Effect of Pressure on Bubble Growth Within Liquid Droplets at the Superheat Limit[1]

C. T. Avedisian
Sibley School of Mechanical
and Aerospace Engineering,
Cornell University,
Ithaca, N.Y. 14853
Assoc. Mem. ASME

A study of high-pressure bubble growth within liquid droplets heated to their limits of superheat is reported. Droplets of an organic liquid (n-octane) were heated in an immiscible nonvolatile field liquid (glycerine) until they began to boil. High-speed cine photography was used for recording the qualitative aspects of boiling intensity and for obtaining some basic bubble growth data which have not been previously reported. The intensity of droplet boiling was found to be strongly dependent on ambient pressure. At atmospheric pressure the droplets boiled in a comparatively violent manner. At higher pressures photographic evidence revealed a two-phase droplet configuration consisting of an expanding vapor bubble beneath which was suspended a pool of the vaporizing liquid. A qualitative theory for growth of the two-phase droplet was based on assuming that heat for vaporizing the volatile liquid was transferred across a thin thermal boundary layer surrounding the vapor bubble. Measured droplet radii were found to be in relatively good agreement with predicted radii.

1 Introduction

Intimate contact between a volatile liquid dispersed in another immiscible nonvolatile liquid can be an effective means for transferring heat. Such contact can also suppress nucleate boiling due to a lack of preferred nucleation sites. The volatile liquid may then be heated to temperatures substantially higher than its saturation temperature. There is a practical limit to the temperature a liquid can reach before vaporization must occur. At this temperature an intrinsic phase transition is initiated by the random molecular processes of homogeneous nucleation. If growth of the initial vapor bubbles is sufficiently rapid, explosive boiling can result. The potential for these "vapor explosions" has been recognized in connection with liquid natural gas spills on water, during fuel/coolant interactions in a liquid metal fast breeder reactor [1, 2] and during droplet combustion of high boiling-point fuels which contain a volatile additive [3].

However, evidence indicates that a phase transition is not necessarily explosive when the limit of superheat is reached [4–8]. Homogeneous nucleation theory gives no information concerning the *intensity* of vaporization. This intensity is dependent on the difference in pressure between the gas within the initial vapor bubble and the surrounding liquid. Such a pressure difference exists during the early stages of growth. Indeed, Henry and Fauske [9] and Buchanan and Dullforce [10] theorized that vapor explosions are possible only when bubble growth is inertially controlled. If this excess pressure is reduced sufficiently, vapor explosions could be eliminated. One of the aims of the present work was to demonstrate this experimentally.

The configuration chosen for study was that of droplets of a volatile pure liquid heated in an immiscible nonvolatile liquid. This configuration is relevant to many situations in which vapor explosions are initiated.

To the author's knowledge no work has been reported on bubble growth within liquid droplets heated to their homogeneous nucleation temperatures at pressures above atmospheric. We report here the results of such a study. The present work is distinguished from previous studies [e.g., 11] in that our efforts were concerned with bubbles growing within liquids of finite volumes (i.e., droplets) and not within an infinite sea of superheated liquid, and that the liquids in which the bubbles grew were at reduced temperatures greater than .9.

Our initial efforts were concerned with a study of bubble growth within pure liquid n-octane droplets. High-speed ciné photography was used both to record the qualitative aspects of boiling intensity of the test droplets, and to obtain some basic bubble growth data which have not previously been reported. The objectives were to (*i*) study the effect of ambient pressure on the growth rate of bubbles within liquid droplets heated to their limits of superheat, and (*ii*) develop a simple physical model for boiling of the superheated droplets.

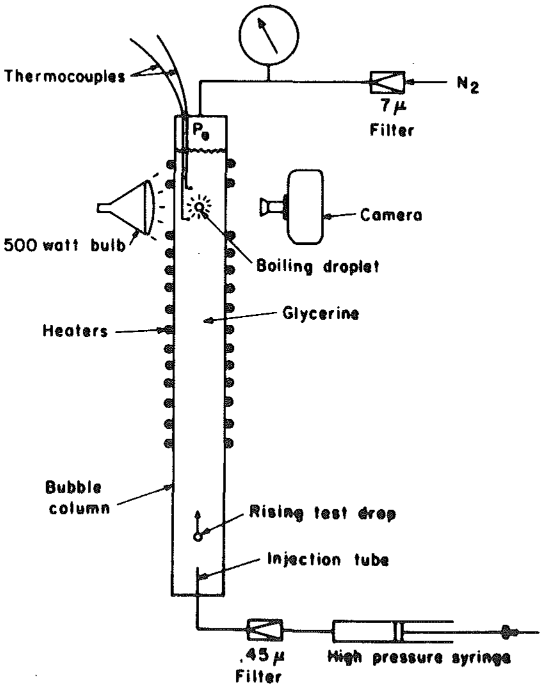

Fig. 1 Schematic diagram of experiment

---

[1] Part of this paper was presented at the 20th ASME/AIChE National Heat Transfer Conference, Milwaukee, Wisconsin, August 2–5, 1981. Paper No. 81-HT-11.

Contributed by the Heat Transfer Division for publication in the JOURNAL OF HEAT TRANSFER. Manuscript received by the Heat Transfer Division September 7, 1981.

2 Experiment

2.1 Description of the Apparatus. The experiment was a modification of that used by Skripov and Ermakov [4, 5] and Avedisian and Glassman [6] at high pressures. Droplets of a light volatile test liquid were injected into the bottom of a vertical column (Fig. 1) containing a heavier immiscible nonvolatile field liquid. A stable temperature gradient was imposed on the field liquid such that temperature was hotter at the top of the column than the bottom. As the droplets rose, they were progressively heated until they began to boil. The temperature of boiling was obtained by measuring the temperature in the field liquid at the level in the column at which vaporization was observed. Droplet surface temperatures were estimated to be within 1.5°K of the ambient temperature for rise velocities and field liquid temperature gradients typical of the present experiments.

The above method was combined with high-speed cine photography to record the boiling intensity of the droplets. Previous studies by Apfel and Harbison [12] and Mori and Komitori [13] concerned unsupported ethyl ether droplets boiling in glycerine under an effective pressure of .101 MPa.

The bubble column consisted of a heavy walled glass tube 56.8-cm long with nominal dimension of 3.6-cm i.d. and 5.8-cm o.d. The tube was heated by a split aliminum tube clamped to the bubble column and held in place by two band heaters and connecting bolts. The tube was pressurized directly with filtered nitrogen gas. The droplet injection system was similar to that employed by Avedisian and Glassman [6].

The droplets were photographed with a Hycam 16-mm high-speed rotating prism camera equipped with a 75-mm lens and extension tubes. The camera was mounted next to the level of the column at which the droplets were observed with the naked eye to boil. Direct back lighting was used with a GE DXB 500 W bulb, the intensity of which was regulated by a variac. Because the droplets were moving past the field of view of the camera at velocities typically between 20 mm/s and 60 mm/s, some luck was involved in synchronizing the camera start-up with the initiation of boiling. For this reason, maximum camera framing rates of about 1000 frame/s were used. (The framing rate was determined by an electronic timer which put marks on the film in .001 s intervals.) These rates gave us at least 4 s of filming time for a 100 ft. role of film. This was time enough to start the camera before the droplets entered the lens field of view and still have a high probability of photographing their vaporization. A number of successful shots of droplets undergoing what is believed to be homogeneous nucleation at various ambient pressures were obtained and are shown in Figs. 2 to 4.

Droplet vaporization rates were obtained by studying individual frames from the high-speed movies on a motion picture analyzer. Overall droplet diameters (Figs. 2 to 4) were used in our subsequent analysis to avoid possible ambiguities of discerning dimensions of the vapor bubbles within the test droplets due to the backlighting technique employed. Also, only measurements in the undistorted vertical direction were used (distortion due to the curvature of the glass tube).

2.2 Selection of Liquids. The test and field liquids were chosen to satisfy the following requirements: (*i*) $T_{\text{sat2}}(P_0) > T_0$, (*ii*) both liquids exhibit low mutual miscibility, (*iii*) availability of physical property data, and (*iv*) $\sigma_2 > \sigma_1 + \sigma_{12}$. The first requirement ensures that the test droplet can be heated to its limit of superheat. The fourth requirement assures that the probability for homogeneous nucleation will be greater in the bulk of liquid 1 than at the liquid 1/liquid 2 interface or within the bulk of liquid 2 [14].

In the present work, droplets of pure n-octane were heated in a field liquid of glycerine. The normal paraffin/glycerine combination satisfies the above requirements and has been found by others [6, 7, 15, 16] to yield reproducible measurements of the limits of superheat of the n-alkanes over a wide range of pressures. The n-octane was obtained from Humphrey Chemical Co. with a stated purity of 99 percent. The glycerine was Eastman "spectrograde." The liquids were used directly as received except for normal filtering.

Nomenclature

A_{cap} = surface area of spherical cap
A_{lv1} = surface area of liquid 1/vapor 1 interface
C_i = constant defined in equation (12)
F = h/R
h = dimension of spherical segment defined in Fig. 9
h_{fg1} = latent heat of vaporization of liquid 1
J = nucleation rate
K = Boltzman constant
k = liquid thermal conductivity
k_f = molecular evaporation rate of species 1
m = molecular mass of species 1
N = number density of molecules within liquid 1
$\bar{P}$ = nondimensional pressure, $P/[\rho_{l2}(C_1\alpha_{l1}/R_0)^2]$
P = pressure
q_1, q_2 = heat-transfer rates over the surface of the vapor bubble at the liquid 2/vapor 1 interface (q_2) and the liquid 1/vapor 1 interface (q_1)
r = radial dimension ($r > R$)
R = radius of two-phase droplet
$\bar{R}$ = gas constant
R_f = final radius of vapor bubble
R_0 = initial liquid droplet radius
t = time
T = temperature
T_0 = limit of superheat of liquid 1, and field liquid temperature
$\bar{T}$ = nondimensional temperature, T/T_0
T_{sati} = saturation temperature of i at P_0
T_t = thermodynamic limit of superheat at P_0 (Fig. 5)
v = molar volume of superheated liquid
V_{l1} = volume of spherical segment of liquid 1 suspended from the vapor bubble
y = nondimensional droplet radius, R/R_0

Greek Symbols

α = liquid thermal diffusivity
Γ = growth probability of a critical size nucleus
ΔA^* = energy of forming a critical size nucleus
ΔP = $P_v - P_0$
ϵ = liquid to vapor density ratio of species 1, $\rho_{l1}(T_0)/\rho_{v1}(T_v)$
ρ = density
σ = surface tension
σ_1 = liquid 1/vapor 1 surface tension
σ_2 = liquid 2/vapor 2 surface tension
σ_{12} = liquid 1/liquid 2 interfacial tension
τ = nondimensional time, $(C_1\alpha_{l1}/R_0^2)t$
ν = kinematic viscosity

Subscripts

0 = ambient (field liquid)
v = vapor bubble
c = critical point property
sat = saturation conditions corresponding to P_0 or T_0
$l1$ = liquid 1
$l2$ = liquid 2
i = species i ($i = 1, 2$)

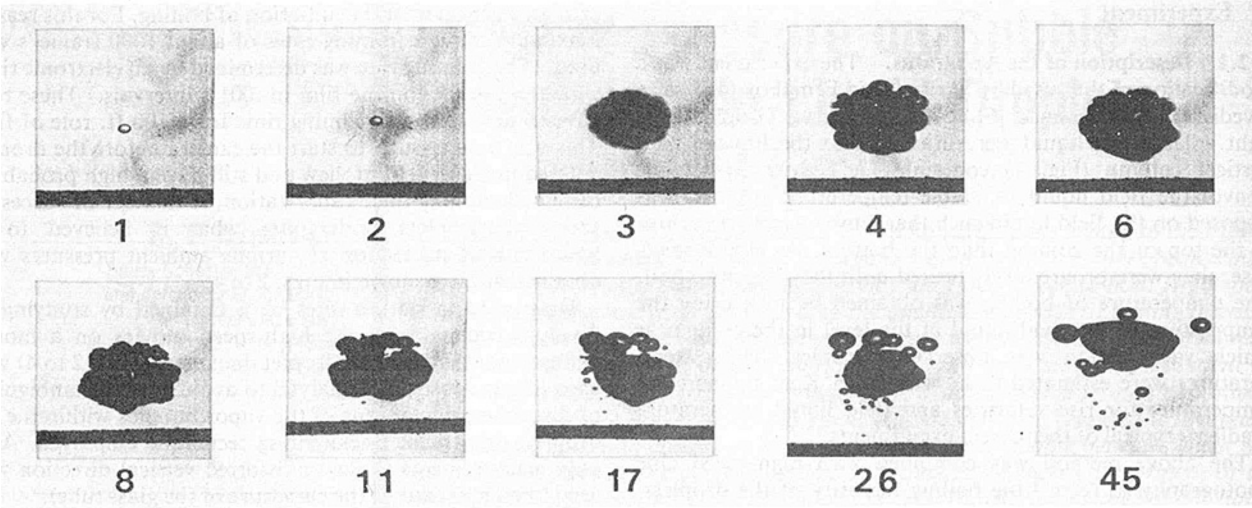

Fig. 2 N-octane droplet boiling in glycerine at $P_0 = .101$ MPa. Number of frame in the motion picture sequence is shown below each photograph. $T_0 \simeq 514°K$, $R_0 \simeq .3$ mm, framing rate = 1033 frames/s.

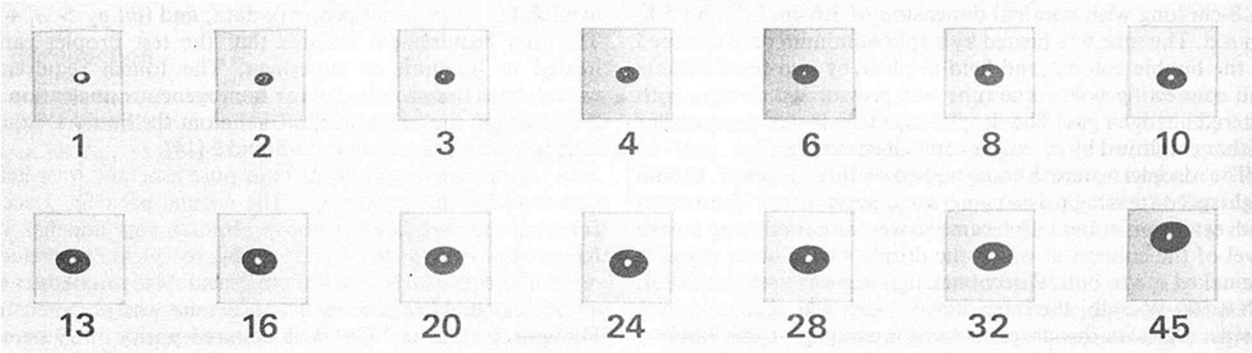

Fig. 3 N-octane droplet boiling in glycerine at $P_0 = .687$ MPa. Number of frame in the motion picture sequence is shown below each photograph. $T_0 \simeq 525°K$, $R_0 \simeq .4$ mm, framing rate = 933 frames/s.

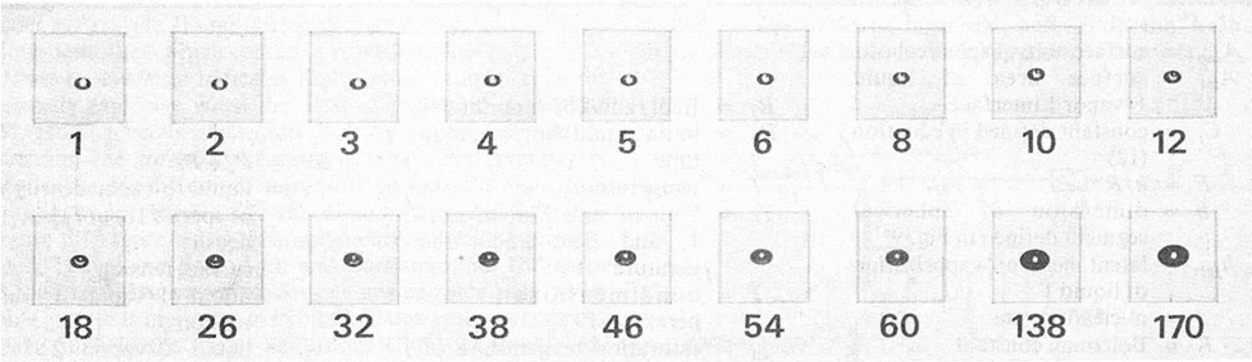

Fig. 4 N-octane droplet boiling in glycerine at $P_0 = 1.22$ MPa. Number of frame in the motion picture sequence is shown below each photograph. $T_0 \simeq 531°K$, $R_0 \simeq .3$ mm, framing rate = 900 frames/s.

2.3 Experimental Observations. High-speed motion pictures of n-octane droplets boiling in glycerine were taken at pressures of .101 MPa, .687 MPa, and 1.22 MPa. The corresponding reduced temperatures ranged from about .9–.94.

At atmospheric pressure the n-octane droplets boiled with a "popping" sound. The droplets appeared to vaporize in an instant with the naked eye. There was little ambiguity about the vertical position in the column at which boiling was observed. As pressure was increased, the audible sound accompanying boiling completely disappeared. For instance, at around .6 MPa the only way to detect boiling was by observing a sudden increase in velocity of the rising droplets.

Figure 2 shows a series of photographs of an octane droplet boiling in glycerine under a pressure of .101 MPa. The photographs were taken from a typical sequence of motion picture frames. A framing rate of 1033 frames was used. The droplet temperature in the first frame was approximately 514°K. Boiling was so intense that complete vaporization occurred in less than 2 ms at a time between the first and third frames in Fig. 2. The stages of growth between these two frames could thus not be recorded by our method because the process was too fast.

The vapor cloud illustrated in frame 3 of Fig. 2 underwent an oscillatory motion, followed by disintegration into a cloud of bubbles (45th frame). The mechanism for this break-up is

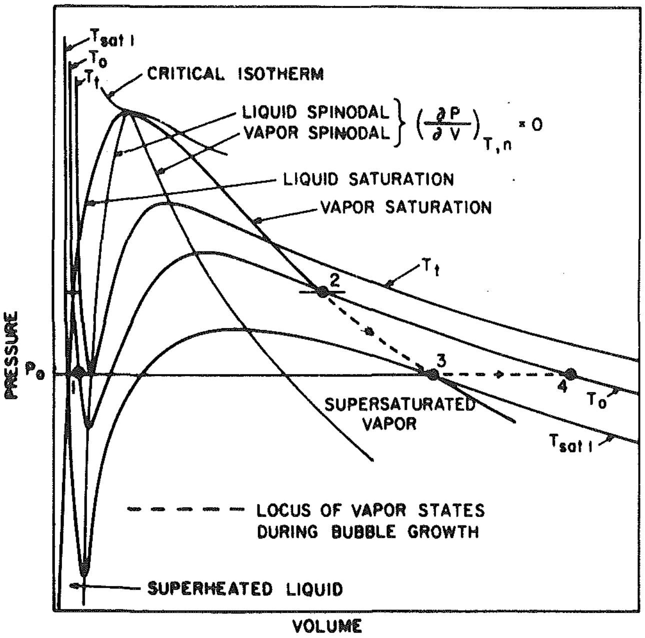

Fig. 5 Pressure-volume phase diagram for a pure substance. "1" represents liquid state; "2" is the initial state in the critical size nucleus; "3" is the vapor state immediately after liquid 1 completely vaporizes; "4" is the state of the final vapor bubble.

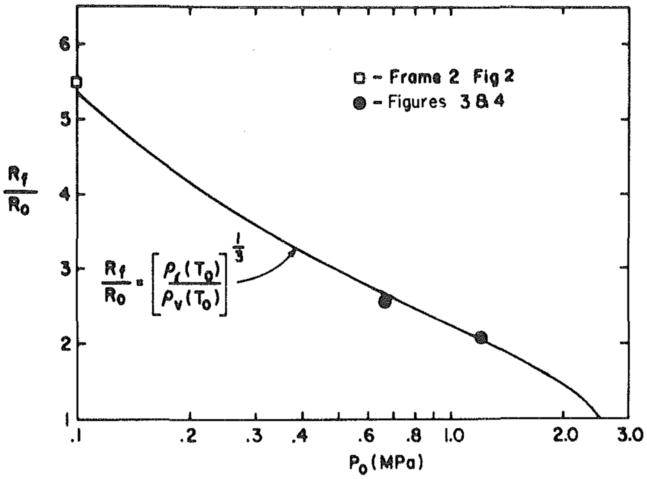

Fig. 6 Variation of final vapor bubble size with ambient pressure

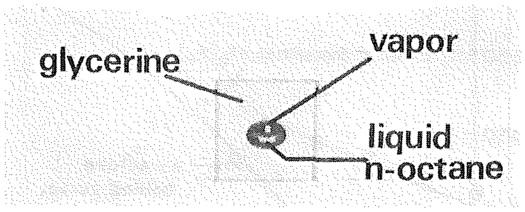

Fig. 7 Photograph of vaporizing two-phase, n-octane droplet in glycerine at 1.22 MPa and $T_0 \simeq 531°K$

probably a Taylor unstable oscillation of the bubble surface. The unstable interface for this effect (liquid over vapor) effectively exists over the upper hemisphere of the bubble; it is here where the deformation of the bubble surface appears most pronounced, as shown in the frames subsequent to frame 6.

The origin of the darkened region or "ring" in the second frame of Fig. 2 is unknown at present. It could have been the remnants of a pressure or shock wave emanating from the droplet surface just prior to the droplet bursting into vapor, but this is just conjecture. The ring was not observed in all the movies which were taken at atmospheric pressure. At pressures above atmospheric, the ring was never observed.

Quite different results were observed at ambient pressures of .687 MPa and 1.22 MPa, as shown in Figs. 3 and 4. The time for complete vaporization, boiling intensity, and size of the final vapor bubble were observed to be strongly affected by changes in ambient pressure. In particular, explosive boiling such as occurred at atmospheric pressure (Fig. 2) was entirely absent at elevated pressures. In addition it took over four times longer for complete vaporization to occur at 1.22 MPa than at .687 MPa. At these pressures, boiling was characterized by growth of apparently only one bubble within the octane droplet (as suggested by Figs. 2 to 4). This single bubble continued to grow until all the liquid octane completely vaporized, after which the bubble size remained constant.

Figure 5 schematically illustrates the initial and final states which are believed to characterize a phase transition via homogeneous nucleation of a liquid droplet in an infinite medium at temperature T_0. ($T_0(P_0)$ is less than the thermodynamic limit of superheat, $T_t(P_0)$, defined by the spinodal curve for a pure liquid ($\partial P/\partial V|_{T,n} = 0$).) During vaporization the vapor temperature drops from T_0 to close to $T_{sat1}(P_0)$ (2→3), after which the vapor becomes superheated as thermal equilibrium is regained (3→4). From mass conservation

$$\frac{R_f}{R_0} \approx \left\{\frac{\rho_{l1}(T_0)}{\rho_{v1}(T_0)}\right\}^{1/3} \tag{1}$$

Using the Peng-Robinson [17] equation of state to estimate superheated liquid and vapor densities, equation (2) is plotted in Fig. 6. As $P_0 \to P_c$, then $T_0 \to T_c$, $\rho_{l1} \to \rho_{v1}$ and therefore $R_f \to R_0$. This fact explains the relative decrease in final bubble size with increasing P_0 as shown in Figs. 3 and 4. At P_0 = .101 MPa by the first accessible time of observation (2nd frame in Fig. 2) the vapor bubble has grown past the size at which excess pressure between vapor and ambient liquid is zero. The subsequent oscillatory motion of the liquid/vapor interface was followed by fragmentation of the bubble. Such explosive vaporization as that illustrated in Fig. 2 did not, therefore, yield a single final bubble.

Figure 7 illustrates the two-phase droplet configuration typically observed at elevated pressures. It consisted of a single vapor bubble beneath which was suspended a puddle of the vaporizing liquid. Such two-phase droplets have been observed by others [e.g., 18–20]. In our present application, the initial bubbles were believed to form by homogeneous nucleation (section 3.2) and not as a result of any pre-existing gas bubbles or dissolved gases in the liquid. Although this two-phase droplet configuration was not observed in the explosive boiling sequence illustrated in Fig. 2, the camera framing rate was too slow to observe the stages of bubble growth in the time between the first three frames.

3 Physical Model

3.1 Introduction. Two steps in the boiling process pertinent to our study are (*i*) an initial or *homogeneous nucleation* phase during which the aforementioned critical size nuclei form within the liquid, and (*ii*) a second or *bubble growth* stage in which the initial microscopic bubble grows as the superheated liquid vaporizes. The first step is absent in most practical boiling situations due to the presence of pre-existing nucleation aids (e.g., dissolved gases, particles, or air bubbles). In the present study, these effects are minimal.

3.2 Homogeneous Nucleation of Bubbles in Liquids. Critical size nuclei form by random density fluctuations within the liquid. The stochastic nature of the process precludes a precise description of the steps involved in nucleus formation. Only an approximate rate at which the initial vapor bubbles form within a given volume of liquid can be determined. This rate is proportional to the exponential of the energy required to form a critical size nucleus:

$$J \simeq \Gamma\, k_f N \exp\left(-\frac{\Delta A^*}{KT_0}\right) \tag{2}$$

The energy of the critical size nucleus, ΔA^*, is

$$\Delta A^* = \frac{16\pi\,\sigma^3}{3(P-P_0)^2} \tag{3}$$

It is more convenient for our purposes to write equation (2) in terms of temperature:,

$$T_0 \simeq \Delta A^*\left[K\, ln\left\{\frac{N\,\Gamma k_f}{J}\right\}\right]^{-1} \tag{4}$$

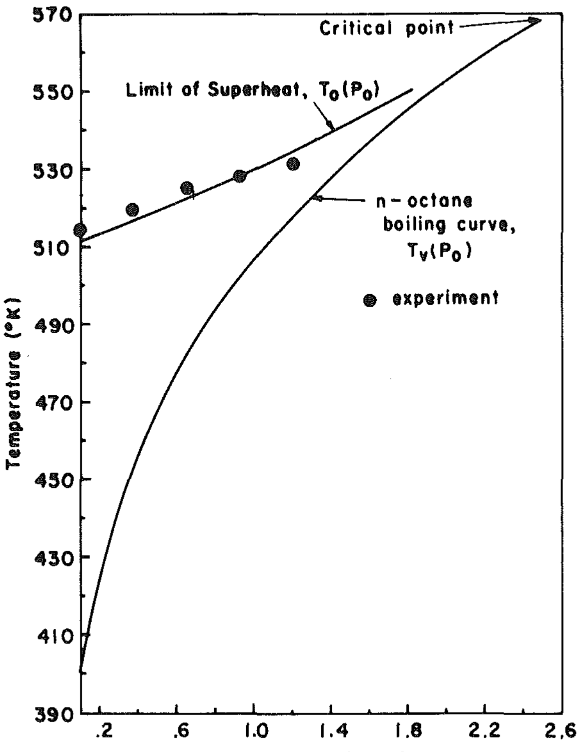

Fig. 8 Variation of limit of superheat with ambient pressure of n-octane

Equation (4) defines the homogeneous nucleation temperature corresponding to the rate J.

In equation (4) the number density of molecules, N (molecules/cm^3), was approximated as

$$N \simeq 6.02\times 10^{23}/v \tag{5}$$

where v is the molar volume of the superheated liquid (estimated from a correlation for saturated liquids [21]). The nucleus vapor pressure was approximated as

$$P \simeq P_e \exp\left[\frac{v}{\bar{R}T_0}(P_0-P_e)\right] \tag{6}$$

The equilibrium vapor pressure, P_e, was evaluated from a correlation given by Gomez-Nieto and Thodos [22]. The molecular evaporation rate, k_f, was estimated by the ideal gas collision frequency,

$$k_f \simeq \frac{8P\sigma^2}{(P-P_0)^2}\left(\frac{2\pi}{mKT_0}\right)^{1/2} \tag{7}$$

Finally surface tension was estimated from the generalized relation

$$\sigma = \sigma_0\left(1-\frac{T_0}{T_c}\right)^{\mu} \tag{8}$$

where for octane, $\sigma_0 \simeq 55.72$, $\mu \simeq 1.3$ [7], and $T_c = 568.8$.

The physical properties appearing in equations (3-8) were estimated by assuming a smooth continuation of the properties at saturation into the region of metastable states. This has been shown to be a reasonably accurate procedure [23].

Γ in equation (2) is the probability of a nucleus of critical size growing by the evaporation of a single molecule. For simplicity, $\Gamma \simeq 1$ was used in this work—every critical size nucleus grows and none decay [14].

An estimate of J commensurate with experiment is required to solve for temperature in equation (4). Experimental conditions were similar to those reported by Avedisian and Glassman [6]. They estimated a nucleation rate of 10^5 nuclei/cm^{3}s. Figure 8 therefore illustrates predicted limits of superheat corresponding to $J = 10^5$. The data shown in the figure represent an average of the vaporization temperatures of approximately ten droplets at the corresponding pressure. The experimentally measured superheat temperatures are in quite good agreement with estimated limits of superheat. This agreement was not unexpected as others have also found similar results for other liquids in bubble column experiments performed at pressures above atmospheric [6, 23-26]. This result substantiates the belief that the type of boiling illustrated in Figs. 2 to 4 was initiated by a homogeneous nucleation mechanism, and not the result of nucleation from

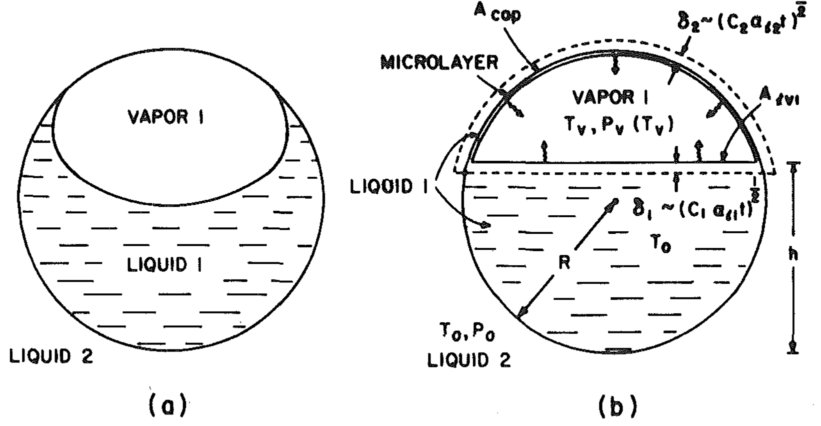

Fig. 9 (*a*) Schematic illustration of real two-phase droplet; (*b*) Geometric and heat-transfer model used in the analysis air bubbles, particles, etc. It also shows that the mere attainment of the limit of superheat is insufficient to ensure a violent boiling process (i.e., a vapor explosion).

3.3 Physical Model for Bubble Growth. A simple model for vaporization of a two-phase droplet was developed in connection with the following assumptions: (*i*) droplet expansion is spherically symmetric, (*ii*) T_0, P_0, and properties are constant, (*iii*) the field liquid is nonvolatile and only supplies heat to the droplet, (*iv*) heat transfer occurs by transient conduction across a thin thermal boundary layer surrounding the vapor bubble, (*v*) the interior of the droplet is at a uniform pressure, and (*vi*) internal liquid motion in the droplet (e.g., acceleration of the liquid at the liquid 1/vapor 1 interface) is neglected. The entire droplet thus uniformly expands as the vapor bubble grows. While not strictly valid, this latter assumption will be useful for estimating the time domain for the various processes controlling vaporization of the two-phase droplets.

To further simplify the development, we modeled the geometry of the two-phase droplet depicted at high pressures in Figs. 3, 4, 7, and 9(*a*) by the representation shown in Fig. 9(*b*). The liquid 1/vapor 1 interface is assumed to be planar. This facilitates a description of the appropriate volume and surface areas required in the analysis.

The model was also used to obtain information on atmospheric pressure vaporization, even though no proof of the assumed droplet geometry at this pressure could be given. This was because significant period for bubble growth at atmospheric pressure was inaccessible by our experimental method. However, the present approach can still be used to obtain an order of magnitude of the time domain over which the various mechanisms controlling bubble growth occurs.

The extended Rayleigh equation [27] relates the vapor pressure within the bubble cap to the temporal variation in radius. In nondimensional form, this equation is

$$y\frac{d^2y}{d\tau^2}+\frac{3}{2}\left(\frac{dy}{d\tau}\right)^2+\left(\frac{4\nu_{l2}}{C_1\alpha_{l1}}\right)\frac{dy}{d\tau}$$

$$\left(\frac{2\sigma_{12}R_0}{\rho_{l2}(C_1\alpha_{l1})^2}\right)\frac{1}{y}=\bar{P}_v-\bar{P}_0 \tag{9}$$

The viscous term in equation (9) is very small in the present application and was neglected. The surface tension term is initially small, and becomes of increasing importance as growth proceeds. The final vapor bubble (equation (1)) is in static mechanical equilibrium and Laplaces equation applies. Although $\bar{P}_v \neq \bar{P}_0$ due to the finite size of the final vapor bubble, this small final excess pressure is unimportant in the present analysis and was neglected.

The heat-transfer model used to relate $\bar{T}_v$ to y is illustrated in Fig. 9(*b*). Thermal boundary layers exist around the vapor cap in both liquid 2 and at the liquid 1/vapor 1 interface. A thin microlayer of liquid 1 is assumed to be present on the inside surface of the cap. Its existence is justified in terms of the tendency of liquid 1 to spread on liquid 2. Changes in the microlayer volume relative to corresponding changes in the puddle volume were neglected due to the presumed thinness of the microlayer.

An energy balance on the bubble cap yields

$$q_1+q_2=h_{fg1}\rho_{l1}\frac{dV_{l1}}{dt} \tag{10}$$

For simplicity we treated the phase boundaries as semi-infinite media undergoing transient conduction. Hence.

$$q_i\simeq k_{li}A_{lvi}T_0\frac{(\bar{T}_v-1)}{(C_i\alpha_{li}t)^{1/2}} \tag{11}$$

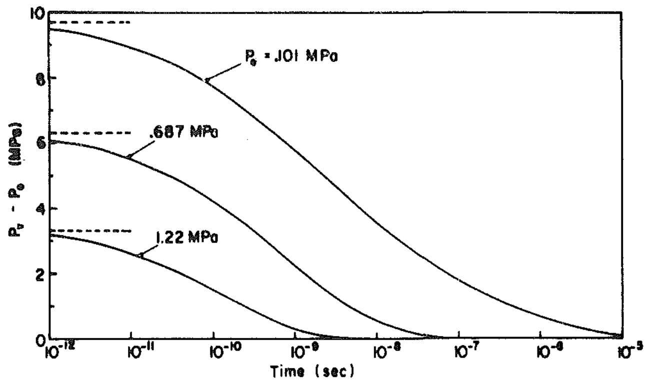

Fig. 10 Calculated variation of ΔP with time at pressures P_0 of .101 MPa, .687 MPa, and 1.22 MPa for an n-octane droplet ($R_0 \simeq$ .3mm). Small and large time asymptotes correspond to the nucleation pressure and saturation pressure ($P_v = P_0$), respectively.

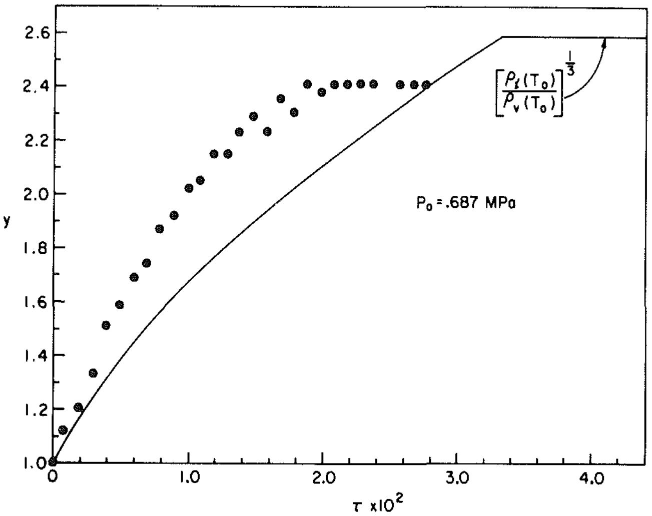

Fig. 11 Comparison between calculated and measured two-phase droplet radii at P_0 = .687 MPa

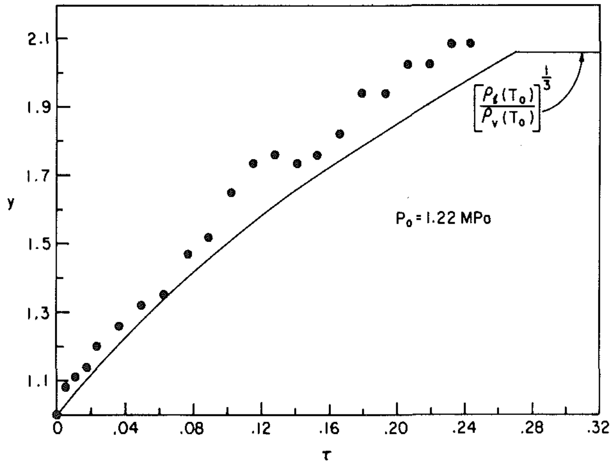

Fig. 12 Comparison between calculated and measured two-phase droplet radii at P_0 = 1.22 MPa

where $C_i = \pi$ ($i=1$, 2 and $A_{lv2} = A_{\text{cap}}$). This approximation has been shown to be surprisingly good in describing heat transfer to spherically symmetric expanding vapor bubbles which exist at surfaces and in infinite media (e.g., [28–31]). Equation (11) has also been used in approximating the heat flux to vaporizing bubbles in situations involving heat transfer over part of the surface of the bubbles [29–34]. In these studies the effects of the thermal boundary layer, radial liquid motion in the field liquid, and sphericity were accounted for by appropriately adjusting the value of C_i. (These studies do not strictly apply to the present problem because of the finite volume of the vaporizing liquid.) C_i is thus more in the vein of an experimentally adjustable parameter, although $C_i = \pi$ gave qualitative agreement with experiment as discussed below.

From geometry we can write that

$$A_{lv1} = \pi R_0^2 F(2-F) y^2 \tag{12}$$

$$A_{\mathrm{cap}} = 2\pi R_0^2 (2-F) y^2 \tag{13}$$

$$V_{l1} = \frac{1}{3} \pi R_0^3 F^2 (3-F) y^3 \tag{14}$$

where $F \equiv h/R$. The total droplet mass (liquid + vapor) at any instant during boiling is equal to the mass of the initial liquid droplet. Hence, we have that

$$F^2(3-F) = \frac{4(\epsilon - y^3)}{y^3(\epsilon - 1)} \tag{15}$$

Solving for F gives

$$F = 2\cos\left[\frac{1}{3}\cos^{-1}\left\{1 - \frac{2(\epsilon - y^3)}{y^3(\epsilon-1)}\right\} + \frac{4\pi}{3}\right] + 1 \tag{16}$$

Combining equations (10–14) and solving for $\bar{T}_v$ yields

$$\bar{T}_v = 1 - \frac{4 h_{fg1} C_1}{C_{pl1} T_0 (\epsilon - 1)} \cdot \frac{\tau^{1/2} \dfrac{dy}{d\tau}}{(2-F)\left[F + \dfrac{k_{l2}}{k_{l1}}\left(\dfrac{C_1 \alpha_{l1}}{C_2 \alpha_{l2}}\right)^{1/2}\right]} \tag{17}$$

The problem as formulated does not explicitly require vapor phase dimensions $(R-h)$ due to equation (16), and thus is at least qualitatively amenable to verification.

Equations (9), (10), (16), and (17), together with the initial condition

$$y(0) = 1, \dot{y}(0) = 0 \tag{18}$$

(i.e., the critical size nucleus is small compared with R_0) are a set of four equations for the unknowns y, $\bar{T}_v$, $\bar{P}_v$, and F. They were solved numerically over a range of pressures, P_0. Properties were evaluated at $1/2\,(T_0 + T_v)$. T_0 was estimated by solving equation (4) at each pressure using a nucleation rate of 10^5.

Figure 10 shows the variation of excess pressure within the vapor bubble, $P_v - P_0$, with time corresponding to three different ambient pressures. The initial pressure differences approximately correspond to the limit of superheat of octane. As P_0 increases, $\Delta P \rightarrow 0$ earlier in the growth of the bubble. Thus, the driving force for a vapor explosion is diminished earlier as P_0 increases. Growth then becomes controlled by the supply rate of heat to the vapor cap. Since experimentally accessible times are greater than 1 ms, growth is most likely controlled by heat transfer at .687 MPa and 1.22 MPa for the vaporization typical of that illustrated in Figs. 3 and 4. Equation (17) can then be directly integrated to give the variation of y with τ as $\bar{T}_v$ is constant. Equation (9) is therefore *not* needed in the analysis since $P_v \rightarrow P_0$ for the conditions of our high-pressure experiments. Note, too, that vaporization at these two pressures is not explosive.

At .101 MPa a pressure difference, ΔP, exists almost into the experimentally accessible time domain. Vaporization is correspondingly explosive (Fig. 2). While this observation does not conclusively show that inertially controlled growth is capable of producing a vapor explosion, neither does it disprove this contention. Further experimental work is required to elucidate the vaporization process in the time scales which were inaccessible by our method.

A comparison between experimentally measured and predicted droplet radii is shown in Figs. 11 and 12. Similar data could not be obtained for atmospheric pressure boiling by our experimental method. Considering our various approximations and experimental accuracy, there is qualitative agreement between calculated and measured radii. Also, measured radii exhibit evidence of approaching a maximum value given by equation (1). (R_0 is slightly larger due to subsequent superheating of the vapor after the liquid completely vaporizes. This further increase is comparatively small and was neglected.)

4 Conclusions

The boiling of droplets heated to their limits of superheat revealed that ambient pressure strongly affects the bubble growth rate. At .101 MPa droplets of n-octane under 1 mm dia exploded into vapor with an audible "popping" sound when they were heated to within 2°K of the theoretical homogeneous nucleation temperature; the boiling process occurred in less than 2 ms. At pressures above .6 MPa, the intensity of vaporization was considerably reduced, with droplets of the same size requiring over 30 ms to completely vaporize.

Homogeneous nucleation theory was used to provide the initial conditions for a simplified model of droplet boiling which was based on vaporization of a two-phase, liquid-vapor droplet. Predicted droplet radii were shown to be in qualitative agreement with measured radii. The results suggest that vapor explosions are not likely to occur when bubble growth is controlled by heat transfer to the vaporizing liquid. The results also show that while a necessary condition for a vapor explosion is that the liquid be heated to its spontaneous nucleation temperature, sufficient conditions must include consideration of the dynamics of the subsequent growth of the initially formed critical size nuclei.

Acknowledgments

The author wishes to thank Professor S. George Bankoff of Northwestern University for various discussions. Thanks are also due for the services provided by the Cornell University Computer Center. This work was supported by the National Science Foundation under Grant No. CPE-8106348 with Dr. David O. Cooney as project monitor.

References

1 Reid, R. C., "Superheated Liquids: A Laboratory Curiosity and, Possibly, an Industrial Curse, Part II: Industrial Vapor Explosions," *Chemical Engineering Education*, Summer 1978, p. 108.

2 Bankoff, S. G., "Vapor Explosions: A Critical Review," *Proceedings of the 6th International Heat Transfer Conference*, Aug. 7-11, 1978.

3 Lasheras, J. C., Fernandez-Pello, A. C., and Dryer, F. L., "Initial Observations on the Free Droplet Combustion Characteristics of Water-In-Fuel Emulsions," *Combusiton Science and Technology*, Vol. 21, 1979, pp. 1-14.

4 Skripov, V. P., and Ermakov, G. V., "The Limit of Superheating of Liquids," *Russian Journal of Physical Chemistry*, Vol. 37, No. 8, Feb. 1963, pp. 1047-1048.

5 Skripov, V. P., and Ermakov, G. V., "Pressures Dependence of the Limiting Superheating of a Liquid," *Russian Journal of Physical Chemistry*, Vol. 38, No. 2, Feb. 1964, pp. 208-213.

6 Avedisian, C. T., and Glassman, I., "High-Pressure Homogeneous Nucleation of Bubbles Within Superheated Binary Liquid Mixtures," ASME JOURNAL OF HEAT TRANSFER, Vol. 103, No. 2, 1981, pp. 272-280.

7 Eberhart, J. G., Kremsner, W., and Blander, M., "Metastability Limits of Superheated Liquids: Bubble Nucleation Temperatures of Hydrocarbons and Their Mixtures," *Journal of Colloid and Interface Science*, Vol. 50, No. 2, Feb. 1975, pp. 369-378.

8 Blander, M., Hengstenberg, D., and Katz, J. L., "Bubble Nucleation in

n-Pentane, n-Hexane, n-Pentane + Hexadecane Mixtures, and Water," *Journal of Physical Chemistry*, Vol. 75, No. 23, 1971, pp. 3613-3619.

9 Henry, R. E., and Fauske, H. K., "Nucleation Processes in Large Scale Vapor Explosions," ASME JOURNAL OF HEAT TRANSFER, Vol. 101, May 1979, pp. 280-287.

10 Buchanan, D. J., and Dullforce, T. A., "Mechanism for Vapor Explosions, *Nature*, Vol. 245, Sept. 1973, pp. 32-34.

11 Dergarabedian, P., "The Rate of Growth of Vapor Bubbles in Superheated Water," ASME *Journal of Applied Mechanics*, Vol. 20, 1953, pp. 537-545.

12 Apfel, R. E., and Harbison, J. P., "Acoustically Induced Explosions of Superheated Liquids," *Journal of the Acoustical Society of America*, Vol. 57, No. 6, June 1975, pp. 1371-1373.

13 Mori, Y. H., and Komotori, K., "Boiling of Single Superheated Drops in an Immiscible Liquid," *Heat Transfer—Japanese Research*, Vol. 5, No. 3, 1976, pp. 75-95.

14 Avedisian, C. T., "Superheating and Boiling of Water in Hydrocarbons and of Hydrocarbon Mixtures," PhD thesis, Princeton University, 1980.

15 Holden, B. S., and Katz, J. L., "The Homogeneous Nucleation of Bubbles in Superheated Binary Liquid Mixtures," *AIChE Journal*, Vol. 24, No. 2, March 1978, pp. 260-267.

16 Renner, T. A., Kucera, G. H., and Blander, M., "Explosive Boiling of Light Hydrocarbons and Their Mixtures," *Journal of Colloid and Interface Science*, Vol. 52, No. 2, Aug. 1975, pp. 391-396.

17 Peng, D. Y., and Robinson, D. B., "A New Two-Constant Equation of State," *Industrial and Engineering Chemistry Fundamentals*, Vol. 15, No. 1, 1976, pp. 59-64.

18 Sideman, S., and Taitel, Y., "Direct Contact Heat Transfer with Change of Phase: Evaporation of Drops in an Immiscible Liquid Medium," *International Journal of Heat and Mass Transfer*, Vol. 7, 1964, pp. 1273-1289.

19 Selecki, A., and Gradon, L., "Equation of Motion of an Expanding Vapour Drop in an Immiscible Liquid Medium," *International Journal of Heat and Mass Transfer*, Vol. 19, 1976, pp. 925-929.

20 Simpson, H. C., Beggs, G. C., and Sohal, M. S., "Nucleation of Butane Drops in Flowing Water," *Proceedings of the Sixth International Heat Transfer Conf.*, 1978, Paper No. PI-10.

21 Hankinson, R. W., and Thomson, G. H., "A New Correlation for Saturated Densities of Liquids and Their Mixtures," *AIChE Journal*, Vol. 25, No. 4, July 1979, pp. 653-663.

22 Gomez-Nieto, M., and Thodos, G., "Generalized Vapor Pressure Equation for Nonpolar Substances," *Industrial and Engineering Chemistry Fundamentals*, Vol. 17, No. 1, 1978, pp. 45-51.

23 Skripov, V. P., *Metastable Liquids*, Wiley, New York, 1974.

24 Mori, Y., Hijikata, K., and Nagatani, T., "Effect of Dissolved Gas on Bubble Nucleation," *International Journal of Heat and Mass Transfer*, Vol. 19, 1976, pp. 1153-1159.

25 Hijikata, K., Mori, Y., and Nagatini, T., "Experimental Study on Bubble Nucleation in the Oscillating Pressure Field," ASME JOURNAL OF HEAT TRANSFER, Vol. 100, Aug. 1978, pp. 460-465.

26 Forest, T. W., and Ward, C. A., "Homogeneous Nucleation of Bubbles in Solutions at Pressures above the Vapor Pressure of the Pure Liquid," *Journal of Chemical Physics*, Vol. 69, No. 5, Sept. 1978, pp. 2221-2230.

27 Bankoff, S. G., "Diffusion-Controlled Bubble Growth," in *Advances in Chemical Engineering*, Vol. 6, Academic Press, New York, 1966, pp. 1-60.

28 Zuber, N., "The Dynamics of Vapor Bubbles in Nonuniform Temperature Fields," *International Journal of Heat and Mass Transfer*, Vol. 2, 1961, pp. 83-98.

29 Donald, M. B., and Haslam, F., "The Mechanism of the Transition from Nucleate to Film Boiling," *Chemical Engineering Science*, Vol. 8, 1958, pp. 287-294.

30 Jones, O. C., and Zuber, N., "Bubble Growth in Variable Pressure Fields," ASME JOURNAL OF HEAT TRANSFER, Vol. 100, 1978, pp. 453-459.

31 Mikic, B. B., Rohsenow, W. M., and Griffith, P., "On Bubble Growth Rates," *International Journal of Heat and Mass Transfer*, Vol. 13, 1970, pp. 657-666.

32 Jongenelen, F. C. H., Groeneweg, F., and Gouda, J. H., "Effects of Interfacial Forces on the Evaporation of a Superheated Water Droplet in a Hot Immiscible Oil," *Chemical Engineering Science*, Vol. 33, 1978, pp. 777-781.

33 Bankoff, S. G., and Choi, H. K., "Growth of a Bubble at a Heated Surface in a Pool of Liquid Metal," *International Journal of Heat and Mass Transfer*, Vol. 19, 1976, pp. 87-93.

34 Van Stralen, S. J. D., "The Mechanism of Nucleate Boiling in Pure Liquids and in Binary Mixtures—Part 1," *International Journal of Heat and Mass Transfer*, Vol. 9, 1966, pp. 995-1020.