The Effect of Surface Tension on Factors in Boiling Heat Transfer

JOHN B. ROLL and JOHN E. MYERS
Purdue University, Lafayette, Indiana

The investigation of boiling heat transfer has been pursued vigorously over the past several years. Yet with all this research the mechanism of boiling heat transfer remains at best poorly defined. This paper is another hopeful attempt to explain some of the phenomena observed in boiling research.

LITERATURE

Until recently it has been generally accepted that the high, heat transfer rates experienced in boiling heat transfer were a direct result of the high degree of turbulence caused by bubble motion in the vicinity of the heated surface. The presentations of Jakob (*1*), Rohsenow (*2*), Forster and Zuber (*3*), and Levy (*4*) attack the problem along this line. The paper by Forster and Greif (*5*), who consider the mechanism to be one of vapor-liquid exchange is a variation on the theme of bubble-induced, liquid motion. Recently an entirely different mechanism, that of microlayer vaporization, has been presented by Moore and Mesler (*6*). Further support for this mechanism has been presented by Hendricks and Sharp (*7*). As envisioned by Moore and Mesler the mechanism of microlayer vaporization takes place as follows: "As a bubble grows on the surface it exposes the heating surface, wet with a microlayer of liquid, to the interior of the bubble. This microlayer rapidly vaporizes, removing heat rapidly from the surface until it is completely vaporized." Although not mutually exclusive the two mechanisms are obviously not both the prime mechanism for heat removal in boiling heat transfer. This situation has been discussed by Zuber (*8*) who suggests that the phenomena of nucleate boiling includes two regimes. In the first, at low heat flux, the heat transfer rate is determined largely by the updraught induced circulation. In the second, at moderate and high heat fluxes, the dominate mode of heat transfer is the latent heat transport process associated with large bursts of vapor from a pulsating microlayer.

The mechanism of bubble growth has been extensively investigated. With various ramifications the mechanism of bubble growth has been reported successively by Plesset and Zwick (*9*), Forster and Zuber (*10*), Zuber (*11*), Scriven (*12*), Forster (*13*), and Han and Griffith (*14*). When reduced to a first-order approximation each of the derivations can be written as

$$\frac{dr}{dt} = C \frac{k\theta}{\lambda\rho v} \frac{1}{\sqrt{\pi\alpha t}} \tag{1}$$

where

$$1 < C < \sqrt{3} \tag{2}$$

The mechanism of bubble departure was investigated originally by Fritz (*15*). His derivation was based upon a static balance between the upward buoyant force and the downward surface tension force at the bubble base. Apparently no subsequent presentations have appeared, and authors have been content to use the Fritz equation when an expression for maximum bubble size was required.

It appears that there is a contradiction between the microlayer vaporization model for heat transfer and the Fritz model for bubble departure. In the Fritz model a large perimeter of contact for the metal surface-vapor-liquid triple interface is a requirement. On the other hand the microlayer vaporization model almost precludes such a large perimeter. As a bubble grows, according to Moore and Mesler, a microlayer is formed which flash vaporizes to remove heat from the plate. This vaporization may uncover successively larger portions of the plate. However, especially in the early stages of growth, the existence of a large perimeter of interface means that a correspondingly smaller microlayer exists for subsequent heat removal. The model presented in the present paper reduces to some extent this apparent contradiction.

EXPERIMENT

The experimental evidence presented in support of the model developed herein was obtained during an investigation into the effects of surface tension on boiling heat transfer (*16*). The apparatus was basically that which was constructed by Kurihara (*17*). Boiling took place from the horizontal end of a copper cylinder to which heat was supplied electrically. The surface temperature was determined by the extrapolation of temperatures within the cylinder as determined by imbedded thermocouples.

For the series of runs reported in this paper high-speed photography was used to record the bubble growth characteristics. For this a camera was used at a film speed of 800 to 900 frames/sec. The camera was placed approximately 20 in. from the site of boiling at an angle of 15 deg. to the horizontal. By projecting the developed film strips frame-by-frame it was possible to determine the volume-time relationships for selected

---

John B. Roll is with the Division of Reactor Development, United States Atomic Energy Commission, Washington, D. C. John E. Myers is a Fulbright lecturer at the University of Toulouse, France.

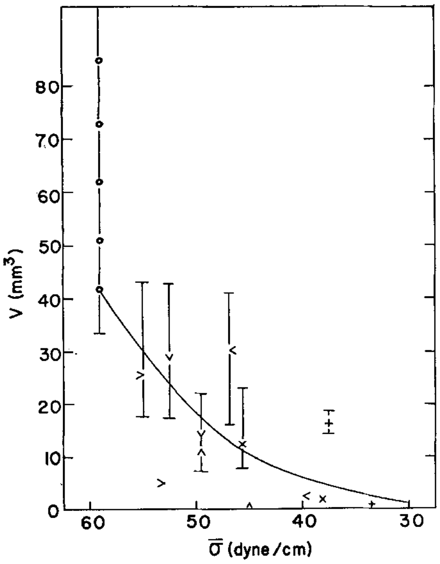

Fig. 1. Bubble volume vs. mean surface tension. ◎ Water only, < Aerosol OT, > Aerosol AY, V Aerosol IB, Λ Aerosol MA, X Hyonic PE-200, + Hyonic PE-300, I range of average at each site.

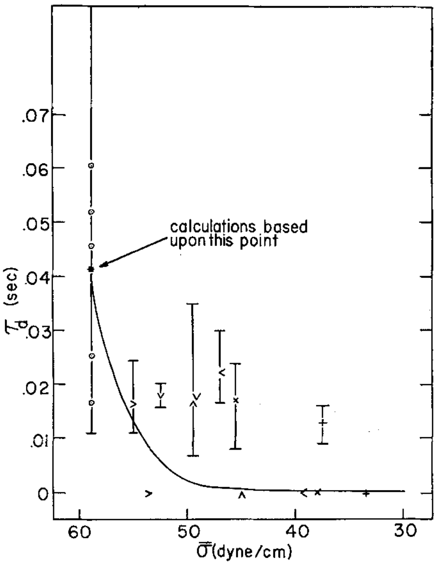

Fig. 2. Delay time vs. mean surface tension. ◎ Water only, < Aerosol OT, > Aerosol AY, V Aerosol IB, Λ Aerosol MA, X Hyonic PE-200, + Hyonic PE-300, I range of average at each site.

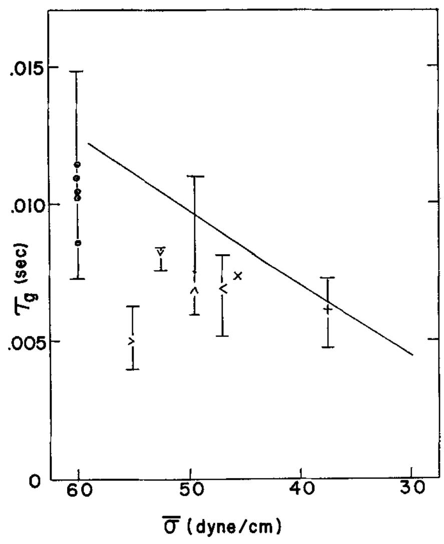

Fig. 3. Growth time vs. mean surface tension. ◎ Water only, < Aerosol OT, > Aerosol AY, V Aerosol IB, Λ Aerosol MA, X Hyonic PE-200, + Hyonic PE-300, I range of average at each site.

bubbles. From these primary data it was possible to calculate the following:

1. The average growth rate dV/dt as determined from the slope of the best visually-fitted line through the points of bubble volume vs. time.
2. The maximum bubble volume V determined as the point where the data either end or deviate appreciably from the best-fitting straight line.
3. The growth time τ_g which is equal to maximum bubble volume divided by average growth rate.
4. The delay time τ_d which is the time during which there is no bubble growing from the site.

For the surface active agents(surfactants) considered in this research values of the dynamic surface tension were determined (*16*) in a study of air-bubble formation in aqueous solutions at a rate of 1,800 bubbles/min. This system was only approximately similar to a boiling system; hence the measured values of dynamic surface tension (which lay between 30 and 60 dynes/cm. at 90°C.) would not be expected to apply directly to the boiling system. It was found that the best representation of the data was accomplished by defining an effective surface tension $\bar{\sigma}$ which was the arithmetic average of the static surface tension of the boiling solution at 100°C. and the dynamic surface tension as measured by the air-bubble apparatus:

$$\bar{\sigma} = \frac{1}{2}(\sigma_{100} + \sigma_d) \qquad (3)$$

This variable is used in Figures 1, 2, and 3 to show the dependence of V, τ_d and τ_g on surface tension.

RESULTS

A total of seventeen runs were made. The average heat flux in these runs was 24,100 B.t.u./hr. sq.ft. Of these twelve were made with two concentrations of each of six surfactants, and five were made with water only. The results in Figures 1, 2, and 3 show a range of values of the dependent variable at each given value of $\bar{\sigma}$. This range is not the result of errors in experimental measurement but merely reflects the variation in V, τ_d, and τ_g for a given boiling system. For example in a given run approximately ten bubbles were studied on each of several sites. Hence a given point on Figure 1 represents an average value of V for as many as fifty bubbles, that is all the bubbles examined for a given run. Since there was no way to find and photograph bubbles produced from the same sites in different runs, it is to be expected that different averages would be obtained for different runs. If enough bubbles were examined from a very large number of sites, it would be expected that the averages would check for successive runs made at the same conditions. Notwithstanding the apparent random scatter of the data, by considering each surfactant separately the following general observations can be made:

1. The bubble volume decreases with decreasing surface tension.
2. The growth time decreases with decreasing surface tension.
3. The delay time decreases to zero as the surface tension is lowered.
4. The frequency, which is the reciprocal of the sum of the growth and delay times, increases by an order of magnitude as surface tension is lowered.

It was seen from the films that during patch nucleation the bubbles seemed to exist as close packed spheres with no delay time. As used here the term "patch nucleation" refers to the evolution of a very large number of bubbles from a patch of heated surface as opposed to the usual sequential formation of bubbles from a given site. Another observation from the films was that the horizontal axis of the growing bubble was always greater than the vertical axis. The eccentricity was as great as 2 with water and approached 1 with the surfactant solutions.

It was not possible to record growth rate or growth time for the high surfactant concentrations. At these concentrations patch nucleation occurred and obscured the individual bubble growth characteristics. For these runs delay time was recorded as zero, and the final average volume was estimated.

DISCUSSION OF RESULTS

It is possible to develop a model for bubble growth and departure which predicts the phenomena observed in this research and which if correct lends support to the microlayer vaporization mechanism of boiling as presented above. Hsu (*18*) has recently presented a paper in which the results agree quite well with previously reported data. In his model (which forms the basis of the present development) he considers a cycle as follows. At the beginning of the bubble cycle relatively cool bulk liquid, which has filled the space left by a departed bubble, surrounds the nucleus at the active site. As time goes on this liquid is warmed by heat conduction, and a thermal boundary layer develops. He assumes that this thermal layer heats up in a manner analogous to that of conduction into a flat plate of finite thickness. In order to simplify the resulting equations an infinitely thick flat plate will be assumed here, the solution of which can be approximated by (*1*):

$$\theta(x, t) = \theta_w \left[1 - \frac{x}{2\sqrt{\alpha\tau}} \right] \text{ for } \frac{x}{2\sqrt{\alpha\tau}} < 0.75 \quad (4)$$

It should be noted that the denominator $2\sqrt{\alpha\tau}$ does not correspond to that of the first term of the series solution $\pi\sqrt{\alpha\tau}$. However in the range of interest use of a 2 rather than a π tends to compensate for dropping the rest of the series. The initial bubble superheat is obtained in terms of the critical radius of the nucleus by combining the well-known equation

$$r^* = \frac{2\sigma}{\Delta P} \quad (5)$$

with an integrated form of the Clausius-Clapeyron equation. This gives the superheat at nucleation as

$$\theta_b = \frac{2\sigma\, T_{\text{sat}}}{\lambda\rho_v\, r^*} \quad (6)$$

Hsu considered the distance from the heater surface to the top of the bubble nucleus x_b to be identical to the diameter of the active cavity and to be related to the bubble radius r by

$$x_b = 1.6\, r^* \quad (7)$$

Equation (6) becomes

$$\theta_b = \frac{1.6\,\beta}{x_b} \quad \text{with} \quad \beta = \frac{2\sigma\, T_{\text{sat}}}{\lambda\rho_v} \quad (8)$$

The bubble nucleus will not grow unless the surrounding liquid is warmer than the bubble at nucleation; hence there is a net heat flux into the bubble to provide the heat of vaporization. When the bubble starts to grow, the delay time ends. Accordingly the end of the delay time is reached when $\theta(x, t)$ given by Equation (4) equals θ_b given by Equation (8) at $x = x_b$.

When one uses the above simplified derivation by Hsu as a point of departure, the effect of changes in the surface tension on the delay time can be derived as follows: For a given wall temperature and saturation temperature Equation (4) will define a family of lines of $\theta(x, t)$ vs. x with τ as the parameter. For a given set of liquid conditions Equation (8) will define a family of curves of θ_b vs. x_b with σ as the parameter. These two families of curves are plotted in Figure 4. The intersection of the curve corresponding to $\sigma = 58.85$ with the line corresponding to the observed delay time for water will determine x_b for the heater surface of the particular experiment. This in turn is identical with the characteristic microdimension of the heater surface and as such does not change upon addition of a surfactant. In other words a particular grade of surface roughness is capable of maintaining a particular maximum size of subnuclei. Thereafter when the surface tension is lowered, the delay time will correspond to the line passing through the intersection of the proper θ_b vs. x_b curve and the vertical line at the value of x_b representative of the heater surface of the experiment. This intersection therefore also determines the value of θ_b for that particular combination of θ_w, σ, and surface condition.

By combining Equations (4) and (8) one gets

$$x_b = \sqrt{\alpha\,\tau_d} - \left[\alpha\,\tau_d - \frac{3.2\,\beta\sqrt{\alpha\,\tau_d}}{\theta_w} \right]^{1/2} \quad (9)$$

For subsequent changes in surface tension (which are reflected in changes in β), having established the characteristic x_b, one obtains

$$\theta_b = \frac{1.6\,\beta}{x_b} \quad (10)$$

and

$$\tau_d = \frac{1}{\alpha} \left[\frac{x_b\,\theta_w}{2(\theta_w - \theta_b)} \right]^2 \quad (11)$$

Thus by knowing the delay time and surface temperature for pure water boiling from a given surface the delay time and bubble temperature can be calculated when the surface tension has been lowered. Note that there is a conjugate root for Equation (9). Previous experiments (*17*) with the apparatus used here have shown that there are no single cavities as large as those defined by Equation (5), but that active cavities were probably formed by a combination of many subcritical sized cavities. Therefore it is concluded that such a number of subcritical cavities will combine as will produce a minimum-sized critical cavity, and accordingly only that root corresponding to the minimum critical radius is used in Equation (9). It should be noted that the above derivation assumes constant surface temperature. It has been shown (*6, 18*) that neither constant surface temperature nor constant heat flux are attained. However in order to provide a simple, first approximation the constant temperature boundary condition was chosen.

The bubble volume is now considered. There have been several attempts to characterize the bubble growth rate in a superheated liquid. Among them are

Plesset and Zwick (*9*) and Scriven (*12*):

$$\frac{dr}{dt} = \sqrt{3}\,\frac{k\theta_w}{\lambda\rho_v}\,\frac{1}{\sqrt{\pi\alpha t}} \quad (12)$$

Forster and Zuber (*10*):

$$\frac{dr}{dt} = \frac{\pi}{2}\,\frac{k\theta_w}{\lambda\rho_v}\,\frac{1}{\sqrt{\pi\alpha t}} \quad (13)$$

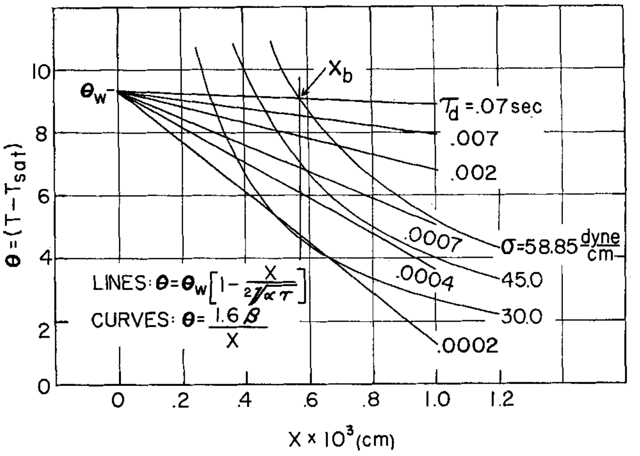

Fig. 4. Graphical solution to determine x_b.

Forster (*13*):

$$\frac{dr}{dt} = \frac{k\theta_w}{\lambda \rho_v} \frac{1}{\sqrt{\pi \alpha t}} - \frac{k^2 \theta_w^2}{\lambda^2 \rho_v^2 \alpha} \frac{1}{\pi H} \tag{14}$$

Zuber (*11*):

$$\frac{dr}{dt} = \left[\frac{k\theta_w}{\lambda \rho_v} \frac{1}{\sqrt{\pi \alpha t}} - \frac{q_b}{\lambda \rho_v} \right] \frac{\pi}{2} \tag{15}$$

Equations (12) and (13) were derived with the assumption of a uniformly superheated liquid; Equation (14) assumed a temperature field proportional to exp $(-x/H)$; Equation (15) assumed a nonuniform but unspecified field. As an approximate equation to describe bubble growth Equation (13) is used in the form

$$\frac{dr}{dt} = \frac{M}{2} \sqrt{\frac{\pi \alpha}{t}} \quad \text{where} \quad M = \frac{k\theta}{\lambda \rho_v \alpha} \tag{16}$$

Several people have investigated the free rise of bubbles in liquids. One such work, Harturian and Sears (*19*), reports results in the form

$$u_t = \left[\frac{8}{3} \frac{gr}{C_d} \right]^{1/2} \tag{17}$$

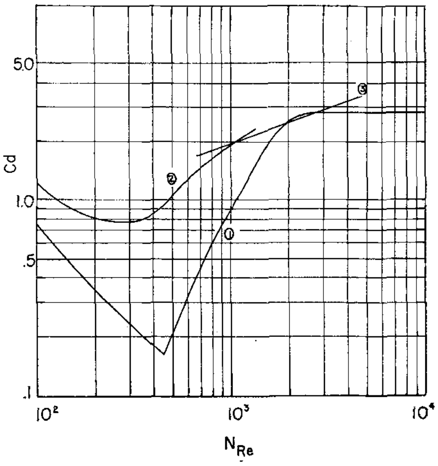

Fig. 5. Drag coefficient for rising bubbles. (1) Pure water; (2) surfactant solutions; (3) assumed relation for this application.

Their values of the drag coefficient are shown in Figure 5.

If the significant bubble velocity is considered to be defined by

$$u_b = 2 \frac{dr}{dt} = \frac{dD}{dt} = \frac{M^2 \alpha \pi}{r} \tag{18}$$

where the latter representation can be readily obtained from Equation (16), then the Reynolds number can be written as

$$N_{Re} = \frac{D u_b \rho}{\mu} = \frac{2 M^2 \alpha \pi \rho}{\mu} \tag{19}$$

In these experiments it was found that N_{Re} was 2,580 for the water runs and 1,085 for the runs with $\overline{\sigma} = 38$ (approximate minimum observed here). Accordingly a straight line was drawn on Figure 5 over this range which gave an effective C_d vs. N_{Re} relationship to be used in the first approximation.

When one considers a force balance on a bubble growing in a superheated field without attachment to the heated surface, it follows that

$$\text{buoyant force} - \text{drag force} - \text{acceleration force} = 0 \tag{20}$$

or mathematically

$$g V \rho_L - \frac{C_d A_f \rho_L u_b^2}{2} - \frac{V \rho_L}{2} \left(1 + \frac{3}{8} \right) \frac{d u_b}{dt} = 0 \tag{21}$$

In Equation (21) the virtual mass of the accelerating bubble has been approximated by ½(1 + 3/8) times the mass of displaced liquid (*20*). Also the inertia of the bubble has been neglected.

In bubble growth in a boiling system the driving force is thermal not hydrodynamic. Therefore the growth rate is determined by Equation (16). The velocity predicted by Equation (16) is greater than that for the equilibrium condition embodied in Equation (21). Thus in the early stages of growth a bubble is out of balance and is held down on the plate by the drag and acceleration forces. Only when Equation (21) is satisfied will the bubble begin to rise out of the superheated field because of the hydrodynamically induced velocity (that is free bubble rise) rather than be held down on the plate because of the thermally induced velocity (that is bubble growth). By combining Equations (16), (18), and (21) the value for the bubble radius when the force balance is satisfied is determined as

$$r_{b.o.} = (\pi M^2 \alpha)^{2/3} \left[\frac{3\left(C_d - \frac{11}{12} \right)}{8g} \right]^{1/3} \tag{22}$$

Hence the criteria for bubble departure (and accordingly approximate cessation of bubble growth) are embodied in Equation (22) and not in a force balance between the buoyant force and the surface tension force. Spherical volumes calculated from the radius determined in Equation (22) and delay times calculated from Equation (11) are plotted on Figures 1 and 2. These calculations are based upon the average superheat and delay times observed for the water runs. The curves on Figures 1 and 2 are not correlations of the data plotted on these graphs.

Implied in this development is the fact that in evaluating bubble growth rates the superheat to be considered is not the wall superheat but the bubble superheat as defined by Equation (10). This can be checked by referring to Figure 3, where observed growth time has been plotted vs. the characteristic surface tension $\overline{\sigma}$ along with τ_g determined by combining Equations (16), (18), and (22):

$$\tau_g = (\pi M^2 \alpha)^{1/3} \left[\frac{3\left(C_d - \frac{11}{12} \right)}{8g} \right]^{2/3} \tag{23}$$

As with Figures 1 and 2 the line on Figure 3 is not a correlation of the data shown on the same figure. The line is plotted from Equation (23) and is shown on the same plot as the data merely to indicate that the theory predicts the trends observed experimentally.

When one considers the mechanism of bubble departure, the point of divergence between the model presented here and the previously-held model of Fritz is the nature of the force resisting bubble motion. The Fritz model claims that the resisting force is that of surface tension acting at the perimeter of contact at the bubble base. An implication of this assumption would be that at the point of departure the bubble would be elongated with the vertical axis greater than the horizontal axis. The model presented here claims that the resisting force is the hydrodynamic force of the liquid acting on the bubble surface. An implication of this assumption is that at the point of departure the bubble will be elongated with the horizontal axis greater than the vertical axis. Observations made in this research, as well as those reported photographically by Lowery and Westwater (*21*) and Hendricks and Sharp (*7*) and by sketches of Moore and Mesler (*6*) and Han and Griffith (*14*), support the contentions that at departure the horizontal axis of the bubble is indeed greater than the vertical axis and that the principal resisting force is one of hydrodynamics and not surface tension.

CONCLUSIONS

A model has been developed to explain how surface tension changes are reflected by changes in delay time, growth time, and volume. Alterations in the delay time can be explained by considerations of nucleation. Alterations in the growth time and volume are to be explained as secondary effects of nucleation. That is the growth rate is changed because at lower surface tension the bubble nucleates at a lower superheat and the growing bubble finds itself enveloped in a thermal layer of lower superheat. This in turn alters the final or break off (a misnomer) volume as per the hydrodynamic buoyancy force balance. Finally the combination of lower growth rate and smaller final volume with decreased surface tension results in a slightly decreased growth time.

The trends exhibited by the reported data are represented by this model. Evidence recently obtained (*7*, *6*), tends to support the microlayer vaporization concept of heat removal. Acceptance of this model for heat transfer precludes the acceptance of the buoyancy-surface tension force-balance model for the bubble departure. The new model for bubble growth and departure presented here is consistent with the microlayer vaporization concept of heat removal (and with the induced turbulence model) as well as with data obtained by varying the surface tension of the liquid. It should be noted that the data with which the results of this model are compared are at relatively low heat flux. Accordingly care should be exercised when using it in the regime of high heat flux described by Zuber (*8*).

As envisioned by the authors a model consistent with the requirements of boiling heat transfer would include the following points. The bubble is initiated when the temperature of the liquid in the boundary layer equals that of the equilibrium bubble of critical size. Bubble growth is governed by a thermal driving force. The result is that the instantaneous value of dr/dt is greater than the upward free rise velocity for a bubble of the same size. Therefore the bubble is held down on the surface by hydrodynamic forces. While it is so held down, microlayer vaporization occurs at its base. When the hydrodynamic force acting downward is balanced by the buoyant force acting upward, the bubble begins to rise out of the heated layer, bubble growth ceases, and the attached base, if formed, is broken. The surface forces at this point of attachment play an insignificant role in determining the point of bubble departure. When this tail of vapor breaks off, the bubble has already begun to rise, the condition for rise having been achieved prior to this alleged break off.

ACKNOWLEDGMENT

The authors wish to thank the United States Atomic Energy Commission for financial support given John B. Roll during the course of this research.

NOTATION

A_f = frontal area of bubble, (sq.cm.)
C_d = drag coefficient
D = diameter of sphere of volume equivalent to bubble, (cm.)
g = acceleration of gravity, (cm./sec.^{2})
H = constant in Equation (14)
k = thermal conductivity, (cal./sec. cm. °C.)
M = constant defined in Equation (17)
ΔP = pressure difference across bubble surface, (g./sq.cm.)
q_b = heat flux through base of bubble, (cal./sec. sq. cm.)
r = radius of bubble of diameter D, (cm.)
r^* = critical radius for nucleation, (cm.)
t = time, (sec.)
T = temperature, (°C.)
T_{sat} = saturation temperature, (°C.)
u_b = bubble velocity, (cm./sec.)
u_t = terminal velocity for free rising bubble, (cm./sec.)
V = bubble volume, (cc.)
x_b = distance from boiling surface to top of bubble, (cm.)
N_{Re} = defined in Equation (20)

Greek Letters

α = thermal diffusivity, (sq.cm./sec.)
β = constant defined in Equation (8)
θ = $T - T_{\text{sat}}$, (°C.)
θ_w = $T_{\text{surface}} - T_{\text{sat}}$, (°C.)
θ_b = bubble temperature minus liquid saturation temperature, defined in Equation (6)
λ = latent heat of vaporization, (cal./g.)
ρ_v = vapor density, (g./cc.)
σ_d = dynamic surface tension, (dyne/cm.)
σ_{100} = static surface tension at 100°C., (dyne/cm.)
$\bar{\sigma}$ = surface tension defined in Equation (3)
τ_d = delay time, (sec.)
τ_g = growth time, (sec.)
μ = liquid viscosity, (g./cm. sec.)

LITERATURE CITED

1. Jakob, Max, "Heat Transfer," Vol. 1, Wiley, New York, (1958).
2. Rohsenow, W. M., *Trans. Am. Soc. Mech. Engrs.*, **73**, 969 (1951).
3. Forster, H. K., and N. Zuber, *A.I.Ch.E. Journal*, **1**, 531 (1955).
4. Levy, S., *J. Heat Trans.*, **81C**, 37 (1959).
5. Forster, K. E., and R. Greif, *ibid.*, p. 43.
6. Moore, F. D., and R. B. Mesler, *A.I.Ch.E. Journal*, **7**, 620 (1961).
7. Hendricks, R. C., and R. R. Sharp, Paper presented at A.I.Ch.E. Los Angeles meeting (February, 1962).
8. Zuber, N., *Int. J. Heat and Mass Trans.*, **6**, 53 (1963).
9. Plesset, M. S., and S. A. Zwick, *J. Appl. Phys.*, **23**, 95 (1952).
10. Forster, H. K., and N. Zuber, *ibid.*, **25**, 474 (1954).
11. Zuber, N., *AECU-4439* (1959).
12. Scriven, W. E., *Chem. Eng. Sci.*, **10**, 1 (1959).
13. Forster, K. W., *Phys. Fluids*, **4**, No. 4, p. 448 (1961).
14. Han, C. Y., and P. Griffith, *Tech. Rept. No. 19, AEC Document NP-11491.*
15. Fritz, W., *Physik Z.*, **36**, 379 (1935).
16. Roll, J. B., Ph.D. thesis, Purdue University, Lafayette, Indiana (1962).
17. Kurihara, H. M., and J. E. Myers, *A.I.Ch.E. Journal*, **6**, 83 (1960).
18. Hsu, Y. Y., *Am. Soc. Mech. Engrs., Paper 61-WA-177.*
19. Harturian, R. A., and W. R. Sears, *J. Fluid Mech.*, **3**, 27 (1958).
20. Milne-Thomson, L. M., "Theoretical Hydrodynamics," 2 ed., Macmillan Company, New York (1950).
21. Lowery, A. J., and J. W. Westwater, *Ind. Eng. Chem.*, **49**, 1445 (1957).

Manuscript received July 10, 1963; revision received November 22, 1963; paper accepted November 26, 1963. Paper presented at A.I.Ch.E. Houston meeting.