimate. Define the partial differences

$$\Delta \phi_i = \phi_i(x_i^{(1)}, \ldots, x_{j-1}^{(1)}, x_j^{(2)}, x_{j+1}^{(1)}, \ldots, x_n^{(1)}) - \phi_i(x_i^{(1)})$$  \hspace{1cm} (2)

and in terms of them the matrices

$$(\beta_{ij})^{-1} = \delta_{ij} - \frac{\Delta \phi_i}{\Delta x_j}, \quad \left(\begin{array}{c}
\delta_{ij} = \begin{cases} 1, & i = j \\
0, & i \neq j \end{cases}
\end{array}\right)$$  \hspace{1cm} (3)

$$\alpha_{ij} = \delta_{ij} - \beta_{ij}.$$  

Then the estimate

$$x_i^{(3)} = \sum_{j=1}^{n} \left[ \alpha_{ij} x_j^{(1)} + \beta_{ij} x_j^{(2)} \right]$$  \hspace{1cm} (4)

is accurate to twice as many significant figures as $x_i^{(1)}$ or $x_i^{(2)}$.

To prove the statement, suppose that

$$x_i = \xi_i$$  \hspace{1cm} (5)

are the required solutions of (1), and that

$$x_i^{(1)} = \xi_i + \epsilon_i$$  \hspace{1cm} (6)

are the first estimates. Here the $\epsilon_i$ represent the errors in $x_i^{(1)}$. Under the iteration procedure, the next estimate will then be

$$x_i^{(2)} = \phi_i(x^{(1)}) = \phi_i(\xi + \epsilon)$$

$$= \phi_i(\xi) + \sum_j \frac{\partial \phi_i}{\partial x_j}(\xi) \epsilon_j + 0(\epsilon^2);$$

or, since by assumption

$$\phi_i(\xi) = \xi,$$  \hspace{1cm} (7)

$$x_i^{(2)} = \xi + \sum_j \frac{\partial \phi_i}{\partial x_j}(\xi) \epsilon_j + 0(\epsilon^2).$$

We wish to form a set of weighted means

$$x_i^{(3)} = \sum_j (\alpha_{ij} x_j^{(1)} + \beta_{ij} x_j^{(2)})$$  \hspace{1cm} (8)

which differ from the $\xi_i$ only in $0(\epsilon^2)$. From (6), (7) we find that

$$x_i^{(2)} = \sum_j \left[ \alpha_{ij} [\xi_j + \epsilon_j] + \beta_{ij} [\xi_j + \sum_k \frac{\partial \phi_j}{\partial x_k}(\xi) \epsilon_k] \right] + 0(\epsilon^2)$$

$$= \sum_j (\alpha_{ij} + \beta_{ij}) \xi_j + \sum_k (\alpha_{ik} + \sum_j \beta_{ij} \frac{\partial \phi_j}{\partial x_k}(\xi) \epsilon_k) + 0(\epsilon^2).$$  \hspace{1cm} (9)

The error in $x_i^{(3)}$ will thus be of order $\epsilon^2$ if

$$\alpha_{ij} + \beta_{ij} = \delta_{ij}, \quad \alpha_{ik} + \sum_j \beta_{ij} \frac{\partial \phi_j}{\partial x_k}(\xi) = 0.$$  \hspace{1cm} (10)

On eliminating $\alpha_{ij}$ from Eqs. (10), we obtain

$$\delta_{ik} = \beta_{ik} - \sum_j \beta_{ij} \frac{\partial \phi_j}{\partial x_k} = \sum_j \beta_{ij} (\delta_{jk} - \frac{\partial \phi_j}{\partial x_k}),$$
so that unless the determinant \(| \delta_{jk} - (\partial \phi_i/\partial x_k)(\xi) | \) vanishes, the \( \beta_{ij} \) are given by the matrix reciprocal to \( \delta_{ij} - \partial \phi_i/\partial x_j \):

\[
\beta_{ij} = [\delta_{ij} - (\partial \phi_i/\partial x_j)(\xi)]^{-1}. \tag{11}
\]

If the \( \partial \phi_i/\partial x_j(\xi) \) are known, then the \( \beta_{ij} \) are given by (11), the \( \alpha_{ij} \) by the first of Eqs. (10), and the mean estimate \( x_i^{(3)} \) by (8). The error in the \( x_i^{(3)} \) is of order \( \epsilon^2 \) by construction. It may be noted that this result does not depend upon convergence of the iteration procedure in (1).

In general, the \( \partial \phi_i/\partial x_j(\xi) \) are not known if the \( \xi_i \) are not known. These may be approximated, however, by the values of the partial differences \( \Delta \phi_i/\Delta x_j \) defined by Eq. (2), without affecting the order of the error in the \( x_i^{(3)} \). For, from (2),

\[
\frac{\Delta \phi_i}{\Delta x_j} = \frac{\partial \phi_i}{\partial x_j}(x^{(1)}) \pm \frac{1}{2} \frac{\partial^2 \phi_i}{\partial x_j^2}(x^{(1)}) + \cdots = \frac{\partial \phi_i}{\partial x_j}(\xi) + O(\epsilon). \tag{12}
\]

We now define

\[
\beta_{ij} = \left[ \delta_{ij} - \frac{\Delta \phi_i}{\Delta x_j} \right]^{-1} = \left[ \delta_{ij} - \frac{\partial \phi_i}{\partial x_j}(\xi) \right]^{-1} + O(\epsilon), \tag{13}
\]

and put

\[
\alpha_{ij} \equiv \delta_{ij} - \beta_{ij}. \tag{14}
\]

This means that \( \alpha_{ij} + \beta_{ij} = \delta_{ij} \) as in Eq. (10), while

\[
\alpha_{ik} + \sum_j \beta_{ij} \partial \phi_j/\partial x_k(\xi) = 0(\epsilon).
\]

But this last error affects the \( x_i^{(3)} \) only in order \( \epsilon^2 \), according to Eq. (9), and thus does not change the order of the error in the mean estimate.*

The proof breaks down formally when the determinant \( \Delta = | \delta_{ij} - \partial \phi_i/\partial x_j(\xi) | \) vanishes. In this case the system (1) may not have a unique solution. For, set

\[
\psi_i(x_1, \ldots, x_n) \equiv x_i - \phi_i(x_1, \ldots, x_n); \tag{15}
\]

then \( \Delta \) represents the Jacobian of the transformation of variables

\[
\psi_i(x_1, \ldots, x_n) = \eta_i \tag{16}
\]

from \( x_i \) to \( \eta_i \), evaluated at the point \( \eta_i = 0 \). The vanishing of the Jacobian signifies, in general, the existence of a family of solutions (depending upon one or more parameters) which passes through \( \eta_i = 0 \), and correspondingly, unique solutions to (1) cannot exist. If it should happen that \( \Delta = 0 \) defines an isolated singular point, then it can be shown that the weighted mean procedure based on the \( \Delta \phi_i/\Delta x_j \) (for which \( \beta_{ij} \) still exists) will converge to that point; however, the convergence in this case goes as \( O(\epsilon) \), not \( O(\epsilon^2) \), and the method becomes unsuited for numerical computation.

* Clearly, an equally good estimate for the \( \partial \phi_i/\partial x_j(\xi) \) would be the \( \partial \phi_i/\partial x_j \) evaluated at \( x_i^{(1)} \) or \( x_i^{(2)} \) if these are readily obtainable, the convergence being relatively insensitive to the choice of \( \beta_{ij} \) provided \( \alpha_{ij} + \beta_{ij} = \delta_{ij} \).
Appendix II. Numerical Solution for the Collapsing Bubble. The system (68) may be written

\[ pp'' + \frac{7}{6} p^2 + \frac{3}{p^{4/3}} \left[ \frac{1}{p^{1/3}} + \phi \right] = 0, \quad \phi = \phi(\theta), \quad (1), \quad (2) \]

\[ rp - 1 = \left( \frac{2}{\pi c} \right) \int_0^u \theta'(v)(u - v)^{1/2} dv, \quad r = r(\theta). \quad (3), \quad (4) \]

In order to obtain a scheme for numerical integration of the system, we first subdivide the range of values of \( u \) into intervals defined by the points

\[ 0 = u_0 < u_1 < \cdots < u_k < \cdots < u_n < \cdots. \]

The intervals corresponding to (5) are in general not equal, but chosen as the integration proceeds.

For convenience, write

\[ u_{n+1} - u_n \equiv h, \quad (6) \]

and assume that \( p_k = p(u_k), \theta_k = \theta(u_k), r_k = r(\theta_k), \phi_k = \phi(\theta_k) \) are known for \( 0 \leq k \leq n \).

If the interval \( u_{k+1} - u_k \) is sufficiently short, \( \theta'(u) \) within the interval may be approximated by

\[ m_k = \frac{\theta_{k+1} - \theta_k}{u_{k+1} - u_k}. \quad (7) \]

The integral in (3) evaluated at the point \( u = u_{n+1} \) may then be estimated as

\[ \int_0^{u_{n+1}} \theta'(v)(u_{n+1} - v)^{1/2} dv \approx \sum_{k=0}^{n} m_k \int_{u_k}^{u_{k+1}} (u_{n+1} - v)^{1/2} dv \]

\[ = \frac{3}{4} \sum_{k=0}^{n} m_k [(u_{n+1} - u_k)^{3/2} - (u_{n+1} - u_{k+1})^{3/2}]. \]

Define

\[ I_0 = 0 \]

\[ I_n = \frac{4}{3\pi c} \sum_{k=0}^{n} m_k [(u_{n+1} - u_k)^{3/2} - (u_{n+1} - u_{k+1})^{3/2}]. \quad (8) \]

Then with the use of (6) and (7), Eq. (3) at \( u = u_{n+1} \) becomes

\[ r_{n+1} p_{n+1} - 1 = I_n + \left( \frac{4h^{1/3}}{3\pi c} \right)(\theta_{n+1} - \theta_n). \quad (9) \]

The value of \( r_{n+1} \) in (9) may be estimated in terms of \( \theta_{n+1} \) by an expansion of \( r \) about a value \( \theta = \bar{\theta} \) near \( \theta_{n+1} \) which uses equilibrium vapor pressure data,* say

\[ r_{n+1} = r(\theta_{n+1}) = \bar{r}[1 + \bar{b}_1(\theta_{n+1} - \bar{\theta}) + \bar{b}_2(\theta_{n+1} - \bar{\theta})^2 + \cdots]. \quad (10) \]

* The obvious choice for the first few steps of integration is \( \bar{\theta} = 0 \), so that \( \bar{r} = 1 \) initially.
We thus obtain for (9) the equation
\[ p_{n+1} = 1 + I_n + (4h^3/3\pi c)[(\theta_{n+1} - \bar{\theta}) - (\theta_n - \bar{\theta})] + \cdots, \] 
(11)
in which the only unknowns are \( \theta_{n+1} \) and \( p_{n+1} \). Eq. (11) is most easily solved for \( \theta_{n+1} \) by an iteration procedure based on the equation
\[ (\theta_{n+1} - \bar{\theta}) = \frac{p_{n+1} - 4h^3}{3\pi c (\theta_n - \bar{\theta}) - I_n - 1}. \]
(12)
To obtain \( p_{n+1} \), we use the differential equation (1). At each point \( u = u_n \), make the approximations
\[ p'_n = \frac{p_{n+1} - p_n}{u_{n+1} - u_n}, \]
\[ p''_n = \frac{(p_{n+1} - p_n)}{(u_{n+1} - u_n)}, \]
(13)
Under these approximations, the formula
\[ p(u) = p_n + (u - u_n)p'_n + \frac{1}{2}(u - u_n)^2 p''_n \]
is exact for \( u = u_{n-1}, u_n, u_{n+1} \). If \( u_n - u_{n-1} = u_{n+1} - u_n = h \), (13) gives
\[ p'_n = \frac{p_{n+1} - p_{n-1}}{2h}, \quad p''_n = \frac{p_{n+1} - 2p_n + p_{n-1}}{h^2}, \]
(14)
so that the differential equation at \( u = u_n \) is approximated by the difference equation
\[ p_{n+1}^2 + [\frac{2\Delta p_n}{2} - 2p_{n-1}]p_{n+1} \]
\[ + [(p_{n+1}^2 - 4\Delta p_n^2 + \frac{2\Delta p_n p_{n-1}}{3}) + 72h^2/7p^{1/3}(p_{n-1}^{1/3} + \phi_n)] = 0. \]
(15)
Given \( \theta_n \), Eq. (15) may be solved for the positive root \( p_{n+1}, \phi_n = \phi(\theta_n) \) being obtainable from equilibrium vapor pressure data.

In order to keep the differences in \( p \) and \( \theta \) small and ensure that a positive root \( p_{n+1} \) of the difference equation exists, it becomes necessary to decrease \( h \) as the numerical integration proceeds. At the step where a new value of \( h \) is introduced, the approximations (13) rather than (14) must be used. The difference equation which applies at that step is not (15), therefore, but one obtainable from (13).

To start the integration, a fictitious point \( u_{-1} = -u_1 \) is used. Corresponding to the initial conditions \( p'(0) = 0 \) and the approximation (14), we must then choose \( p_{-1} = p_1 \). Since \( p_0 = 1 \), the difference equation (15) for \( n = 0 \) simplifies to the linear equation
\[ p_1 = 1 - \frac{3}{2}h^2(1 + \phi_0) \]
(16)
where $\phi_0 = \phi(\theta_0) = \phi(0)$. The temperature equation (12) becomes

$$\theta_1 = \frac{p_1 - 1}{(4h^1/3\pi c) - p_1(b_1 + b_2\theta_1 + \cdots)}$$  \hspace{1cm} (17)

for $n = 0$, since $I_0 = \theta_0 = \bar{\theta} = 0$, $\bar{r} = 1$. For sufficiently small $\hbar$, (17) may be approximated by

$$\theta_1 = \frac{p_1 - 1}{(4h^1/3\pi c) - \bar{b}_1}.$$  \hspace{1cm} (18)

It should be noted that $\bar{r}$, $\bar{b}_1$, $\bar{b}_2$, $\cdots$ depend on $\bar{\theta}$, and change with each new expansion of $r(\theta)$. Because these parameters, as well as $\hbar$, may be constant over several integration steps, we have not given them indices which depend on $u$ (i.e. on $n$).

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